Appendix A

Sacramento Stormwater Quality Partnership Quality Assurance Project Plan (QAPP)

October 2018

Quality Assurance Project Plan (QAPP)

Sacramento Stormwater Quality Partnership

Prepared by

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A PROJECT MANAGEMENT

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A.2 DISTRIBUTION LIST

Table 1. Distribution List for this QAPP

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A.3 PROJECT ORGANIZATION

The project's roles and responsibilities are defined in **Table 2.**

Table 2. Project Roles and Responsibilities

Role	Person	Responsibility
City Project Manager	Dalia Fadl	Provide oversight and coordinate with the monitoring manager prior to any monitoring events
County Project Manager	Dave Tamayo	Provide oversight and coordinate with the monitoring manager prior to any monitoring events
Project Manager	Brian Laurenson	Project oversight and coordination with the clients.
Monitoring Manager and QA Officer	Steve Maricle	Implements monitoring program and manages field crews for mobilization. Project coordination and oversight, data management, and reporting. Ensure that the laboratory quality assurance plan and QAPP criteria are met through routine monitoring and auditing of the systems.
Data Management Officer	Jenny Bayley	Processes collected data for completeness and ensures that the data meets the criteria set forth in this QAPP.
Sub-consultant Project Manager	Beth Smiley	Monitoring event preparation, mobilization, and oversight. Oversees collection of water quality samples and shipment to laboratories
Equipment Technical Advisor	Jeff Walker	Development and maintenances of sample collection equipment and sensors. Ensures continuous data meets QAQC objectives.

A.4 BACKGROUND

The Sacramento Stormwater 2018/2019 National Pollutant Discharge Elimination System (NPDES) monitoring program is comprised of several components as required in the NPDES Monitoring and Reporting Program (MRP, Order No. R5-2008-0142). The joint permit allows stormwater discharge from the municipal and county agencies collectively known as the Sacramento Stormwater Quality Partnership (Partnership). This permit was renewed on April 17, 2015 and included modifications to the original monitoring programs.

As part of the permit renewal, the Partnership is required to continue the urban discharge monitoring programs at all three sites. During the 2018/2019 wet season, a Partnership consultant team led by Larry Walker Associates (LWA) and CDM will collect Urban Discharge monitoring samples from Strong Ranch Slough in Sacramento County and at the North Natomas Detention Basin and Sump 111, both located in the City of Sacramento.

Urban Discharge monitoring will occur between September 1, 2018 and June 1, 2019 during three wet weather events and one dry weather event. All four events of the season will cover the complete list of NPDES Monitoring and Reporting Program (MRP) "Table B" constituents.

A.5 PROJECT DESCRIPTION

A.5.1 Monitored Constituents

The Partnership will monitor the constituents specified in the Permit. The following water quality monitoring elements are to be included:

- Bacteriological (fecal coliform and *Escherichia coli*)
- General characterization parameters (total and dissolved organic carbon, hardness, biochemical and chemical oxygen demand, alkalinity, turbidity, electrical conductivity)
- Solids (suspended sediment, total and dissolved solids)
- Nutrients (total phosphorus, total Kjeldahl nitrogen, nitrate + nitrite, orthophosphate as P)
- Filtered and unfiltered total metals (copper, nickel, lead and zinc)
- Methylmercury, and total mercury
- Total Petroleum Hydrocarbons (TPH)
- Pesticides (organophosphate, pyrethroids, and fipronil)
- Polycyclic Aromatic Hydrocarbons (PAHs)
- Sensor parameters (Flow, turbidity, water temperature, dissolved oxygen, electrical conductivity, pH and redox)

A.5.2 Monitoring Schedule

This QAPP covers monitoring activities during the 2018/2019 fiscal year (July 2018 to June 2019). Three wet weather events and one dry weather event will be conducted during the monitoring year (September 2018 through June 2019).

A.5.2.1 Storm Event Schedule

The Partnership will target three storm events that are based on the following criteria:

- **First Flush Event** – A first flush event is a storm event in which precipitation totals are greater than 0.25 inches. Beginning in September the Partnership will target an event that is forecasted to meet the first flush criteria at each of the monitoring sites.

- **Mid-Season Storm Event** – Following the first flush event, the Partnership will target a winter storm event (November through January) that is forecasted to be greater than 0.50 inches with a probability greater than 75%. The preceding antecedent conditions must also be dry (precipitation less than 0.10 inches) for at least 72 hours.

- **Late-Season Event** – The final wet weather event of the season will be late season event (January through March). The storm's forecast should be greater than 0.50 inches with a probability greater than 75%. The preceding antecedent conditions must also be dry (precipitation less than 0.10 inches) for at least 72 hours.

The Monitoring Manager will target sample collection events where all sites are likely to meet the precipitation criteria and will observe urban runoff. The criteria and schedule can be modified by the Monitoring Manager, based on seasonal precipitation amounts and sampling logistics.

A.5.2.2 Dry Event Schedule

The Partnership will target one dry weather event during the 2018/2019 monitoring year. The dry weather event will occur between January and May of the monitoring year and will occur during a period of dry weather, which is when project wide precipitation amounts are less than 0.10 inches for at least three days. Urban runoff flows should also be at baseline levels and not elevated from any storm flows.

A.5.3 Sampling Locations

Monitoring will be conducted within the City of Sacramento at the North Natomas detention Basin No. 4 and at Sump 111 and within the Count of Sacramento at Strong Ranch Slough. One site at each location will be monitored throughout the wet season. These areas and their site locations are shown in **Figure 1**. The proposed monitoring sites and their coordinates are shown in Table 3.North Natomas Detention Basin No. 4 is a collection point for stormwater drained from a 470 acre area of residential development in North-West Sacramento before it is pumped into the East Drainage Canal, which is a tributary to the Main Drainage Canal that eventually drains into the Sacramento River.

Table 3

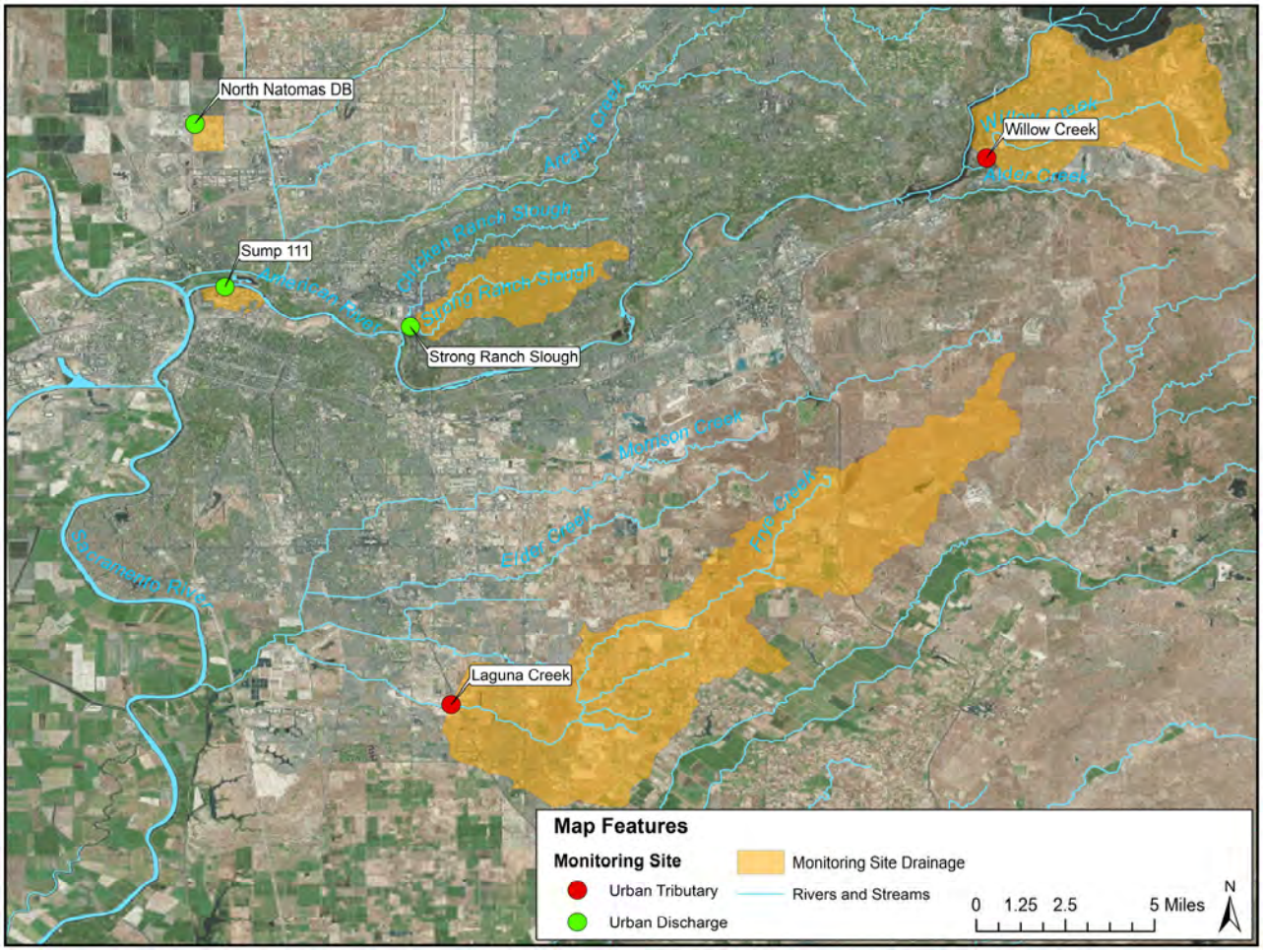

Figure 1 Area Overview and Site Locations

Strong Ranch Slough (UR2S)

Strong Ranch Slough drains a 4,446 acre mixed-use area of the County of Sacramento. At the sampling point, a trapezoidal channel conveys runoff from Strong Ranch Slough into a holding pond (D5 Basin) before being conveyed to the American River via pump or gravity flow.

Sump 111 (UR3)

Sump 111 is a collection point for stormwater drained from an industrialized 439 acre area of the City of Sacramento. Three storm pumps and one summer pump convey water to the American River.

North Natomas Detention Basin No. 4 (UR5)

North Natomas Detention Basin No. 4 is a collection point for stormwater drained from a 470 acre area of residential development in North-West Sacramento before it is pumped into the East Drainage Canal, which is a tributary to the Main Drainage Canal that eventually drains into the Sacramento River.

Table 3. Monitoring Locations

Site Name	Site ID	Longitude	Latitude
Strong Ranch Slough	UR2S	38.585154	-121.418113
Sump 111	UR3	38.601520	-121.492846
North Natomas Detention Basin No. 4	UR5	38.667779	-121.506603

A.6 QUALITY OBJECTIVES AND CRITERIA

The objective of this project is to collect high quality data to characterize, as closely as possible, the effects urban runoff on stormwater discharges. This objective will be achieved by using standard accepted methods to collect and analyze surface water. This program will meet this objective by evaluating all of the collected laboratory data in terms of detection limits, precision, accuracy, representativeness, comparability, and completeness.

A.6.1 Measurement Quality Objectives

Continuous sensors and field meters will be chosen based on the criteria outlined in **Table 4**. Instruments will either meet or exceed these performance criteria.

Method detection limits (MDL) and reporting limits (RLs) must be distinguished for proper understanding and data use. The MDL is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The RL represents the concentration of an analyte that can be routinely measured in the sampled matrix within stated limits and with confidence in both identification and quantitation.

These RLs and MDLs in **Table 4** should be considered as maximum allowable reporting limits to be used for laboratory data reporting. Note that samples diluted for analysis may have sample-specific RLs that exceed these RLs. This will be unavoidable on occasion, but the data must still be qualified when this occurs. However, if samples are consistently diluted to overcome matrix interferences, the analytical laboratory will be required to notify the Monitoring Manager how the sample preparation or test procedure in question will be modified to reduce matrix interferences so that project RLs can be met consistently.

Table 4. Analytical Methods and Project Reporting Limits for Field Parameters

Constituent	Method	Units	Range	Project RL
Depth	Pressure Transducer	cm	NA	1
Velocity	Pressure or Area Velocity	feet/sec	NA	0.1
pH	Electrometric	std. units	0-14	NA
Conductivity	Graphite Electrodes	µs/cm	0-10000	2.5
Temperature	High Stability Thermistor	deg C	-5 – 50	NA
Turbidity	4-Beam	NTU	0-1000	1
Dissolved Oxygen	Optical	mg/L	0-50	0.5
Oxidation Reduction Potential	Electrical	mV	-1000-1000	NA
Fluorescent Dissolved Organic Matter (FDOM)	Fluorescent	ppb	0-1250	1

Table 5. Analytical Methods and Project Method Detection and Reporting Limits for Laboratory Analyses

Constituent	Method	Units	Project MDL	Project RL
Escherichia coli	SM 9221 B&E	MPN/100mL	1	2
Fecal Coliform	SM 9221 B&E	MPN/100mL	1	2
Total Suspended Solids	SM 2540D	mg/L	1	2
Total Dissolved Solids	SM 2540C	mg/L	1	2
Suspended Sediment	ASTMD 3977-97	mg/L	2	3
Turbidity	EPA 180.1	mg/L	0.75	1.0
Conductivity	SM 2510B	mg/L	10	10
Total Organic Carbon	SM 5310B	mg/L	0.05	1.0
Dissolved Organic Carbon	SM 5310B	mg/L	0.05	1.0
Total Phosphorus (as P)	SM 4500-PE	mg/L	0.005	0.01
Total Kjeldahl Nitrogen	SM 4500-NH3C	mg/L	0.07	0.1
Nitrate + Nitrite (as N)	EPA 353.2	mg/L	0.02	0.1
Chemical Oxygen Demand	EPA 410.4	mg/L	20	50
Biochemical Oxygen Demand	SM 5210	mg/L	5	5
Alkalinity	SM 2320 B	mg/L	1.2	10
Conductivity	SM 2510B	mg/L	10	10
Methylmercury	EPA 1630	ng/L	0.02	0.05
Total Mercury	EPA 1631	ng/L	0.2	0.5
Copper (Total and Dissolved)	EPA 200.8	µg/L	0.07	0.5
Iron (Total and Dissolved)	EPA 200.8	µg/L	1.0	2.0
Lead (Total and Dissolved)	EPA 200.8	µg/L	0.25	0.5
Zinc (Total and Dissolved)	EPA 200.8	µg/L	0.7	1.0
Total Hardness	EPA 130.2	mg/L	0.7	1.0
TPH Gasoline	SW846 5030	µg/L	4.7	50
TPH Diesel and Motor Oil	EPA 8015M	µg/L	97	200
OP Pesticides	EPA 625	ng/L	1	5
PAHs	EPA 625	ng/L	1	5
Pyrethroids + Diazinon + Chlorpyrifos + Fipronil	EPA 8270M	ng/L	0.1-2.0	1.5-15

A.6.2 Project Acceptance Criteria

This project will use the acceptance criteria outlined in

Table 6 to validate and assess any collected data.

Table 6. Project Acceptance Criteria for Laboratory Analyses

Parameter	Accuracy	Precision	Recovery	Completeness
Sensor Measurements				
Depth	±20%	NA	NA	90%
Water Velocity	±20%	NA	NA	90%
pH	±0.2 pH units	±0.5 pH units	NA	90%
Temperature	±0.5 °C	5%	NA	90%
Dissolved Oxygen	±0.5 mg/L	10%	NA	90%
Turbidity	5%	5%	NA	90%
Conductivity	5%	5%	NA	90%
Oxidation Reduction Potential	5%	5%	NA	90%
FDOM	5%	5%	NA	90%
Laboratory Analyses				
Conventionals	80 – 120%	0 – 25%	80 – 120%	90%
Nutrients	80 – 120%	0 – 25%	90 – 110%	90%
TPHs	80 – 120%	0 – 25%	80 – 120%	90%
Metals[1] (total and dissolved)	75 – 125%	0 – 25%	75 – 125%	90%
Mercury (total and methyl)	70 – 130%	0 – 25%	70 – 130%	90%
Pesticides and PAHs	50 – 150% or 3x std. deviation	0 – 25%	50 – 150% or 3x std. deviation	90%

1 Copper, lead, iron, and zinc

A.6.2.1 Representativeness

Representativeness can be defined as the degree to which the environmental data generated by the monitoring program accurately and precisely represent actual environmental conditions of interest. For this project, this objective is addressed by the overall design of the monitoring program. Specifically, assuring the representativeness of the data is addressed primarily by selecting appropriate locations, methods, times, and frequencies of sampling for each environmental parameter, and by maintaining the integrity of the sample after collection. Each of these elements of the quality assurance program is addressed elsewhere in this document. Representativeness is also assured by avoiding the introduction of bias in sampling and analytical methods where possible, by recognizing potential sources of bias inherent in the sampling design or methodology, and by controlling these sources of bias where possible.

A.6.2.2 Accuracy

Accuracy is a measure of how close a measurement is to the true value. Accuracy is assessed by evaluating field and method blanks, laboratory control spikes, matrix spikes and surrogate analytes. Accuracy is evaluated in field and method blanks by determining if there is

contamination present in the quality control sample. Contamination is defined as detection of the analyte above the MDL.

Laboratory control spike, matrix spike and surrogate accuracy checks consist of measurements of the recovery of a "spike" of a known concentration, followed by the calculation of percent recovery according to the following formula:

$$R = 100\% * \left[\frac{Cs - C}{s}\right]$$

Where: R = Percent recovery

Cs = spiked sample concentration

C = sample concentration (for spiked matrices)

S = concentration equivalent of spike added

Laboratory control spikes are "spikes" of laboratory created blank water, whereas matrix spikes and surrogates are "spikes" of the sample matrix water.

A.6.2.3 Precision

The precision of data is a measure of the reproducibility of the measurement. Precision is assessed by evaluation of the results for replicate samples and analyses, including field duplicate samples and laboratory duplicate analyses of environmental and QA samples.

Precision is expressed and assessed as the relative percent difference between two measured results. Generally, relative percent difference (RPD) is calculated as:

$$RPD = 100\% * \frac{[R1 - R2]}{\left[\frac{R1 + R2}{2}\right]}$$

Where: *RPD* = the Relative Percent Difference

R_1 = first replicate result,

R_2 = second replicate result.

A.6.2.4 Completeness

Completeness is a measure of the amount of successfully collected and validated data relative to the amount of data planned to be collected for the project, and is usually expressed as a percentage value. Completeness refers to the complete event process of sample reception, chain-of-custody documentation, storage and in-house preservation, extraction, analysis, and laboratory quality assurance and control samples and measures.

A.7 SPECIAL TRAINING AND CERTIFICATION

Organizations and individuals involved in monitoring for this project are expected to have familiarity with this QAPP and its appendices. All staff performing field procedures will receive training to ensure that the work is conducted correctly and safely. The QA officer is responsible for oversight of training and maintaining any documentation.

A.8 DOCUMENTATION AND RECORDS

The project contains documents that aid in the processing and validation of the analytical data as well as the generation of year end deliverables. The data generation documents will be maintained on an event basis according to the timing and process outlined in **Figure 2**. The deliverable documents will be created once all monitoring data is collected and processed, near the end of the monitoring year.

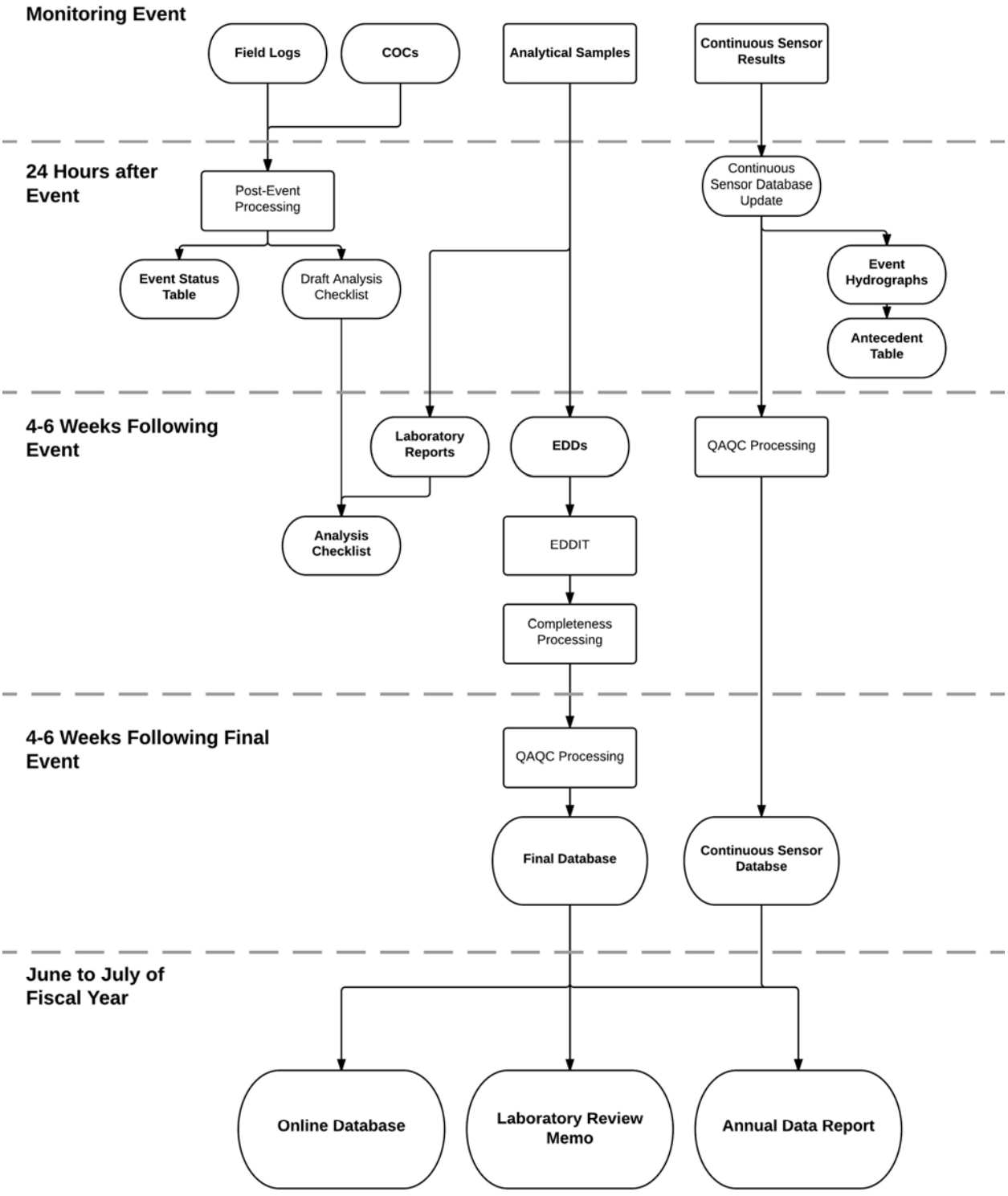

Figure 2. Data Processing and Generation Flow Chart

The following sections summarize are some of the documents and files that this program will generate.

A.8.1 Field and Laboratory Generated Documents

All field activities must be documented to ensure defensibility of any data used for project changes and data interpretation. Hard copies of these files will be stored by the Monitoring Manager and digital versions will be stored in the project specific folder and maintained by the Monitoring Manager. Examples of these files are included in the Sampling and Analysis Plan (SAP). These records will be maintained for at least five years following the completion of the monitoring year.

- Field Logs – Field activities will be documented during each site visit in a field log by the Field Crew.
- Chain of Custody (COC) – The Field Crew will create COCs for any sample that is collected and transferred to a laboratory.
- Analytical Data Reports - Analytical data reports will consist of a hardcopy or equivalent electronic report in each laboratory's standard format, and in an electronic format. All final data reports will include the results of Quality Assurance analyses and a narrative summary of Quality Assurance data for the environmental results reported.
- Electronic Data Deliverables (EDDs) – An EDD will be created for each laboratory report and they will comply with SWAMP standards.
- Continuous Sensor Outputs - Any continuous data measurements collected during this project will be, at the minimum, downloaded monthly. The QA Officer will validate the continuous data prior to inclusion in the database. The database will be stored a project specific folder and maintained by the Monitoring Manager.

A.8.2 Data Generation Documents

These documents will be created and updated on an event basis or as determined by the Monitoring Manager. They will be stored in project specific folders, which will be backed up. These records will be maintained for at least five years following the completion of the monitoring year.

- Event Status – Summary table outlining the events conducted in the current monitoring year. Includes date of event and sites sampled.
- Antecedent Conditions – Event tables describing precipitation based event conditions. Includes sample timing, precipitation timing, storm summaries, and descriptions of storms preceding the event.
- Event Hydrographs – Site specific hydrographs that summarize the rainfall rate, flow rate, cumulative storm flow, and cumulative storm precipitation amount.

- Analysis Checklist – Documents analyses that are requested on the COC and cross-checks it against laboratory results. Contains sites sampled, analyses requested (including QAQC), and analysis received from the laboratories.

- Continuous Database – Annual database containing the continuous results from the monitored sites.

- EDDIT Database – Database tool for entering and analyzing laboratory EDDs.

A.8.3 Deliverable Documents

These deliverables will be created at the conclusion of the monitoring year.

- Annual Data Report - Annual report summarizing the data collected during the monitoring year. Includes conclusions and recommendations for improvement to the program.

- Laboratory Assessment Memo – End of the monitoring year assessment of the laboratory performance. Laboratories will be sent surveys that include requests for updated RLs, MDLs, and pricing. Includes recommendations for modifications to analytical methods and laboratories for future monitoring years.

- Analytical Results Database - Update of the Partnership online database with the processed and verified data from the just completed monitoring year.

B DATA GENERATION AND ACQUISITION

B.1 SAMPLING PROCESS DESIGN

The sampling process design is discussed in depth in the SAP in **Appendix B**.

B.2 SAMPLE COLLECTION METHODS

The following sections outline the standard collection methods that this project will use. The SAP contains a more detailed approach that includes site-specific sampling instructions.

B.2.1 Water Column Samples

This section contains protocol for sampling water quality samples and actions that should be taken by the field crew team to minimize contamination. To reduce potential contamination, sample collection personnel must adhere to the following general sampling rules at all times while collecting or handling water samples:

- No smoking.
- Always wear clean, powder-free, nitrile or similar surgical-quality gloves when handling sample bottles.
- Never sample near a running vehicle. Do not park vehicles in immediate sample collection area (even non-running vehicles).
- Minimize the amount of time any sample bottle is left open.
- Do not set sample bottle lids down where they may accumulate contamination.
- Prevent foreign material (blowing dust, leaves, etc.) from entering any open sample bottle.
- Do not breathe, sneeze, or cough in the direction of an open sample bottle.
- Avoid allowing rainwater to drip from rain gear into sample bottles.
- Never touch the inside surfaces of sample bottles or sample bottle lids, even with gloved hands.
- Never touch the exposed end of a sample tube.

B.2.1.1 Clean Sampling Technique

All water samples will be collected using clean techniques that are designed to minimize sample contamination. Samples are collected using rigorous protocols, based on *EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (*USEPA 1996). This technique is designed for trace metals, but it will be used for all water sample collection. Samples are collected using rigorous protocols, based on EPA Method 1669, as summarized below:

- Samples are collected only into rigorously pre-cleaned sample bottles.

- Pre-cleaned sample bottles and related equipment (tubing, spare bottle lids, etc.) are placed in double zip-lock bags by the laboratory performing the cleaning process.
- At least two persons, wearing clean, powder-free nitrile gloves at all times, are required on a sampling crew.
- One person ("dirty hands") touches and opens only the outer bag of all double bagged items (such as sample bottles, tubing, and lids), avoiding touching the inside of the bag.
- The other person ("clean hands") reaches into the outer bag, opens the inner bag, and removes the clean item.
- After a grab sample is collected, or when a clean item must be re-bagged, it is done in the opposite order from which it was removed.
- Clean, powder-free nitrile gloves are changed whenever something not known to be clean has been touched.
- Water samples are most cleanly obtained by surface grab, using clean powder-free nitrile gloved hands, and facing into a flowing body of water. If samples are taken from depth, the only non-contaminating method generally available is pumping. A peristaltic pump is used with a short piece of freshly cleaned silicone tubing in the pump. The remainder of the sampling tubing must be Teflon. Once cleaned, silicone tubing quickly absorbs air borne contaminants, and therefore must be double bagged until use.

For this program, clean techniques must be employed whenever handling any of the tubing, composite bottles and lids, and grab samples.

B.2.1.2 Direct Submersion: Hand Technique

Where practical, all grab samples will be collected by direct submersion at mid-stream, mid-depth using the following procedures.

1. Wear clean powder-free nitrile gloves when handling containers and lids. Change gloves if soiled or if the potential for cross-contamination occurs from handling sampling materials or samples.
2. Use pre-labeled sample containers as described in the Sample Container Labeling section.
3. Remove the lid, submerge the container to mid-stream/mid-depth, let the container fill and secure the lid.
4. Place the sample on ice.
5. Collect the remaining samples including quality control samples, if required, using the same protocols described above.
6. Fill out the COC form, note sample collection time on the field log sheet, and deliver samples to the appropriate laboratory.

B.2.1.3 Intermediate Container Technique

Samples may be collected with the use of a specially cleaned intermediate container, if necessary, following the steps listed below. A secondary container may include a container that is similar in composition to the sample container or a pre-cleaned container made of the same material as the sample container.

1. Wear clean powder-free nitrile gloves when handling bottles and lids. Change gloves if soiled or if the potential for cross-contamination occurs from handling sampling materials or samples.

2. Use pre-labeled sample containers as described in the Sample Container Labeling section.

3. Submerge the intermediate container to mid-stream/mid-depth (if possible), let the container fill, and quickly transfer the sample into the individual sample container(s) and secure the lid(s).

4. Place the sample(s) on ice.

5. Collect remaining samples including quality control samples, if required, using the same protocols described above.

6. Fill out the COC form, note sample collection time on the field log sheet, and deliver the samples to the appropriate laboratory.

B.2.1.4 Pumping

The use of a peristaltic pump is will be necessary for sites that are inaccessible to direct submersion or the intermediate container technique. Samples may be collected with the use of a peristaltic pump and specially cleaned tubing following the steps listed below.

1. Wear clean powder-free nitrile gloves when handling bottles, lids, and pump tubing. Change gloves if soiled or if the potential for cross-contamination occurs from handling sampling materials or samples;

2. Use pre-labeled sample containers as described in the Sample Container Labeling section;

3. Attach pre-cleaned tubing into the pump, exercising caution to avoid allowing tubing ends to touch any surface known not to be clean. A separate length of clean tubing must be used at each sample location for which the pump is used;

4. Place one end of the tubing below the surface of the water. To the extent possible, avoid placing the tubing near the bottom of the channel so that settled solids are not pumped into the sample container.

5. Hold the other end of the tubing over the opening of the sample container, exercising care not to touch the tubing to the sample container.

6. Pump the necessary sample volume into the sample container and secure the lid;

7. Place the sample on ice;

8. Collect remaining samples including quality control samples, if required, using the same protocols described above; and

9. Fill out the COC form, note sample collection time on the field log sheet, and deliver the samples to appropriate laboratory.

B.2.1.5 Sample Filtration[1]

USGS will filter any dissolved metal samples upon receipt, but if a secondary laboratory is used, then dissolved metals must be filtered in the field. Dissolved metals samples are field filtered immediately after collection. The recommend type vacuum filter has an intake reservoir (500 mL), an applied vacuum attachment, and a filtrate receiver reservoir. To minimize the risk of contamination, filter blanks for metals should be analyzed, anytime a new filter product is used. The recommended filtration procedure is as follows, however, based on results of filter blanks, the procedure can be modified to ensure that contamination is negligible (<10% of environmental concentration).

1. The sample will be either collected with an intermediate container or pumped directly into the reservoir. If the sample is a composite, it will need to be composited into the reservoir to.

2. The "discharge" end of sample collection pump apparatus pump (flexible) tubing is attached to the filter vacuum valve and the pump is reversed to apply vacuum suction on the filter apparatus.

3. After sufficient filtrate (>300 mL) is collected in the receiver reservoir, the vacuum suction is removed.

4. The receiver reservoir is removed and the filtrate is transferred to the laboratory-provided bottle.

5. The chain of custody should clearly indicate that the sample was field filtered in the notes and the sample ID so that it can be distinguished from the total recoverable metals sample

B.2.2 Field Measurements

Field measurements for conductivity, turbidity, dissolved oxygen, temperature, and pH shall be taken at each sampling station, each time the station is sampled. Field measurements shall be collected soon after grab samples have been taken. They should be located just upstream from the water quality sample collection and approximately mid-depth and mid-channel. Field crews will note the exact time measurements are taken.

B.2.3 Flow Measurements

Flow data will be collected by continuous sensors installed at each sampling location. During site visits, field crews will provide estimates for channel or discharge depth.

[1] http://www.epa.gov/waterscience/methods/method/inorganics/1669.pdf

B.2.4 QC Sample Collection

The field crew will collect QC samples for each event, based on the schedule outlined in **Table 11**. The following are collection methods for any required QC samples.

B.2.4.1 Equipment Blanks

Blank water will be run through any laboratory cleaned equipment before the sampling event occurs.

B.2.4.2 Field Blanks

Field blanks will be collected before collecting any other samples at a site. The field blank will be collected in the same method as the environmental sample.

Pump

Blank water will be run through the pump before being collected in the respective sampling container.

Direct Fill

Blank water will be poured directly into the sampling container

Intermediate Container

Blank water will be poured into the clean intermediate container and then transferred to the sample container.

Composite Container

Blank water will be poured into a clean composite container and then transferred to the laboratory for analyses.

The field crew will also collect a dissolved metals filter blank, by filling the filter reservoir with blank water and applying vacuum suction.

B.2.4.3 Field and Laboratory Duplicates

Field duplicates will be collected immediately following the collection of the corresponding environmental sample. Field duplicates will be collected in the same manner as the environmental sample. If laboratory duplicates are required, the field crew will use sample containers that can contain twice the optimum volume for an analysis. The analytical laboratory will then be responsible for analyzing the sample for both an environmental and duplicate result.

B.2.4.4 Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

If MS/MSDs are required for a specified analyte then additional volume will be collected directly after the environmental sample collection. MS/MSDs require the collection of three times the optimum (

Table 9**)** sample volume.

B.2.5 Sample Container Sizes, Preservation and Collection Method

Sample containers must be pre-cleaned and/or certified free of contamination according to the specification for appropriate analytical methods. **Table 7** provides the requirements for sample volume, bottle type and preservation for each analyte.

Table 7. Constituents to be Analyzed, Sample Volume Required, and Sample Type

Constituent	Method[1]	Sample Container	Preservation	Maximum Analytical Hold Time
BOD_5	SM 5210	Plastic/Glass	0-6˚C	48 Hours
Alkalinity	SM 2320	Plastic/Glass	0-6˚C	14 days
Total Dissolved Solids	SM 2540-C	Plastic/Glass	0-6˚C	7 days
Total Suspended Solids	SM 2540-D	Plastic/Glass	0-6˚C	7 days
Turbidity	EPA 180.1	Plastic/Glass	0-6˚C	48 Hours
Electrical Conductivity	SM 2540-C	Plastic/Glass	0-6˚C	28 days
Suspended Sediment	ASTMD 3977-97	Plastic/Glass	0-6˚C	120 days
COD	EPA 410.4	Plastic/Glass	H_2SO_4, 0-6˚C	7 days
Total Phosphorus (as P)	SM 4500-PE	Plastic/Glass	H_2SO_4, 0-6˚C	28 days
Total Kjeldahl Nitrogen	SM 4500-NH3	Plastic/Glass	H_2SO_4, 0-6˚C	28 days
Nitrate + Nitrite (as N)	EPA 353.2	Plastic/Glass	H_2SO_4, 0-6˚C	28 days
Total Organic Carbon	SM 5310B	Plastic/Glass	H_2SO_4 or HCl, 0-6˚C	28 days
Dissolved Organic Carbon	SM 5310B	Plastic/Glass	Filter then H_2SO_4, 0-6˚C	28 days
Hardness, total	SM 2340	Plastic/Glass	HNO_3, 0-6˚C	6 months
Metals, total (Cu, Ni, Pb, Zn)	EPA 200.8	Plastic/Glass	HNO_3, 0-6˚C	6 months
Metals, dissolved (Cu, Ni, Pb, Zn)	EPA 200.8	Plastic/Glass	HNO_3, 0-6˚C	6 months
Methylmercury	EPA 1630	Teflon/Glass	HCl, 0-6˚C	6 months
Total Mercury	EPA 1631	Teflon/Glass	HCl, 0-6˚C	90 days
OP Pesticides	EPA 625	Glass	0-6˚C	7 days
PAHs	EPA 625	Glass	0-6˚C	7 days
Pyrethroids + (Diazinon , Chlorpyrifos, Fipronil)	EPA 8270M	Glass	0-6˚C	3/7 days

1 SM = Standard Methods for the Examination of Water and Wastewater; EPA = EPA Methods for Chemical Analysis of Water and Wastes.

B.2.6 Cleaning Procedures

Prior to the installation of tubing and bottles, tubing and/or any carboys will be cleaned via the standard protocol outlined in the SAP and a sample will be collected and analyzed for total

mercury, methyl mercury, and TOC. If significant contamination is found, new clean tubing and/or carboys will be used for sample collection.

B.3 SAMPLE HANDLING AND CUSTODY

The Sub-consultant Field Engineer will ensure that all samples are collected and submitted to their respective labs by the maximum hold times listed in **Table 7**. If sample timing or logistics prevent a hold time being met the field crew will contact the Monitoring Manager.

B.3.1 Sample Bottle Labels

The field crew will label all grab sample bottles with a waterproof label, which will contain the project name, sample collection date, analyte, analysis method, site ID and name, storm event number and field crew names. This information will be taken **Table 7**. Composite samples will be labeled with the project name, sample collection date, site ID and name, storm event number and field crew names. Any samples that are to be split from the composite volume will require labels with the same information as the grab samples. Both grab and composite samples shall be labeled using the names listed in **Table 8**. In addition, quality control samples submitted "blind" to the laboratory shall be labeled using the fictitious names also listed in **Table 8**.

Table 8. Site Names for Sample Handling

Station Number	Station Name
UR2S	Strong Ranch Slough
UR3	Sump 111
UR5	North Natomas Detention Basin
UR6	Clear Creek (field blank)
UR7	Newt Creek (field duplicate)

B.3.2 Transport

All samples shall be kept on ice from the time of collection to the time of receipt by laboratory personnel. It is imperative that all samples be analyzed within maximum holding times (**Table 7**). Samples shall be shipped/delivered as specified in

Table 9.

Table 9. Analytical Laboratories

Analytical Laboratory	Analysis	Shipping Method
Caltest Attn: Melinda Kelley 1885 North Kelly Road Napa, CA 94558 707.258.4000	Conventional analyses, Total and dissolved metals Total mercury and methylmercury	Courier
PHYSIS Environmental Laboratories ATTN: Misty B. Mercier 1904 East Wright Circle Anaheim, CA 92806 Phone: 714.602.5320 x202 E-mail: mistymercier@physislabs.com	OP Pesticides and PAHs	Overnight (next morning) delivery
SRCSD EL Attn: Celeste Patena 8521 Laguna Station Road Elk Grove, CA 95758 Phone: 916.875.9027 (direct) 916.875.9000 (main) Fax: 916.875.9069 E-mail: cookm@sacsewer.com	Bacteriological	Drop-off within 6 hours of sampling

B.3.3 Chain of Custody Form

Sample custody procedures are used for documenting information related to sample collection and handling. Sample custody must be traceable from time of sample collection until the results are reported. Chain-of-custody (COC) forms shall be filled out by the field crew for all samples and will remain with the samples until they are received by the analytical laboratory. COCs will contain the following information:

- Sampler name
- Address (where the results will be sent)
- To whom the laboratory results need to be sent
- Sample collection date and time
- Sample location
- Analysis requested (**Table 7**)
- Sample container type and number
- Comments/special instructions

- Samples relinquished by (signature, print name, date)
- Samples received by (signature, print name, date)

In the comments/special instructions section of the COC the field crew will request necessary lab duplicate samples and MS/MSD samples as required by

Table 10 and **Table 11**. The field crew will also note that field dissolved samples were filtered in the field. An electronic data deliverable will be requested for all sample reports. Example lab specific COCs are included in the SAP (**Appendix B**).

B.4 ANALYTICAL METHODS

B.4.1 Project SOPs

Laboratory standard operating procedures (Laboratory SOPs) for all sampling and analytical procedures performed for this program are listed and provided in **Appendix A**. These Laboratory SOPs document any options or modifications from standard method procedures and identify all equipment or instrumentation necessary for the analyses. Corrective measures, responsibilities, and documentation requirements are detailed in the QA Manuals for individual laboratories. Corrective measures to address specific QA problems are also summarized in **Appendix A**.

B.4.2 Sample Disposal Procedures

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals. Procedures for proper disposal are documented in Laboratory SOPs (**Appendix A**).

B.5 QUALITY CONTROL

Quality control (QC) is achieved by collecting and analyzing duplicate, blank, spike and spike duplicate samples to ensure that analytical results are within the specified QC objectives. Field crews will collect QC samples and the QA Officer will use the QC results to validate the collected environmental data. Quality control sample results will be used for data evaluation and interpretation. Quality control samples will be collected for the constituents in

Table 10.

Table 10. Quality Control Samples

	Rinsate Blank	Field Duplicate	Field Blank	MS/MSD
Pyrethroid Pesticides		X	X	X
OP-Pesticides		X	X	X
PAHs	X	X	X	X
Petroleum Hydrocarbons		X		
TOC	X	X	X	
DOC		X		
Nutrients		X		
Total Metals	X	X	X	X
Total Hardness		X		
Dissolved Metals (Filter Blank)		X	X	X
Methylmercury	X	X	X	X
Total Mercury	X	X	X	X
Conventionals		X		
Fecal coliform and *Escherichia coli*		X	X	

B.5.1 Quality Control Sample Collection Schedule

The field crew will collect quality control samples once during each monitoring event. For collection methods and procedures the SAP.

B.5.1.1 Equipment Blanks

Equipment blanks will be collected by the Field Coordinator, prior to each monitoring event. Blank water will be run through pre-rinsed tubing and collected to be analyzed by the laboratory for total metals and mercury. The Field Coordinator will check laboratory results, if they are received before the next event and brand new tubing will be used if contamination is found.

B.5.1.2 Sampling Event Quality Control Samples

For each storm event, the laboratory and field crew will run the QA/QC analyses in **Table 11**.

Table 11. Quality Control Requirement

Quality Control Sample Type	QA Parameter	Frequency	Measurement Quality Objective	Corrective Action
Quality Control Requirements – Field				
Equipment Blanks	Accuracy	After every equipment cleaning	< RL	Identify equipment contamination source. Re-clean or use new equipment.
Field Blank	Accuracy	Once per event	< RL	Examine field log. Identify contamination source. Qualify data as needed.

Quality Control Sample Type	QA Parameter	Frequency	Measurement Quality Objective	Corrective Action
Field Duplicate	Precision	Once per every two events	RPD ≤ 25% if |Difference| ≥ RL	Reanalyze both samples if possible. Identify variability source. Qualify data as needed.
Quality Control Requirements – Laboratory				
Method Blank	Accuracy	Once per analytical batch	< RL	Identify contamination source. Reanalyze method blank and all samples in batch. Qualify data as needed.
Lab Duplicate	Precision	Once per every two events	RPD ≤ 25% if |Difference| ≥ RL	Recalibrate and reanalyze.
Matrix Spike	Accuracy	Once per event	80-120% Recovery for conventionals 75-125% for Metals 70-130% for mmHg 50-150% or historical laboratory control limits (±3 SD) for Organics	Check LCS/SRM recovery. Attempt to correct matrix problem and reanalyze samples. Qualify data as needed.
Matrix Spike Duplicate	Precision	Once per event	RPD ≤ 25% if |Difference| ≥ RL	Check lab duplicate RPD. Attempt to correct matrix problem and reanalyze samples. Qualify data as needed.
Laboratory Control Spike	Accuracy	Once per analytical batch	80-120% Recovery for conventionals 75-125% for Metals 70-130% for mmHg 50-150% or historical laboratory control limits (±3 SD) for Organics	Recalibrate and reanalyze LCS and samples.
Laboratory Control Spike Duplicate	Precision	Once per analytical batch	RPD ≤ 25% if |Difference| ≥ RL	Check lab duplicate RPD. Attempt to correct matrix problem and reanalyze samples. Qualify data as needed.

SD = Standard Deviation

B.5.2 Quality Control Data Validation

The QA Manager is responsible for ensuring all of the laboratory data meet rigorous data validation criteria. Once all of the laboratory data is received, the QA Manager will begin to check the data for accuracy and precision. Quality control samples will be reviewed according to the standards outlined in the following subsections, and qualified as summarized in **Table 12**.

Table 12. Summary of Measurement Quality Objectives

Quality Control Sample Type	SWAMP QA Code
Field Blank	IP
Method Blank	IP
Field Duplicate	FDP
MS/MSD	GB
MSD	IL
LCS/LCSD	EUM
LCSD	IL
Surrogates	GN

B.5.2.1 Accuracy

Accuracy checks consist of measurements of the recovery of a "spike" of a known concentration, followed by the calculation of percent recovery (see Section A.6.2.2). Recoveries will be evaluated based on contamination in blank samples and high or low biases in percent recoveries.

Contamination

Contamination of samples is assessed using equipment, method, and field blanks. Blanks are prepared using reagent grade de-ionized water that is assumed to be void of all constituents for which a given set of analyses are to be performed. These blanks are tested using analytical procedures identical to those used for the environmental samples. The conditions under which the blanks are prepared follow, as closely as possible, the conditions in the field or laboratory, as appropriate for the blank type.

B.5.2.1.1.1 Equipment Blank

Bottle blanks are preseason blanks that check for any contamination in the carboy or tubing cleaning procedures. If contamination is present in the sample results then new tubing or carboys will be used. If tubing and/or carboys are new or are not being used in the sampling design than their respective equipment blank does not need to be run.

B.5.2.1.1.2 Method Blank

Method blanks are prepared by the laboratory using blank water and will be analyzed once per event. The method blank is tested using analytical procedures identical to those used for the environmental samples. A detected concentration in a method blank is an indication of contamination in the analytical process.

When a detected concentration is reported, qualification of the QA/QC data and the corresponding environmental data is carried out according to SWAMP protocols as follows:

- Each method blank result that exceeds the method detection limit (MDL) is qualified with an “IP” (analyte detected in method, trip, or equipment blank).

- Each detected environmental sample with a concentration of less than five times the concentration measured in an associated, detected method blank is considered to be an upper limit of its true concentration due to method blank contamination and is qualified with an “IP” (analyte detected in method, trip, or equipment blank).

Field Blank

A field blank is prepared in the field using procedures that simulate the actual field sampling procedures. A detected value reported for a field blank indicates that contamination has occurred at some point during the field sampling or analytical procedures. The detection of an analyte in a field blank sample does not necessarily mean that the contamination significantly affects a particular environmental result. Field blanks will be collected at one site per event.

When a detected concentration is reported, qualification of the QA/QC data and the corresponding environmental data is carried out according to SWAMP protocols as follows:

- Each field blank result that exceeds the method detection limit (MDL) is qualified with an “IP” (analyte detected in method, trip, or equipment blank).

- Each detected environmental sample with a concentration of less than five times the concentration measured in an associated, detected method blank is considered to be an upper limit of its true concentration due to method blank contamination and is qualified with an “IP” (analyte detected in method, trip, or equipment blank).

Recovery

B.5.2.1.1.3 Laboratory Control Spike

Laboratory control spike (LCS) analyses are batch checks for recovery of a known concentration of a standard solution used to assess the accuracy of the entire laboratory analytical process. LCS samples are standards prepared internally by the laboratory using a known amount of analyte. LCS samples are analyzed in the same manner as the environmental samples. When an out-of-control recovery is reported, qualification of the QA/QC data and the corresponding environmental data will be carried out according to SWAMP protocols as follows:

- Each out-of- control LCS is qualified with “EUM” (LCS is outside of control limits).

- The environmental data associated with the LCS are qualified with “EUM” (LCS is outside of control limits), unless a matrix spike associated with the environmental sample is in control. These environmental data may be considered "high biased" when one or both spike recoveries are greater than the upper recovery limit and the environmental result is above the MDL and "low biased" when one or both spike recoveries are less than the lower recovery limit (the environmental result may be undetected, below the MDL).

B.5.2.1.1.4 Matrix Spike

Matrix spike analysis involves the introduction of a known spike in the original "matrix" (sample solution) and is a measure of the accuracy of the recovery performance of the laboratory. To perform this analysis, the laboratory generally requires an additional volume of sample. Matrix interference can lead to recovery problems and raised detection limits. Re-analysis is the first corrective action once matrix interference problems are identified, but re-analysis is only possible when sufficient sample volume is available. When an out-of-control recovery is reported, qualification of the QA/QC data and the corresponding environmental data will be carried out according to SWAMP protocols as follows:

- Each out-of-control matrix spike is qualified with “GB” (matrix spike recovery not within control limits).
- The environmental samples associated with matrix spikes (i.e., collected at the same location as the matrix spike sample) are qualified with “GB” (matrix spike recovery not within control limits). The environmental samples associated with matrix spikes may be considered "high biased" when one or both spike recoveries are greater than the upper recovery limit and the environmental result is above the MDL and "low biased" when one or both spike recoveries are less than the lower recovery limit (the environmental result may be undetected, below the MDL).

B.5.2.1.1.5 Surrogate

Environmental surrogate matrix spikes are used as a check on the extraction process for organic compounds. Surrogate organic compounds (“surrogates”) are spiked or added to all environmental samples, field-initiated QA/QC samples, and laboratory-initiated QA/QC samples analyzed for trace organics. These surrogate compounds provide a measure of the efficiency of the organic compound extraction process when testing samples using gas chromatography (GC) or gas chromatography-mass spectroscopy (GC/MS) analytical methods.

- Out-of-control surrogate spike recoveries are qualified with “GN” (surrogate recovery is outside of control limits). No environmental data qualification occurs; however, if the corresponding laboratory control spike recoveries are also out-of-control, the laboratory is consulted to determine if and how the environmental results might have been affected.

B.5.2.2 Precision

Precision is the measurement of the difference between samples that are presupposed to be replicates (i.e., collected and analyzed in the same manner). Precision is discussed in more detail in **Section A.6.2.3**.

Field Precision

Field precision will be measured by collecting field duplicate samples directly after the environmental sample and will be submitted to the laboratory as separate samples. These samples will provide a measure of the concentration variability introduced by field procedures. When a field precision RPD exceeds the maximum allowable value (MAV), qualification of the QA/QC data and the corresponding environmental data will be carried out according to SWAMP protocols as follows:

- Each duplicate sample with out-of-control RPDs is qualified with "FDP" (RPD exceeds control limit).

- Each environmental sample associated with a duplicate sample is qualified with "FDP" (RPD exceeds control limit). These environmental samples are considered to be irreproducible due to sampling, variability.

Laboratory Precision

Laboratory precision will be measured through laboratory, laboratory control spike and matrix spike duplicates. When a laboratory precision RPD exceeds the maximum allowable value (MAV), qualification of the QA/QC data and the corresponding environmental data will be carried out according to SWAMP protocols as follows:

- Each duplicate sample with out-of-control RPDs is qualified with "IL" (RPD exceeds laboratory control limit).

- Each environmental sample associated with a duplicate sample is qualified with "IL" (RPD exceeds laboratory control limit). These environmental samples are considered to be irreproducible due to laboratory, sampling, or matrix spike variability.

B.5.2.2.1.1 Laboratory Duplicate

Laboratory duplicates are samples split in the laboratory to measure the precision of the laboratory analysis, including the sub-sampling process (the process of deriving a sample from a parent sample).

B.5.2.2.1.2 Laboratory Control Spike Duplicate

Laboratory control spike duplicate (LCS, Lab Replicate 2 (or greater)) analyses are performed to check the precision of the laboratory control spike recovery. RPDs are calculated from the laboratory control spike and laboratory control spike duplicate percent recoveries. Laboratory control spike duplicates will be run once for each event.

B.5.2.2.1.3 Matrix Spike Duplicate

Matrix spike duplicate (MS1, Replicate 2) analyses are performed to check the precision of the matrix spike recovery. Ideally, triple the normal sample volume is provided to the analytical laboratory for the analysis of a matrix spike and a matrix spike duplicate. RPDs are calculated from the matrix spike and matrix spike duplicate percent recoveries. Matrix spike duplicates will be run at one site for each event.

When a field or laboratory precision RPD exceeds the maximum allowable value (MAV), qualification of the QA/QC data and the corresponding environmental data will be carried out according to SWAMP protocols as follows:

- Each duplicate sample with out-of-control RPDs is qualified with "IL" (RPD exceeds laboratory control limit).

- Each environmental sample associated with a duplicate sample is qualified with "IL" (RPD exceeds laboratory control limit). These environmental samples are considered to be irreproducible due to laboratory, sampling, or matrix spike variability.

B.6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION AND MAINTENANCE

B.6.1 Instruments Requiring Calibration

Equipment and instruments requiring periodic calibration are identified in the SOPs for each analytical or measurement method. These include meters used for field measurements, continuous sensors and all analytical instrumentation.

B.6.1.1 Calibration Procedures and Schedule

Instruments for field measurements and continuous sensors will be calibrated at a frequency recommended by the manufacturer. Within 24 hours of the sampling event start time, the Field Team coordinator will check and calibrate any necessary field instruments.

Calibration procedures are performed according to the manufacturer's SOPs. All calibrations will be documented in a calibration log or field sheet.

B.6.1.2 Corrective Actions for Calibration

Any issues with the calibration of the instrument should be noted in the documentation and the instrument should be recalibrated once the cause is corrected. Before the instrument is used for sampling it should have a clean calibration with no issues. If it is suspected that calibration deficiencies have affected sampling results than those results need to be qualified and reported in the final reports.

B.7 DATA MANAGEMENT

The Monitoring Manager is responsible for all data management and retention. The original data sheets, and reports produced during monitoring will be accumulated into project-specific files. After verification and final database establishment, the raw data files and databases will be copied to a separate database file for storage on site. The original data sheets, statistical worksheets, and reports produced are accumulated into project-specific files. Final report text and tables are also stored on disk. In-house copies of data files are made on CD when submitted. Records will be maintained for at least five years. The records and analyses pertaining to accreditation are kept for a minimum of five years.

C ASSESSMENT AND OVERSIGHT

Compliance with quality control procedures will be assessed routinely during the data collection phase.

- Performance assessments of sampling procedures will be performed by the field sampling crews. These assessments consist of observation of field operations to ensure consistency and compliance with sampling specifications. They are performed continually during sampling. There are no formal reports for this assessment activity.

- Assessment of laboratory QC results will be the responsibility of the QA officer at each laboratory and shall be reported to the Quality Assurance Manager as part of any data reports.

Routine procedures to assess precision and accuracy, criteria for success, and corrective actions have been discussed previously (Section B.5). These assessments will be performed for every sample event.

D DATA VALIDATION AND USABILITY

D.1 DATA REVIEW, VERIFICATION, AND VALIDATION

Data will be reviewed and validated by the QA Manager using the criteria documented in Section B.5. The Project QAPP must be used to accept, reject, or qualify the data generated by the laboratory. The Project Manager shall convey the QA/QC acceptance criteria to the laboratory management. The laboratory management will be responsible for validating the data generated by the laboratory. The laboratory's personnel must verify that the measurement process was "in control" (i.e., that all specified data quality objectives were met or acceptable deviations explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, each laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

Only data that have met data quality objectives, or data that have acceptable deviations explained will be submitted by the laboratory. When QC requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable. The Monitoring Manager will be responsible for determining if the validated laboratory data meets the project acceptance criteria.

After data entry or data transfer procedures are completed for each sample event, data should be inspected for data transcription errors, and corrected as appropriate. After the final QA checks for errors are completed, the data should be added to the final database.

D.2 VERIFICATION AND VALIDATION METHODS

Data verification is the process for evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual specifications. The field crews and laboratories are primarily responsible for data verification.

- Field crews are responsible for verifying field records for completeness and accuracy, including field logs and records of samples collected and COCs, and for field measurement data. The outputs for this verification process are the verified field documents and data, and the sample event summary documents whether all samples were successfully collected and reasons for any lack of completeness.

- Laboratories are responsible for verifying that all samples are analyzed by the project specified methods and meet other project-specific requirements (e.g., reporting limits), and that the data are accurately calculated, transcribed, and reported.

Data validation is an analyte- and sample– specific process that extends the evaluation of data beyond method, procedure, or contractual compliance to determine the quality of a specific data set relative to the end uses. Data validation includes inspection of the verified data and data verification records; a review of the verified data to determine the analytical quality of the data set; and production of a data validation report and qualified data (if applicable). Specific items that will be reviewed during data validation are:

- Chain of custody records

- Documentation of the laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

The Monitoring Manager is responsible for data validation prior to submitting any data to Regional Board. The Project QA Officer will provide independent oversight and resolution of any specific QA issues.

APPENDIX A

Laboratory Standard Operating Procedures

Methods Summary for City of Citrus Heights LID Study
USGS, M. Marvin-DiPasquale

Analysis	Matrix	Sub-sample Vial	Filtered?	Preservation	Holding Time	Reference
Methylmercury	Stormwater	PETG, 125 ml	NO	0.5% tc HCL final, refrig. 4-6°C	6 months	DeWild, J.F., Olson, M.L., and Olund, S.D., 2001, Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection: U.S. Geological Survey Open-File Report 01–445, 19 p.
Mercury, total	Stormwater	PETG, 125 ml	NO	0.5% tc HCL final, refrig. 4-6°C	90 days	EPA, 2002, Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: U.S. Environmental Protection Agency, Office of Water EPA-821-R-02-019, 46 p.
Mercury, reactive	Stormwater	PETG, 125 ml	NO	refrig. 4-6°C	7 days	USGS, 2014, Standard Operating Procedure (SOP): Determination of Reactive Mercury in Surface Water by Direct Tin-Reduction of Inorganic Hg(II), Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry [not published]: U.S. Geological Survey, 13 p.
Total suspended solids (TSS)	Stormwater	NA	Whatman GF/F, 47 mm, preweighed	frozen, -80 C	7 days	APHA, 1981, Section 209 C: Total Nonfiltrable Residue Dried at 103-105 oC, in Franson, M.A.H., ed., Standard Methods for the Examination of Water and Wastewater, 15th Edition: Washington, D.C., Amer. Public Health Association, Amer. Water Works Assoc., Water Pollut. Control Fed., p. 94-95.
Metals, total recoverable (Cu, Ni, Pb, & Zn)	Stormwater	I-CHEM VOA, 40 ml	NO	0.15% tc HNO3 final, refrig. 4-6°C	6 months	USEPA, 1996, Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry: U.S. Environmental Protection Agency, Office of Water, 50 p.
Metals, dissolved metals (Cu, Ni, Pb, & Zn)	Stormwater	I-CHEM VOA, 40 ml	0.1 µm, PALL Acrodisc, syringe	0.15% tc HNO3 final, refrig. 4-6°C	6 months	USEPA, 1996, Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry: U.S. Environmental Protection Agency, Office of Water, 50 p.
Sulfate	Stormwater	Scint vial, 20 ml, glass, combusted	0.1 µm, PALL Acrodisc, syringe	refrig. 4-6°C	28 days	USEPA, 2000, EPA Method 9056A Rev. 1.0 - Determination of Inorganic Anions by Ion Chromatography. : U.S. Environmental Protection Agency, 19 p.

U.S. Department of the Interior
U.S. Geological Survey

Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

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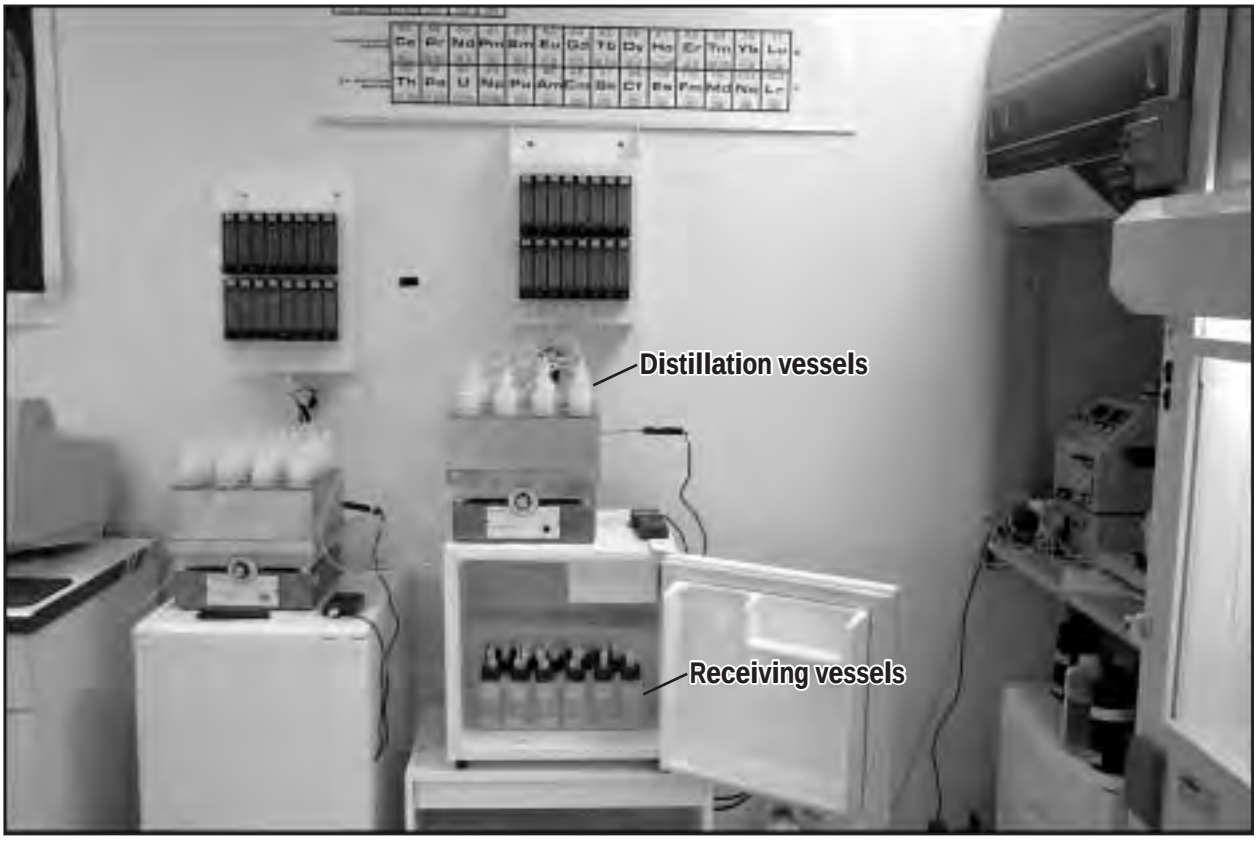

USGS
science for a changing world

Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

By John F. De Wild, Mark L. Olson, and Shane D. Olund

U.S. GEOLOGICAL SURVEY
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Middleton, Wisconsin
2002

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ABBREVIATED WATER-QUALITY UNITS

Abbreviated water-quality units used in this report: Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (µg/L) or nanograms per liter (ng/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. One thousand nanograms per liter is equal to one microgram per liter.

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8\ (°C) + 32.$$

Other Abbreviations Used in this Report:

ng/L	nanograms per liter (parts per trillion)
ng/mL	nanograms per milliliter (parts per billion)
mg/L	milligrams per liter
µg/g	micrograms per gram (parts per million)
g	gram
mg	milligram (10^{-3} grams)
µg	microgram (10^{-6} grams)
ng	nanograms (10^{-9} grams)
pg	picogram (10^{-12} grams)
N	normality (the number of equivalents per liter of solution)
M	molarity (the number of moles of solute per liter of solution)
MΩ	microMohs
cm	centimeters (10^{-2} meters)
mm	millimeters (10^{-3} meters)
µM	micron (10^{-3} millimeters)
L	liters
mL	milliliters (10^{-3} liters)
µL	microliters (10^{-6} liters)
mL/min	milliliters per minute
in	inches

Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

by John F. De Wild, Mark L. Olson, and Shane D. Olund

Abstract

A recent national sampling of streams in the United States revealed low methyl mercury concentrations in surface waters. The resulting median and mean concentrations, calculated from 104 samples, were 0.06 nanograms per liter (ng/L) and 0.15 ng/L, respectively. This level of methyl mercury in surface water in the United States has created a need for analytical techniques capable of detecting sub-nanogram per liter concentrations. In an attempt to create a U.S. Geological Survey approved method, the Wisconsin District Mercury Laboratory has adapted a distillation/ethylation/gas-phase separation method with cold vapor atomic fluorescence spectroscopy detection for the determination of methyl mercury in filtered and unfiltered waters. This method is described in this report. Based on multiple analyses of surface-water and ground-water samples, a method detection limit of 0.04 ng/L was established. Precision and accuracy were evaluated for the method using both spiked and unspiked ground-water and surface-water samples. The percent relative standard deviations ranged from 10.2 to 15.6 for all analyses at all concentrations. Average recoveries obtained for the spiked matrices ranged from 88.8 to 117 percent. The precision and accuracy ranges are within the acceptable method-performance limits. Considering the demonstrated detection limit, precision, and accuracy, the method is an effective means to quantify methyl mercury in waters at or below environmentally relevant concentrations.

INTRODUCTION

Presently (2002), 41 States in the Nation have issued fish consumption advisories because of the high levels of mercury (Hg) in fish (U.S. Environmental Protection Agency, 2001a). Over the past 15 years, scientists have revealed that methyl mercury (CH_3Hg^+) is the specific form of mercury that bioaccumulates most readily in mammals (Bloom, 1992), is the most toxic, and where research priorities are needed to better understand and respond appropriately to this widespread contamination problem. Within the U.S. Geological Survey (USGS), the importance of Hg as a contaminant is demonstrated in that it has been selected as one of five priority issues to be addressed over the next 10 years as part of the National Water-Quality Assessment (NAWQA) program. Because of the increased awareness of environmental Hg contamination, and the understanding that the production and bioaccumulation of CH_3Hg^+ drives the contamination problem, the need for a reliable analytical method for CH_3Hg^+ has increased. Horvat and others (1993) were the first to describe a distillation/ethylation/gas-phase separation method for CH_3Hg^+, which greatly reduces matrix-interference problems, and that largely has been adopted worldwide by Hg research laboratories. Since the start up of the USGS Wisconsin District Mercury Laboratory (WDML) in 1995, an adaptation of this method has been the operational method for CH_3Hg^+ determinations. The purpose of this report is to document the method and describe the results of a methodological test of the WDML's ability to provide quality data at ng/L concentrations for CH_3Hg^+ in water samples.

SUMMARY OF METHOD

Water samples are distilled to remove potential matrix interferences. The pH of the distillate is adjusted to 4.9 (to maximize ethylation potential) using acetate

buffer. The distillate then is ethylated using sodium tetraethyl borate ($NaBEt_4$) and allowed to react for 15 minutes. After reaction with $NaBEt_4$, the distillate is purged with nitrogen gas (N_2) for 20 minutes and the ethylated mercury species are collected on a sample trap containing Carbotrap. These ethylated mercury species are desorbed thermally from the sample trap, separated using a gas chromatographic (GC) column, reduced using a pyrolytic column, and detected using a cold vapor atomic fluorescence spectrometry (CVAFS) detector.

This method may be used to determine CH_3Hg^+ concentrations in filtered or unfiltered water samples in the range of 0.040–5 ng/L. The upper range may be extended to higher concentrations by distilling smaller sample volumes or ethylating less of the distillate.

It should be noted that repeated attempts to analyze reagent grade water spiked with CH_3Hg^+ resulted in low recoveries (40–60 percent). The reasons for these low recoveries have not been resolved; however, other mercury research laboratories also obtain similar recoveries (J. Hurley, University of Wisconsin; C. Gilmour, Academy of Natural Sciences, oral commun., 2001). Therefore, reagent water is not an appropriate water source for spiked standard solutions and should not be used for quality-assurance or quality-control purposes.

Contamination

Methyl mercury analysis, as with all trace metal analysis, is extremely sensitive to contamination. Extreme care must be taken to avoid contamination in the collection and analysis steps of this method. All of the sample collection and analytical equipment that comes in contact with samples must be Teflon or glass and vigorously cleaned prior to and between uses. New Teflon equipment is rinsed with tap water, and cleaned by immersing in a 4 N hydrochloric acid (HCl) bath heated to 65°C for at least 48 hours. Immediately following removal from the bath, the equipment is immersed in fresh reagent grade water and rinsed at least three times with reagent grade water. Following the rinsing step, each sample bottle is filled to 25 percent full volume with 0.12 N HCl and capped. The exterior of the bottles and all other equipment is allowed to air dry on a Hg-clean bench under a laminar flow hood equipped with a High Efficiency Particulate Air (HEPA) filter which is 99.99 percent efficient on particles less than 0.3 microns in diameter. Dry equipment is double bagged in new zip-type bags. After the initial 48 hour cleaning, equipment needs to be immersed in the hot acid for only 24 hours.

Sample Preservation

Samples are acidified with 6N HCl to 1 percent, volume to volume (v/v), and kept in the dark to prevent photodegradation (Krabbenhoft and others, 2001) of CH_3Hg^+. Samples preserved in this manner can be held for up to 6 months before analysis (Bloom, 1995).

Method Detection Limit

The U.S. Environmental Protection Agency (USEPA) has established a fish tissue methyl mercury enforcement standard of 0.3 µg/g (U.S. Environmental Protection Agency, 2001b). A water column concentration of 0.058 ng/L was determined to correspond with a 0.3 µg/g fillet concentration for age-3 largemouth bass (Brumbaugh and others, 2001). To demonstrate that the WDML can accurately quantify methyl mercury in water samples at or below this environmentally important level, a method detection limit study was performed. A method detection limit of 0.04 ng/L was determined from multiple analyses of an unspiked surface-water sample and a spiked ground-water sample (table 1) according to USEPA protocol (U.S. Environmental Protection Agency, 1990). The ground-water sample was collected from a residential well in a 1L Teflon bottle; 0.1 ng of CH_3Hg^+ standard was added to the sample at the lab and the sample was then acidified with 12N HCl to 1 percent (v/v). Each of these samples was distilled in seven separate distillation batches and analyzed over five days.

Table 1. Results from multiple analyses of surface water and ground water for detection limit assay
[All concentrations in nanograms per liter (ng/L)]

	Unspiked surface water	Spiked ground water
	0.134	0.093
	.095	.078
	.123	.095
	.102	.090
	.101	.064
	.116	.090
	.115	.099
	.095	.085
Average	.110	.087
Standard deviation	.014	.011
Percent relative standard deviation	12.9	12.9
Detection limit (standard deviation x 2.998)	.042	.033

Reagents

All reagents and/or dry chemicals used to make reagents must be of high purity and low in Hg.

A. Reagent water: Ultra pure reagent grade water shown to be greater than 18 MΩ starting from a pre-purified source (distilled, RO, and others) and found to be less than 0.1 ng/L Hg. The water is delivered through a 0.2 µM filter, as obtained from a Millipore Academic water-purification system or equivalent.

B. Copper sulfate: 1M $CuSO_4$ in reagent water.

C. Hydrochloric acid: Concentrated HCl found to be less than 0.5 ng/L Hg (EM Science Omni Trace or equivalent).

D. Acetate buffer: 11.8 mL of glacial acetic acid and 27.2 g reagent grade sodium acetate trihydrate diluted to 100 mL with reagent water.

E. Ethylating Reagent: 1 g of Sodium Tetraethyl Borate ($NaBEt_4$; Strem 11-0575) dissolved in 100 mL of 2 percent Potassium Hydroxide (KOH), weight to weight (w/w), solution that has been chilled to form slush. The $NaBEt_4$ solution is divided equally among 9 clean 15 mL Teflon vials that then are capped and frozen. This solution should be kept frozen and made fresh every 2 weeks. Never use $NaBEt_4$ solid or solutions that are yellow in color. *Note: $NaBEt_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaBEt_4$ use should take place in a high-volume fume hood. To discard unused portions of ethylating reagent, empty bottles into a large beaker of 6N hydrochloric acid (HCl) inside a high-volume fume hood. Place beaker on a hotplate and boil down to half-volume, then discard the remaining solution as an acid waste. Triethylboron will boil off into the air where it is oxidized to harmless boric acid.*

F. Nitrogen (N_2). Ultra high purity grade 5.0 N_2 passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

G. Argon (Ar). Ultra high purity grade 5.0 Ar passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

Standards

Upon receipt at the laboratory or on the day of preparation, reagent containers should be labeled with the date received or made and the initials of the person preparing them. The stock and substock standards should be stored outside of the Hg-clean analytical laboratory to prevent contamination of the laboratory.

A. CH_3Hg^+ stock solution (1,000 mg/L CH_3Hg^+ as Hg): 1.252 g of reagent grade methyl Hg chloride (Strem 80-2250) is dissolved in 1L of 2 percent glacial acetic acid, 0.2 percent HCl v/v.

B. CH_3Hg^+ substock solution (1 mg/L CH_3Hg^+ as Hg): Dilute 100 µL of CH_3Hg^+ stock solution to 100 mL with 2 percent glacial acetic acid, 0.2 percent HCl v/v.

C. CH_3Hg^+ working standard (1 ng/mL CH_3Hg^+ as Hg): Dilute 100 µL of CH_3Hg^+ substock solution to 100 mL with 2 percent glacial acetic acid, 0.2 percent HCl v/v. Because measurement errors are present in laboratory processes the exact concentration of the working standard must be determined analytically. The following procedure is used to determine the exact concentration of the working standard.

1. Add 8.0 mL of reagent grade water; 1.0 mL of the CH_3Hg^+ working standard and 1.0 mL of bromine monochloride (BrCl) to four 15 mL Teflon vials.
2. Add 9.0 mL of reagent grade water and 1.0 mL of BrCl to four 15 mL Teflon vials.
3. Double bag and place the eight vials described in steps 1 and 2 into an oven at 50°C overnight and analyze each aliquot for total Hg by USEPA method 1631.
4. Analyze four separate 1.0 mL aliquots of the CH_3Hg^+ working standard for inorganic Hg (Hg(II); readily reducible with $SnCl_2$) using USEPA method 1631 without the BrCl oxidation step.
5. Subtract the average blank concentration determined from analyses of solutions in step 2 from the average concentration determined from analyses of the solutions in step 1 to determine the reagent blank corrected concentration of the working standard.

6. Subtract the average concentration of the Hg(II) in the CH_3Hg^+ working standard, determined in step 4, from the reagent blank corrected value determined in step 5 to determine the actual working-standard concentration.

ANALYTICAL METHOD

Sample Preparation

Samples must be distilled prior to analysis to remove potential matrix interferences such as reduced sulfur containing compounds, calcium, and humic acids associated with dissolved organic carbon (Horvat and others, 1993).

Distillation Equipment

The distillation system (fig. 1a) consists of a solid aluminum heating block, a small refrigerator, Teflon distillation and receiving vessels, and Teflon transfer lines.

A. A custom fabricated aluminum block (fig. 1b) is heated with a Thermolyne type 2200 (or equivalent) hot plate during the distillation step. A temperature probe placed in the center of the block monitors block temperature.

B. A small commercially available refrigerator is used to hold the receiving vials, aid in condensation, maintain distillate at 4°C and protect the distillate from exposure to light. Small holes are drilled in the side of the refrigerator to accommodate the transfer lines.

C. The distillation and receiving vessels are 125 mL Teflon bottles (Nalgene catalogue number 1630-0004 or equivalent). The distillation vessel caps (fig. 1c) and receiving vessel caps (fig. 1d) consists of a Teflon insert (Savillex part number 0738-4-2 or equivalent) molded integrally with two transfer ports equipped with compression fittings for 1/4-in. (6.4 mm) outside diameter (O.D.) tubing. A length of 1/4-in. O.D. tubing is inserted into one of the ports so that it will extend to within 2 mm of the bottom of the distillation and receiving vessels to insure complete sample purging and recondensation, respectively. A short length of 1/4-in. O.D. tubing also must be inserted flush with the lower side of the insert in the remaining port to accommodate the transfer line. The Teflon bottle caps must be machined to accommodate the insert and form an airtight seal for the distillation vessels, whereas the green polypropylene cap included with the insert can be used for the receiving vessels. Teflon transfer lines of 1/8-in. (3.2 mm) O.D. are connected by friction fit from the outlet tubing of the distillation vessel to the inlet tubing of the receiving vessel.

D. Flowmeters capable of maintaining a flow of 60 mL/min of N_2 are placed immediately upstream of the distillation vials to maintain constant and equal flow to all distillation vials. Gas is supplied through 1/8-in. O.D. Teflon line inserted into the inlet tubing of the distillation vessel.

Distillation Procedure

A WDML distillation batch consists of 11 environmental samples, 3 method blanks, a matrix spike, and a matrix spike duplicate. Distillation blanks are reagent grade water acidified with 12N HCl to 1 percent (v/v). The matrix spike and matrix-spike duplicates are prepared by adding a known amount of working standard to two of three bottles containing similar volumes of the same sample.

A. Dispense approximately 60 mL of water (sample or reagent water) into each distillation vessel and add 1 mL of 1M $CuSO_4$ (to bind sulfide–Olson and others, 1997) to each of the bottles in the batch. Record the bottle identifier, tare weight and full weight of each vessel. Cap each of the vials with the distillation cap corresponding to the block position to be occupied by that vial.

B. Dispense approximately 40 mL of reagent water to each of the receiving vessels. Record the bottle identifier, tare weight and bottle plus reagent water weight of each. Cap each of the vials with the receiving cap corresponding to the block position occupied by the matching distillation vessel.

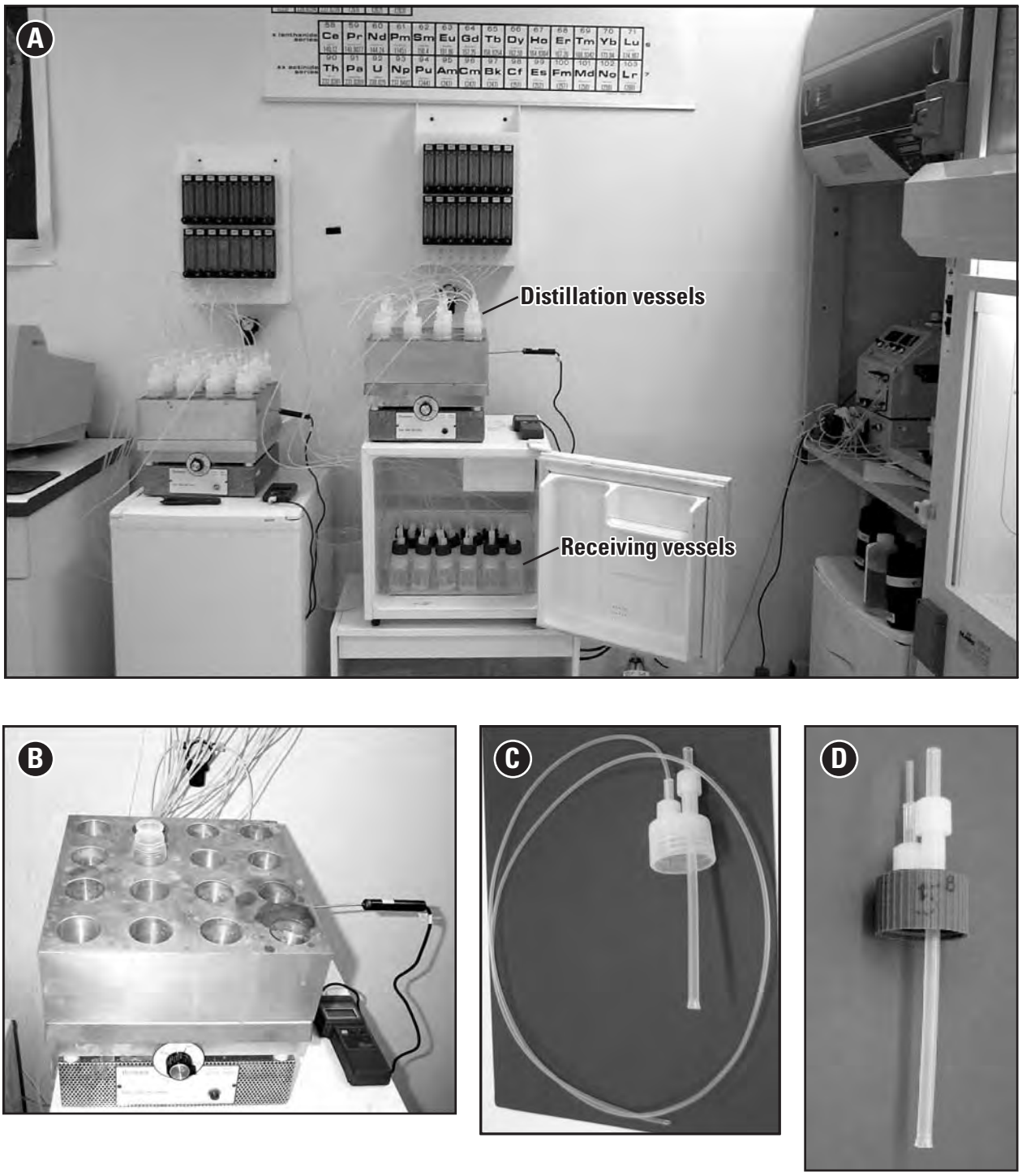

Figure 1. Methyl mercury distillation system: (A) entire system, (B) distillation, (C) distillation vessel cap, and (D) receiving vessel cap.

C. Place the distillation vials in their respective positions in the distillation block and thread the transfer lines through the numbered holes in the refrigerator.
D. Turn on the N_2 flow to the flowmeters and connect the gas lines to the inlet ports of the distillation caps.
E. Place the receiving vial tray in the refrigerator and begin placing the receiving vials into the tray. As the receiving vials are placed into the tray, connect the transfer lines to the inlet ports of the receiving caps. Check for bubbling in the reagent water. This checking verifies a leak-free system.
F. Adjust the flow on the flowmeters to 60 mL/min. Adjust the hot plate temperature to maintain a block temperature of 120 +/- 5°C. This temperature should result in a distillation rate of 6–8 mL per hour but adjustments may need to be made for individual systems.
G. Check the receiving vials to ensure unrestricted flow, the distillation vials to ensure no leakage, and the block temperature for stability periodically throughout the distillation.
H. Remove the transfer lines from the receiving vessels and the distillation vessels from the block when approximately 20 percent of the volume in the distillation vessel remains. The distillation caps as well as the inside of the transfer lines should be rinsed thoroughly with reagent water.
I. Weigh the receiving vessels and record the weight for later determination of the percent of the original sample that was distilled. Cap the bottles and place in a refrigerator at 4°C until analysis (distillates should be analyzed within 48 hours).

Sample Analysis

After the samples have been distilled, they are ready for analysis and should be analyzed within 48 hours. The analysis is a two-step process consisting of purging the mercury species from the distillate and detecting the mercury species with a cold vapor atomic fluorescence detector.

Analytical Equipment

The analytical portion of the process requires two separate systems; one for loading the traps (fig. 2a) and one for desorbing and detecting the Hg species (fig. 3a). The anlalytical equipement used is listed below.

A. Flow meters equipped with needle valves capable of delivering a N_2 flow of 250 mL/min to the reaction vessels.
B. Reaction vessels (figs. 2c and 2d) are 250 mL Erlenmeyer flask with a standard/taper 24/40 neck and a sparging stopper fitted with a four-way valve (fig. 2b).
C. Sample traps (fig. 3b) are made from 7 mm quartz tubes, 10 cm long with a constriction at 3 cm from the outlet end (the trap identifier is placed at this end); about 0.2 g (3 cm in the tube) of Carbotrap (graphitized carbon black, Supelco 2-0287 or equivalent) is placed in the center and contained by quartz wool plugs at either end. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the sample traps to provide a connection point between the sample trap and the reaction vessel, and to provide connection points in the analytical train.
D. An analytical balance capable of measuring to the nearest 0.1g is used to determine sample volumes to the nearest 0.1mL.
E. Pneumatic fixed-volume and variable pipettes ranging from 5 µL to 5 mL.
F. Hewlett Packard model HP3395 integrator or equivalent, connected to a timer, controls the analytical system. The timer is connected to a transformer that is connected to a Nichrome wire coil wrapped to fit around the sample trap.
G. The gas chromatographic column (fig. 3c) is a 4 mm inside diameter (I.D.), 6 mm O.D., glass column 50 cm long and filled with Chromosorb WAW-DMSC 60/80 mesh (Supelco 2-0152) enclosed in a glass sheath 2 cm in diameter and 25 cm long. This column is housed in a cylindrical oven (figs. 3a and 3c) connected to a transformer, which supplies a constant voltage to maintain a temperature of 95 +/- 5°C. Column

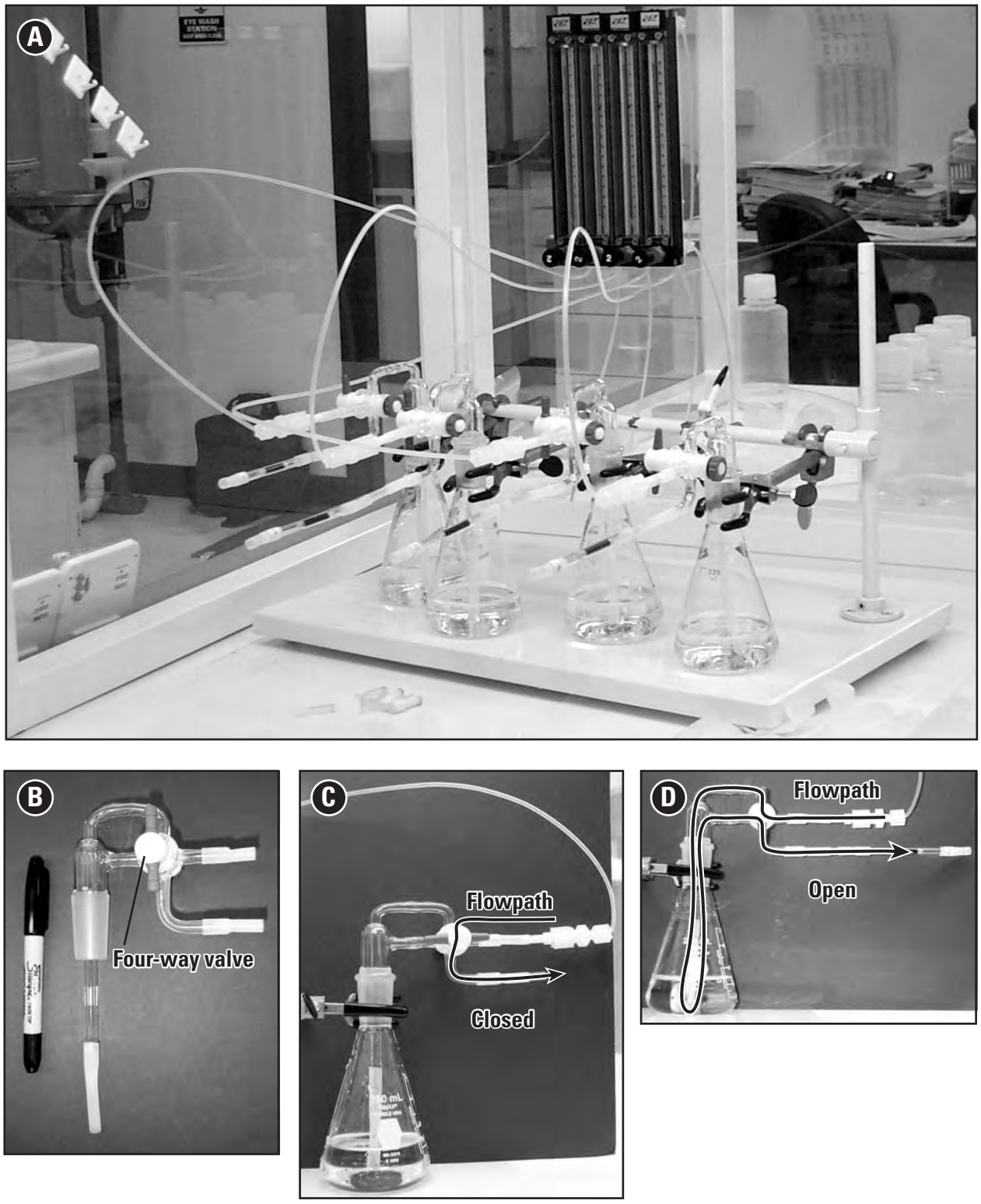

Figure 2. Methyl mercury reaction and purging system: (A) entire system, (B) sparging stopper fitted with a four-way valve, (C) reaction vessel in the closed (reaction) position, and (D) reaction vessel in the open (purging) position.

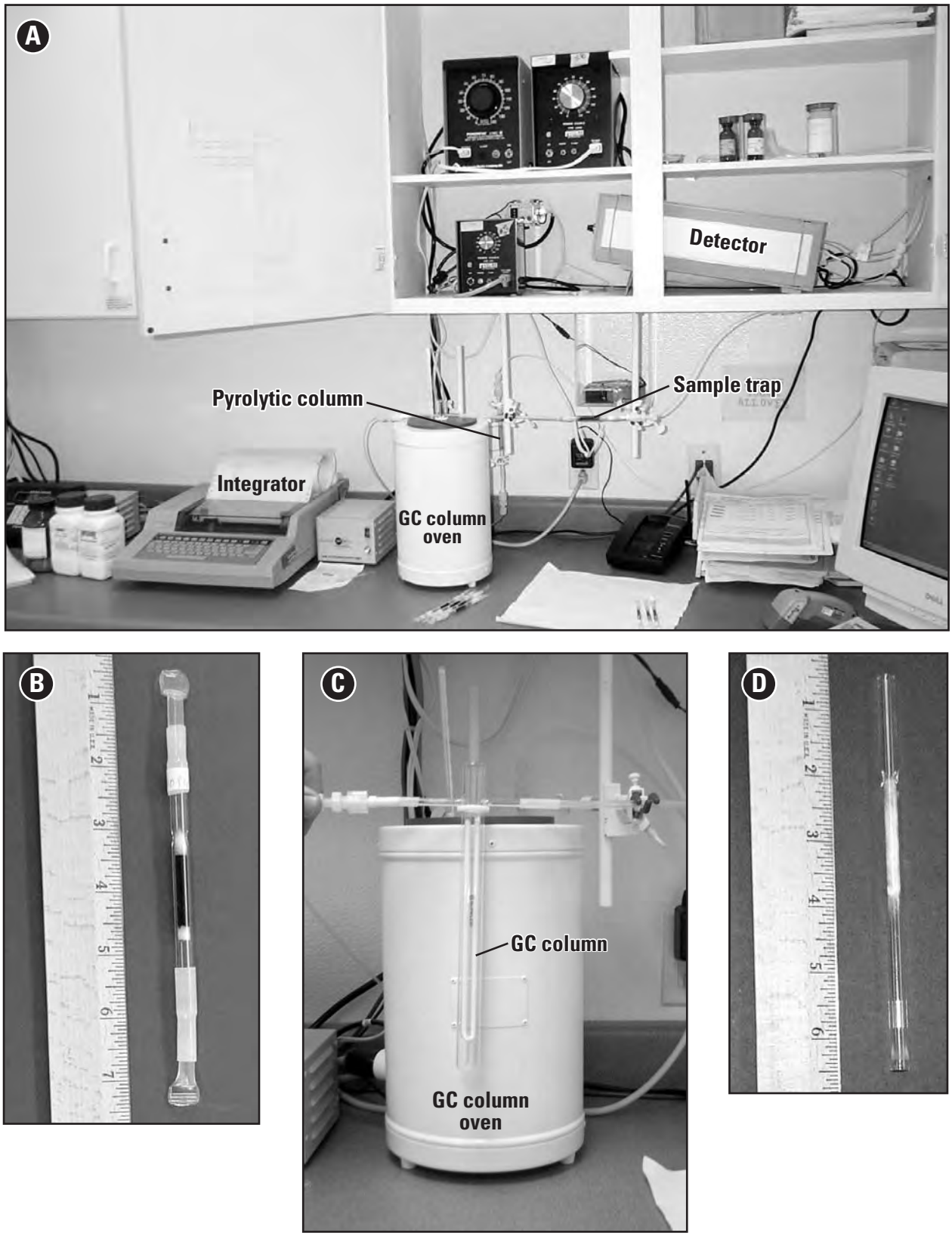

Figure 3. Methyl mercury desorbtion and dectection system: (A) entire system, (B) sample trap, (C) gas chromatographic column, and (D) pyrolytic column.

oven temperature may need to be adjusted on individual systems to insure good peak separation and symmetry.

H. The pyrolytic column (fig. 3d) is a 7 mm quartz tube 15 cm in length with the center 4–5 cm filled with quartz wool. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the pyrolytic column to provide connection points in the analytical train. A length of nichrome wire is wrapped around the tube to cover the length of quartz wool. The wire is connected to a transformer that heats the column to approximately 800°C.

I. The detector is a commercially available Model 2500 CVAFS Mercury Detector from Tekran (Toronto, Ontario) equipped with a mass flow controller capable of maintaining 20 mL/min of Argon flow through the entire analytical train. Detector analog output returns to the HP3395 integrator where the peak areas are recorded.

Analytical Procedure

A WDML analytical batch generally consists of 2 distillation batches, as well as standards and blanks used to evaluate the performance of the analytical train. All chemical additions to the reaction vessels are carried out in a fume hood and then the vessels are transferred to a clean bench below a laminar flow hood equipped with a HEPA filter which is 99.99 percent efficient on particles less than 0.3 microns in diameter.

A. Create a standard curve by adding varying amounts of working standard (typically 100, 50, 25, and 10 µL, but the range needs to cover the expected concentrations in the analytical batch) to approximately 100 mL of reagent water in each of the reaction vessels. Pipette 200 µL of acetate buffer and 100 µL of $NaBEt_4$ to each of the reaction vessels. The $NaBEt_4$ reagent serves to derivatize the two remaining ionic Hg species after the distillation step (inorganic Hg(II) and CH_3Hg^+) to their ethylated forms (diethyl Hg and methylethyl Hg, respectively). Elemental Hg does not react with the $NaBEt_4$. *Note: The $NaBEt_4$ needs to remain near 0°C. It should be removed from the freezer approximately 3 minutes before being added to the reaction vessels and placed in a dark place to partially thaw. A new vial of $NaBEt_4$ should be used each day.*

B. Tighten the sparging stoppers, ensure the four-way valve is in the closed position (fig. 2c), gently swirl the reaction vessels, and allow the reaction to proceed for 15 minutes. After the reaction time has elapsed, remove the plugs from the ends of the sample traps. Place the sample traps onto the outlet of the reaction vessels, with the identification number downstream, turn the four-way valve to the open position (fig. 2d), and allow grade 5 N_2 to purge the vessel at a rate of 250 mL/min for 20 minutes.

C. After the samples have been purged, turn the four-way valve to the closed position and remove the sample trap from the reaction vessel outlet. Remove the N_2 line from the inlet of the four-way valve and place the sample trap on the end of the N_2 line. Allow the N_2 to flow through the sample traps at 250 mL/min for 7 minutes to remove any water vapor that has collected on the sample trap.

D. Four ethylation blanks are prepared by adding approximately 100 mL of reagent grade water, 200 µL of acetate buffer, and 100 µL of $NaBEt_4$ to separate reaction vessels. Then proceed as in step B.

E. While one set of reaction vessels and sample traps are being used to collect the purged sample, the other set can be desorbed and analyzed. Remove the sample traps from the N_2 lines, attach the N_2 lines to the inlets of the four-way valves, and cap both ends of the sample traps.

F. To desorb and analyze the traps, remove the plugs from the ends of the first trap and place it into the analytical train (fig. 3a) by threading it, with the identification number upstream, through the center of the nichrome wire coil. Center the nichrome wire over the Carbotrap, allow the flow to stabilize for approximately 30 seconds, and press start on the integrator. The nichrome wire will heat to 250°C with a ramp time of 30 seconds to desorb the Hg from the sample trap. As the Hg is desorbed from the sample trap it is carried by the Ar carrier gas at a flow of 20 mL/min into the GC column where the elemental Hg, methylethyl Hg and the diethyl Hg are separated. Following separation, the individual Hg species are carried into the pyrolytic column where the methylethyl and diethyl Hg species are reduced thermally to elemental Hg.

G. The CVAFS detector can only detect elemental mercury. The detector then outputs a millivolt signal to the integrator resulting in three distinct peaks (fig. 4).

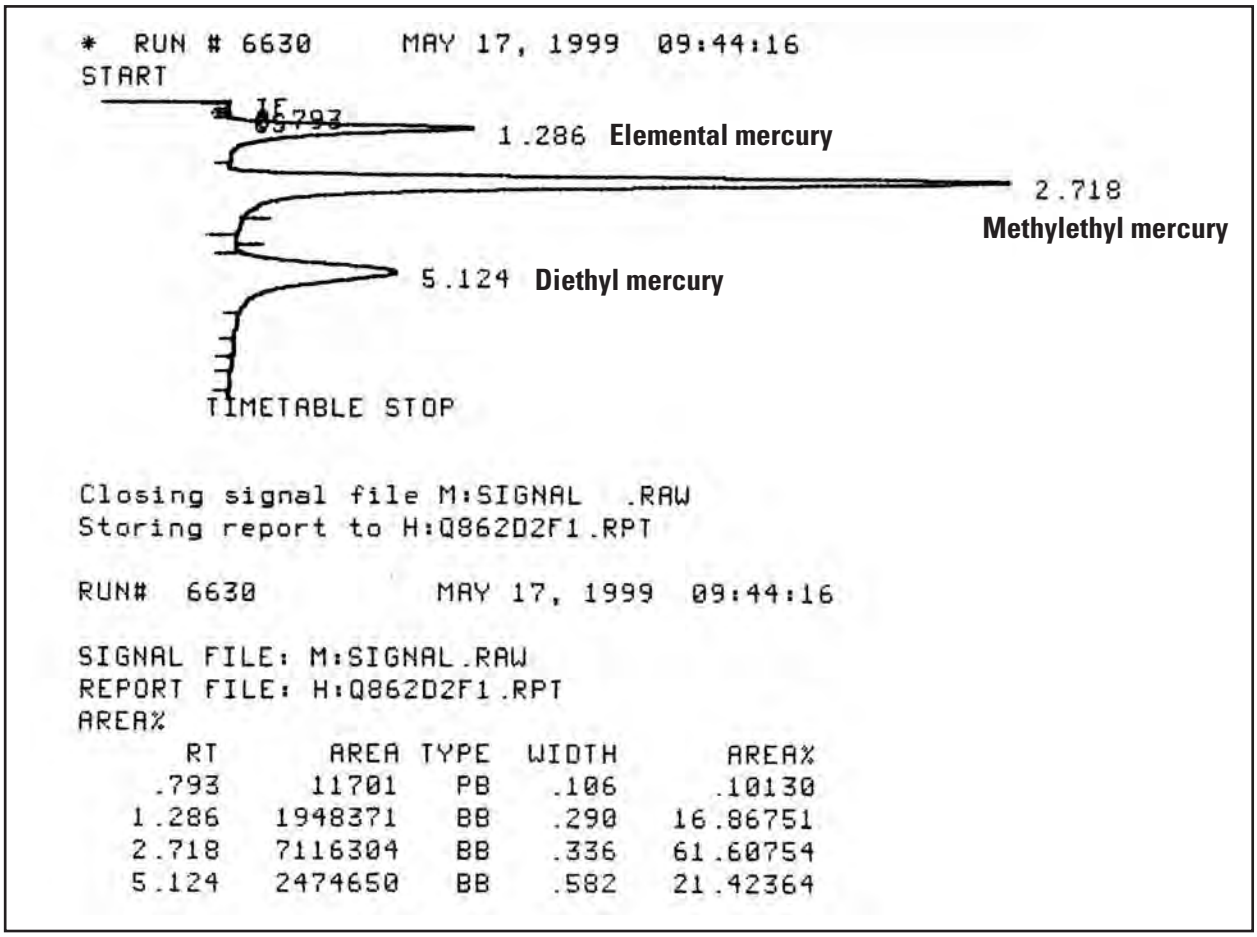

Figure 4. Example of methyl mercury detection chromatograph with peak identities.

H. After the standard curve and the ethylation blanks have been analyzed, and found to meet the daily quality objectives (DQO), the distillates from the batch can be analyzed. The procedure for analyzing the method blanks, environmental samples, matrix spikes and matrix-spike duplicates are identical to the procedure used for the standards and ethylation blanks. Simply dispense an appropriate amount of distillate into the reaction vessel, add the acetate buffer and the $NaBEt_4$ and proceed as in step B. An appropriate amount of sample would be an amount that produces a CH_3Hg^+ peak with an area that falls within the calibration range (for most water samples this amount is the entire distillate volume).

Data Interpretation

The integrator output should show three distinct peaks for a given sample (fig. 4). A peak for the elemental Hg appears at approximately 1 minute and 30 seconds, the methylethyl Hg peak at 2 minutes and 40 seconds, and the diethyl Hg peak appears at 4 minutes and 40 seconds. The methylethyl Hg peak is the peak of interest and the area under its curve is used to calculate concentration of CH_3Hg^+ in the original sample.

Peak areas obtained for the standards during the calibration are corrected for CH_3Hg^+ in the acetate buffer and the $NaBEt_4$ by subtracting the average peak area of the ethylation blanks (DQO is absolute mass less than or equal to 2 pg). Simple linear regression, forcing zero intercept, is applied to the peak area/mass combinations to determine the best-fit line (DQO is a correlation coefficient equal to or greater than 0.995) and establish the equation used to determine the mass of the sample aliquot from its resulting peak area. Each distillation batch contains three method blanks (DQO is an absolute mass less than or equal to 5 pg) to evaluate the contribution of CH_3Hg^+ from the distillation process and reagents. The average mass found in these blanks is subtracted from the mass in the sample dis-

tillates. After correcting for the method blanks, the final sample concentrations are corrected for the fraction distilled (because the fraction of methyl mercury distilled is equal to the fraction of the sample volume distilled), and the difference between the volume of the distillate ethylated and the total volume of distillate recovered. The following series of formulas are used to calculate final concentration.

SAMPLE VOLUME:

$V_s = W_{F1} - W_T$,

where

V_s = sample volume

W_{F1} = weight of reaction vessel with sample

W_T = weight of reaction vessel

FRACTION DISTILLED:

$D = V_S/(W_{F2} - W_W)$,

where

D = fraction distilled

V_S = sample volume

W_{F2} = weight of receiving vessel after distillation

W_W = weight of receiving vessel with reagent water before distillation

MASS OF Hg IN ALIQUOT ANALYZED

$M_A = (PA/S) - MB_{AVE}$,

where

M_A = mass per aliquot

PA = peak area

S = slope of calibration line

MB_{AVE} = average mass found in method blanks

MASS OF Hg IN ORIGINAL SAMPLE

$M_S = (M_A / D)*((W_{F2} - W_{T2})/(W_{F2} - W_A))$,

where

M_S = mass in original sample

M_A = mass per aliquot

D = fraction distilled

W_{F2} = weight of receiving vessel after distillation

W_{T2} = weight of receiving vessel

W_A = weight of receiving vessel after pouring off aliquot to be ethylated

FINAL CH_3Hg^+ CONCENTRATION

$C = M_S / V_S$,

where

C = concentration

M_S = mass in original sample

V_S = sample volume

Table 2a. Results for the analysis of ground water spiked at two different concentrations
[All concentrations in nanograms per liter (ng/L)]

	Ground water spiked at 0.1 ng/L	Percent recovery	Ground water spiked at 1.0 ng/L	Percent recovery
	0.093	95.2	0.927	92.6
	.078	79.9	1.15	114.3
	.095	97.6	.933	93.1
	.090	91.6	.835	83.4
	.064	62.2	.886	88.5
	.090	91.8	1.088	108.6
	.099	101.6	.995	99.4
	.085	87.0	.843	84.2
	.087	88.8	.956	95.5
Average	.087	88.8	.956	95.5
Standard deviation	.011	11.5	.112	11.21
Percent relative standard deviation	12.9	12.9	11.7	11.7

METHOD PERFORMANCE

Precision and accuracy for this method were evaluated using three water sources at two concentrations and analyzed seven times each (U.S. Geological Survey, Office of Water Quality Technical Memorandum 98.05) over a period of five days using different calibration curves. Memorandum 98.05 recommends the use of surface water, ground water, and reagent water as the three sources; however, multiple analyses of reagent water spiked with CH_3Hg^+ resulted in consistently poor recoveries of CH_3Hg^+ for undetermined reasons and, thus, reagent water was not used to evaluate this method. Instead, ground water from a residential well, surface water from a freshwater lake in Canada, and surface water from the Everglades in southern Florida were used to evaluate method performance. The ground water was found to contain no CH_3Hg^+ on initial analysis; therefore, analyte was spiked into this matrix so that it could be evaluated for precision and accuracy. Both surface-water samples contained CH_3Hg^+ at detectable (greater than 0.04 ng/L) concentrations. The USGS requires that sample matrices be evaluated at two different concentrations; therefore, the ground-water sample was spiked at two different concentrations and the surface-water samples were spiked with analyte so that two different concentrations could be evaluated. The results of the analyses of these matrices are presented in tables 2a–c.

Method precision was evaluated by examining the percent relative standard deviation of the concentrations obtained from all analyses of each matrix at each concentration. The percent relative standard deviations ranged from 10.2 to 15.6. Average recoveries of the added analyte obtained at the different concentrations in the different matrices evaluated ranged from 88.8 to 117 percent, which are considered within acceptable method performance limits for accuracy at laboratories using this analytical method (Nicolas Bloom, Frontier Geosciences, Seattle, Washington, written communication, 1999).

SUMMARY AND CONCLUSIONS

This report documents a method for the analysis of CH_3Hg^+ in water samples, and describes the results of a methodological test of the WDML's ability to provide quality CH_3Hg^+ data at ng/L concentrations. Acceptance of this method by the USGS will help to establish a National database of CH_3Hg^+ concentrations from areas across the nation. The need for a reliable method of CH_3Hg^+ detection was precipitated by the National Water-Quality Assessment program's identification of mercury as one of the top five priority issues over the next 10 years coupled with the fact that CH_3Hg^+ is the species of mercury that most readily bioaccumulates in mammals.

The Wisconsin District Mercury Laboratory has adapted a distillation/ethylation/gas-phase separation

Table 2b. Results for the analysis of spiked and unspiked Canada surface water.
[All concentrations in nanograms per liter (ng/L); --, no sample]

	Surface water unspiked	Surface water spiked at 0.627 ng/L[1]	Percent recovery
	0.134	0.638	101.8
	.095	.571	91.0
	.123	.606	96.6
	.102	.668	106.6
	.101	.573	91.4
	.116	.564	89.9
	.115	.482	76.9
	.095	--	--
Average	.110	.586	93.5
Standard deviation	.014	.060	9.57
Percent relative standard deviation	12.9	10.2	10.2

[1]Concentration calculated by adding average concentration of sample to known spike addition

Table 2c. Results for the analysis of spiked and unspiked Everglades' surface water
[all concentrations in nanograms per liter (ng/L)]

	Everglades water unspiked	Everglades water spiked at 1.25 ng/L[1]	Percent recovery
	0.255	1.51	120.8
	.300	1.63	130.1
	.236	1.02	81.6
	.280	1.48	118.2
	.275	1.47	118.0
	.323	1.64	131.2
Average	.278	1.46	116.6
Standard deviation	.031	0.227	18.2
Percent relative standard deviation	11.1	15.6	15.6

[1]Concentration calculated by adding average concentration of sample to known spike addition.

method with cold vapor atomic fluorescence spectroscopy detection for the determination of methyl mercury in filtered and unfiltered waters. A method detection limit of 0.04 ng/L was proven to be achievable from multiple matrices using this method. The accuracy of this method also was tested using multiple matrices at different concentrations and found to be acceptable based on average spike recoveries ranging from 88.8 to 117 percent.

Reagent water is not an appropriate matrix to evaluate method performance as spiked reagent water consistently results in low recovery. Low ionic strength water samples such as snow have also resulted in low recoveries at the WDML as well as other laboratories using this method. Samples high in dissolved organic carbon (DOC) also can be difficult to evaluate because the spike recoveries can be quite inconsistent. When analyzing these types of water samples with these matrices, professional judgment and caution must be used in evaluating method performance.

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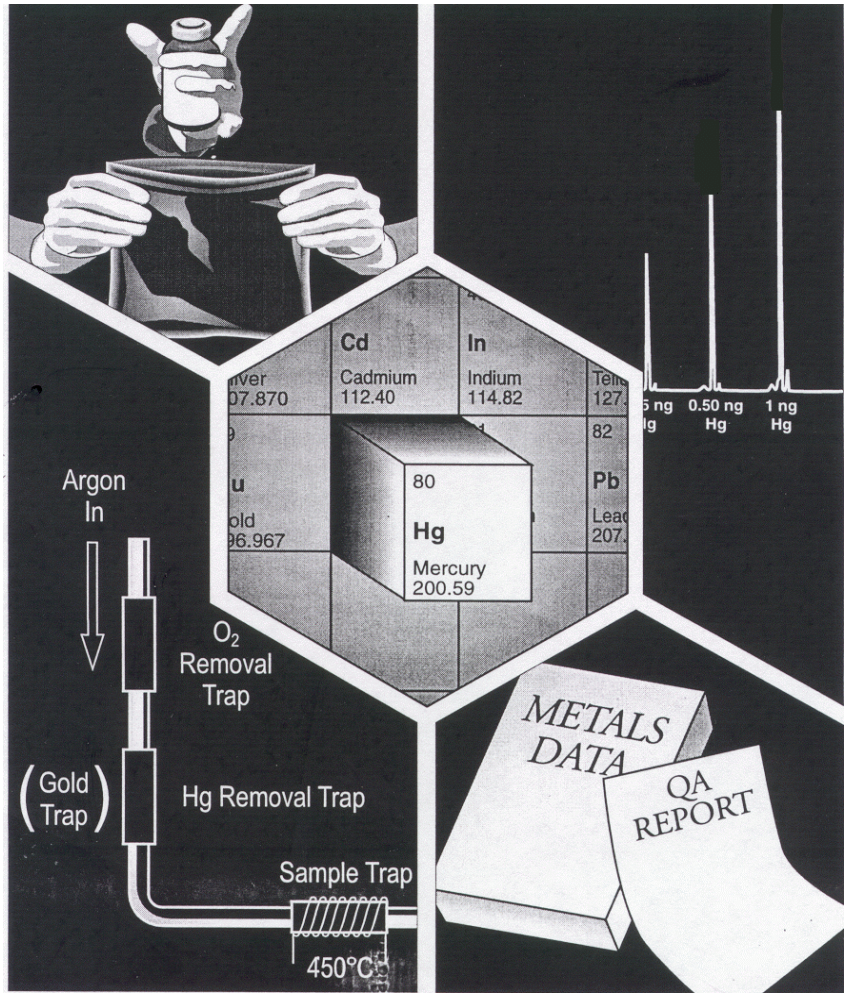
United States
Environmental Protection
Agency

Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

August 2002



United States Environmental Protection Agency
Office of Water 4303
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Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

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Disclaimer

This Method has been reviewed and approved for publication by the Statistics and Analytical Support Branch within EPA's Engineering and Analysis Division. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Introduction

Method 1631 (the "Method") supports technology-based and water quality-based monitoring programs authorized under the Clean Water Act (CWA; the "Act").

CWA Sections 301 and 306 require EPA to publish effluent standards that restrict the direct discharge of pollutants to the nations waters, and CWA Sections 307(b) and (c) require EPA to promulgate nationally applicable pretreatement standards which restrict pollutant discharges into sewers flowing to publicly owned treatment works (POTWs). The effluent limitations guidelines are published at CFR parts 401-503.

CWA Section 303 requires each State to set a water quality standard for each body of water within its boundaries. A State water quality standard consists of a designated use or uses of a water body or a segment of a water body, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. CWA Section 304(a) requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific water body, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by CWA Sections 301(b) and 306.

In 1987, amendments to the CWA required States to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses. Method 1631 was specifically developed to provide reliable measurements of mercury at EPA WQC levels.

In developing methods for determination of trace metals, EPA found that one of the greatest difficulties was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. Method 1631 is designed to preclude contamination in nearly all situations. It also contains procedures necessary to produce reliable results at the lowest WQC levels published by EPA. In recognition of the variety of situations to which this Method may be applied, and in recognition of continuing technological advances, Method 1631 is performance based. Alternative procedures may be used so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this draft Method should be directed to:

U.S. EPA Sample Control Center
6101 Stevenson Avenue
Alexandria, VA 22304-3540
703/461–2100

Note: This Method is performance based. The laboratory is permitted to omit steps or modify procedures provided that all performance requirements in this Method are met. The laboratory must not omit or modify any procedure defined by the term "shall" or "must" and must perform all quality control tests.

Method 1631, Revision E

Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

1.0 Scope and Application

1.1 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 16.1) and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from sea water to sewage effluent (References 16.2–16.5).

1.2 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.

1.3 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 10.4 gives requirements for extension of the calibration range.

1.4 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.

1.5 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 0.2 ng/L when no interferences are present. The minimum level of quantitation (ML) has been established as 0.5 ng/L. An MDL as low as 0.05 ng/L can be achieved for low Hg samples by using a larger sample volume, a lower BrCl level (0.2%), and extra caution in sample handling.

1.6 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 16.6-16.7).

1.7 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."

1.8 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 9.1.2.1 gives the requirements for establishing method equivalency.

1.9 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.

1.10 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 9.2.

1.11 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 Monitoring* (Reference 16.8), that can be used for verification and validation of the data obtained.

1.12 This Method uses either a bubbler or flow-injection system for determination of mercury in water. Separate calibration, analysis, and calculation procedures are provided for a bubbler system (Sections 10.2, 11.2.1, and 12.2) and for a flow-injection system (Sections 10.3, 11.2.2, and 12.3).

2.0 Summary of Method

2.1 A 100- to 2000-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 16.9).

2.2 For dissolved Hg, the sample is filtered through a 0.45-µm capsule filter prior to preservation.

2.3 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 methyl mercury, it should be preserved according to procedures in the method that will be used for determination of methylmercury.

2.4 Prior to analysis, all Hg in a 100-mL sample aliquot is oxidized to Hg(II) with BrCl.

2.5 After oxidation, the sample is sequentially reduced with $NH_2OH{\cdot}HCl$ to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0).

2.6 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, 2, and 3).

2.7 The Hg is 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 2 and 3).

2.8 Quality is assured through calibration and testing of the oxidation, purging, and detection systems.

3.0 Definitions

3.1 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.

3.2 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-µm filter.

3.3 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.

3.4 Definitions of other terms used in this Method are given in the glossary (Section 17.0).

4.0 Contamination and Interferences

4.1 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.

4.2 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 16.9).

4.3 Contamination Control

4.3.1 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.

4.3.1.1 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.

4.3.1.2 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.

4.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. The Sampling Method and Section 5 of this Method give suggestions and requirements for personnel safety.

4.3.2 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 by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class-100 clean room. If a clean room is not available, all sample preparation should be performed in a class-100 clean bench or a nonmetal glove box fed by mercury-and particle-free air or nitrogen. Digestion should be performed in a nonmetal fume hood equipped with HEPA filtration and ideally situated in a clean room.

4.3.4 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.

4.3.5 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.

4.3.6 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.

4.3.7 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.

4.3.7.1 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.

4.3.7.2 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 labware to introduction into the instrument. It may be useful to dedicate separate sets of labware 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 labware can be detected.

4.3.7.3 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.

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

4.3.8.1 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 bubbler blank (bubbler system) or system blank (flow injection system) must be analyzed to demonstrate no carryover at the blank criteria level. For the bubbler system, the blank must be run using the same bubbler and sample trap used to run the high concentration sample. 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.

4.3.8.2 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.

4.3.8.3 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 6.1.2).

4.3.8.4 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.

4.3.8.5 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 9.4.3). If reagent blanks are contaminated, a new batch of reagents must be prepared (see Section 9.4.3.2).

4.4 Interferences

4.4.1 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 $SnCl_2$ should be added in a closed vessel or analysis should proceed immediately. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis (Reference 16.10).

4.4.2 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.

4.4.3 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.

4.4.4 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.

5.0 Safety

5.1 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.

5.1.1 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.

5.1.2 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.

5.2 This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current file of OSHA regulations for safe handling of the chemicals specified in this Method. OSHA rules require that a reference file of material safety data sheets (MSDSs) must be made available to all personnel involved in these analyses (29 CFR 1917.28, Appendix E). It also is suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Personal hygiene monitoring should be performed using OSHA or NIOSH approved personal hygiene monitoring methods. Additional information on laboratory safety can be found in References 16.11-16.14. The references and bibliography included in Reference 16.14 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 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.

5.3.1 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.

5.3.2 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.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 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 mercury vapors.

5.3.7 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.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 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.

5.3.9 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.

5.3.10 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 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg 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.

6.0 Apparatus and Materials

Disclaimer: The mention of trade names or commercial products in this Method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus, materials, or cleaning procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

6.1 Sampling equipment

6.1.1 Sample collection bottles-fluoropolymer or glass, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

6.1.2 Cleaning

6.1.2.1 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 may be shipped to the sampling site containing dilute HCl solution (e.g., 0.04%), containing reagent water, or empty.

6.1.2.2 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.

6.1.2.3 Bottle blanks must be analyzed as described in Section 9.4.7. To verify the effectiveness of the cleaning procedures, bottle blanks must be demonstrated to be free of mercury at the ML of this Method.

6.1.2.4 As an alternative to cleaning by the laboratory, 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 9.4.7) and demonstrated to be free of mercury at the ML of this Method. If mercury is present above this level in any bottle, either the lot must be rejected or the bottles must be re-cleaned.

6.1.3 Filtration Apparatus

6.1.3.1 Filter—0.45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

6.1.3.2 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).

6.1.3.3 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.

6.2 Equipment for bottle and glassware cleaning

6.2.1 Vat, 100–200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

6.2.2 Panel immersion heater, 500-W, all-fluoropolymer coated, 120 vac (Cole-Parmer H-03053-04, 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!*

6.2.3 Laboratory sink—in Class-100 clean area, with high-flow reagent water (Section 7.1) for rinsing.

6.2.4 Clean bench—Class-100, for drying rinsed bottles.

6.2.5 Oven—stainless steel, in Class-100 clean area, capable of maintaining ± 5°C in the 60–70°C temperature range.

6.3 Cold vapor atomic fluorescence spectrometer (CVAFS): The CVAFS system used may either be purchased from a supplier, or built in the laboratory from commercially available components.

6.3.1 Commercially available CVAFS—Tekran (Toronto, ON) Series 2600 CVAFS, Brooks-Rand (Seattle, WA) Model III CVAFS, Leeman Labs Hydra AF Gold*plus* CVAFS, or equivalent

6.3.2 Custom-built CVAFS (Reference 16.15). Figure 2 shows the schematic diagram. The system consists of the following:

6.3.2.1 Low-pressure 4-W mercury vapor lamp

6.3.2.2 Far UV quartz flow-through fluorescence cell—12 mm x 12 mm x 45 mm, with a 10-mm path length (NSG Cells, or equivalent).

6.3.2.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7-nm interference filter (Oriel Corp., Stamford, CT, or equivalent).

6.3.2.4 Photometer and PMT power supply (Oriel Corp. or equivalent), to convert PMT output (nanoamp) to millivolts

6.3.2.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., Seattle, WA, or equivalent).

6.3.2.6 Flowmeter—with needle valve capable of reproducibly keeping the carrier gas flow rate at 30 mL/min

6.4 Hg purging system—Figure 2 shows the schematic diagram for the purging system. The system consists of the following:

6.4.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.

6.4.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm OD fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm OD fluoropolymer tubing because of its greater flexibility.

6.4.3 Acid fume pretrap—10-cm long x 0.9-cm ID fluoropolymer tube containing 2–3 g of reagent grade, nonindicating, 8–14 mesh soda lime chunks, packed between wads of nized glass wool. This trap is cleaned of Hg by placing on the output of a clean cold vapor generator (bubbler) and purging for 1 h with N_2 at 350 mL/min.

6.4.4 Cold vapor generator (bubbler)—200-mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc. or equivalent).

6.5 The dual-trap Hg(0) preconcentrating system

6.5.1 Figures 2 and 3 show the dual-trap amalgamation system (Reference 16.5).

6.5.2 Gold-coated sand traps—10-cm long x 6.5-mm OD x 4-mm ID quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., Seattle, WA, or equivalent). The ends are plugged with quartz wool.

6.5.2.1 Traps are fitted with 6.5-mm ID fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination.

6.5.2.2 At least six traps are needed for efficient operation, one as the "analytical" trap, and the others to sequentially collect samples.

6.5.3 Heating of gold-coated sand traps—To desorb Hg collected on a trap, heat for 3.0 min to 450–500 °C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10-14 vac. Potential is applied and finely adjusted with an autotransformer.

6.5.4 Timers—The heating interval is controlled by a timer-activated 120-V outlet (Gralab, or equivalent), into which the heating coil autotransformer is plugged. Two timers are required, one each for the "sample" trap and the "analytical" trap.

6.5.5 Air blowers—After heating, traps are cooled by blowing air from a small squirrel-cage blower positioned immediately above the trap. Two blowers are required, one each for the "sample" trap and the "analytical" trap.

6.6 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.

6.7 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10 µL to 5.0 mL.

6.8 Analytical balance capable of weighing to the nearest 0.01 g

7.0 Reagents and Standards

Note: The quantities of reagents and the preparation procedures in this section are for illustrative purposes. Equivalent performance may be achievable using quantities of reagents and procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

7.1 Reagent water—18-MΩ 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.

7.2 Air—It is very important that the laboratory air be low in both particulate and gaseous mercury. Ideally, mercury work should be 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. If this is not possible, air coming into the clean bench can be cleaned for mercury by placing a gold-coated cloth prefilter over the intake. Gold-coated cloth filter: Soak 2 m^2 of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% $NH_2OH{\cdot}HCl$ solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to set for several hours, then rinse

with copious amounts of deionized water. Squeeze-dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake prefilter of the laminar flow hood.

CAUTION: Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause interferences with the analysis if gold becomes incorporated into the samples or equipment. The gilding procedure should be done in a remote laboratory if at all possible.

7.3 Hydrochloric acid—trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg. The HCl should be analyzed for Hg before use.

7.4 Hydroxylamine hydrochloride—Dissolve 300 g of $NH_2OH \cdot HCl$ in reagent water and bring to 1.0 L. 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. Flow injection systems may require the use of less $SnCl_2$ for purification of this solution.

7.5 Stannous chloride—Bring 200 g of $SnCl_2 \cdot 2H_2O$ and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free N_2 at 500 mL/min to remove all traces of Hg. Store tightly capped.

7.6 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!*

7.7 Stock mercury standard—NIST-certified 10,000-ppm aqueous Hg solution (NIST-3133). This solution is stable at least until the NIST expiration date.

7.8 Secondary Hg standard—Add approx 0.5 L of reagent water and 5 mL of BrCl solution (Section 7.6) to a 1.00-L Class A volumetric flask. Add 0.100 mL of the stock mercury standard (Section 7.7) 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.

7.9 Working Hg Standard A—Dilute 1.00 mL of the secondary Hg standard (Section 7.8) to 100 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 10.0 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.10 Working Hg Standard B—Dilute 0.10 mL of the secondary Hg standard (Section 7.8) to 1000 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 0.10 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.11 Initial Precision and Recovery (IPR) and Ongoing Precision and Recovery (OPR) solutions—Using the working Hg standard A (Section 7.9), prepare IPR and OPR solutions at a

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.

7.12 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.

7.13 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.

8.0 Sample Collection, Preservation, and Storage

8.1 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.

8.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Glass bottles may be used if Hg is the only target analyte. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Reference 16.4). Polyethylene sample bottles must not be used (Reference 16.15).

8.3 Collect samples using guidance provided in the Sampling Method (Reference 16.9). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for mercury (References 16.4 and 16.15).

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.*

8.4 Sample filtration—For dissolved Hg, a sample is filtered through a 0.45-µm capsule filter (Section 6.1.3.1) in a mercury-free clean area prior to preservation. If the sample is filtered, it must be accompanied by a blank that has been filtered under the same conditions. The Sampling Method describes sample filtration procedures.

8.5 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.

8.5.1 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.

8.5.2 Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Reference 16.16). 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.

8.5.3 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.

NOTE: *Because of the potential for contamination, it is recommended that filtration and preservation of samples be performed in the clean room in the laboratory. However, if circumstances prevent overnight shipment of samples, samples should be filtered and preserved in a designated clean area in the field in accordance with the procedures given in Method 1669 (Reference 16.9). If filtered in the field, samples ideally should be filtered into the sample bottle.*

8.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until sample analysis.

8.7 Sample preservation, storage, and holding time requirements also are given at 40 CFR part 136.3(e) Table II.

9.0 Quality Control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 16.17). 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.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision. This ability is established as described in Section 9.2.

9.1.2 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 16.18), 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., CVAAS) 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.

9.1.2.1 Each time this Method is modified, the laboratory is required to repeat the procedure in Section 9.2 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 10.

Note: If the compliance limit is greater than the concentration of Hg in the OPR/OPR (5 ng/L), the acceptance criteria for blanks and the concentrations of mercury spiked into quality control samples may be increased to support measurements at the compliance limit. For example, if the compliance limit is 12

ng/L (National Toxics Rule, 40 CFR 131.36), the MDL must be less than or equal to 4 ng/L; concentrations of the calibration standards may be 5, 10, 20, 50 , and 100 ng/L; concentrations of the IPR/OPR samples may be 10 ng/L; spike concentrations and acceptance criteria for MS/MSD samples would remain as specified in Section 9.3; and an appropriate blank acceptance criterion would be 5 ng/L.

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 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

9.1.2.2.2 A narrative stating the reason(s) for the modification(s)

9.1.2.2.3 Results from all quality control (QC) tests demonstrating the performance of the modified method, including the following:

(a) Calibration (Section 10)
(b) Initial precision and recovery (Section 9.2.2)
(c) Analysis of blanks (Section 9.4)
(d) Matrix spike/matrix spike duplicate analysis (Section 9.3)
(e) Ongoing precision and recovery (Section 9.5)
(f) Quality control sample (Section 9.6)
(g) Method detection limit (Section 9.2.1)

9.1.2.2.4 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

9.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 9.3 describes the procedure and QC criteria for spiking.

9.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing blanks.

9.1.5 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 9.5 and 9.6 describe these procedures, respectively.

9.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.3.7 and 9.5.3 describe the development of accuracy statements.

9.1.7 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 9.4.2 for the flow-injection system), a

minimum of 3 bubbler blanks (Section 9.4.1 for the bubbler system), 1 OPR sample at the beginning and end of the batch (Section 9.5), a QCS (Section 9.6), and at least 3 method blanks (Section 9.4.4). 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 9.4.2) or a minimum of 3 bubbler blanks (Section 9.4.1)
(b) A minimum of five, non-zero calibration standards (Section 10.2.2.1)
(c) On-going precision and recovery (Section 9.5)
(d) Quality control sample (Section 9.6)
(e) Method blank (Section 9.4.4)
(f) Seven samples
(g) Method blank (Section 9.4.4)
(h) Three samples
(i) Matrix spike (Section 9.3)
(j) Matrix spike duplicate (Section 9.3)
(k) Four samples
(l) Method blank (Section 9.4.4)
(m) Six samples
(n) Matrix spike (Section 9.3)
(o) Matrix spike duplicate (Section 9.3)
(p) Ongoing precision and recovery (Section 9.5)

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 (d) 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 (c) above.

9.2 Initial demonstration of laboratory capability

9.2.1 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 1.5 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.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:

9.2.2.1 Analyze four replicates of the IPR solution (5 ng/L, Section 7.11) according to the procedure beginning in Section 11.

9.2.2.2 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.

9.2.2.3 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 the

precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.3 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 two pairs of MS/MSD samples (four spiked samples total).

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 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 9.3.2), whichever is greater.

9.3.1.2 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.

9.3.2 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 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established *a priori*.

9.3.2.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with identical amounts of the spiking solution and analyze these aliquots as described in Section 11.1.2 to determine the concentration after spiking (A).

9.3.3 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*

9.3.4 Compare percent recovery (R) with the QC acceptance criteria in Table 2.

9.3.4.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 9.5) 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 9.1.2, and repeat analysis of the sample and MS/MSD. However, during the development

of Method 1631, very few interferences have been noted in the determination of Hg using this Method. (See Section 4.4 for information on interferences.)

9.3.4.2 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.

9.3.5 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 9.3.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 200 \times \frac{(|D1-D2|)}{(D1+D2)}$$

Where:
D1 = concentration of Hg in the MS sample
D2 = concentration of Hg in the MSD sample

9.3.6 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.

9.3.7 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 9.3.4, compute the average percent recovery (R_a) and the standard deviation of the percent recovery (s_r). Express the accuracy assessment as a percent recovery interval from $R_a - 2s_r$ 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).

9.4 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.

9.4.1 Bubbler blanks—Bubbler blanks are analyzed to demonstrate that bubbler systems are free from contamination at levels that could affect data quality. At least three bubbler blanks must be run during calibration and with each analytical batch.

9.4.1.1 To analyze a bubbler blank, place a clean gold trap on the bubbler. Purge and analyze previously purged water using the procedure in Section 11, and determine the amount of Hg remaining in the system.

9.4.1.2 If the bubbler blank is found to contain more than 50 pg Hg, the system is out of control. The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed. If the blanks from other bubblers contain less than 50 pg Hg, the data associated with those bubblers remain valid, provided that all other criteria in Section 9 also are met.

9.4.1.3 The mean result for all bubbler blanks (from bubblers passing the specification in Section 9.4.1.2) must be < 25 pg (0.25 ng/L) Hg with a standard deviation (n-1) of <10 pg (0.10 ng/L). If the mean is < 25 pg, the average peak area or height is subtracted from all raw data before results are calculated (Section 12.2).

9.4.1.4 If Hg in the bubbler blank exceeds the acceptance criteria in Section 9.4.1.3, the system is out of control. The problem must be resolved and the system recalibrated. Usually, the bubbler blank is too high for one of the following reasons:

(a) Bubblers need rigorous cleaning;
(b) Soda-lime is contaminated; or
(c) Carrier gas is contaminated.

9.4.2 System blanks— 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.

9.4.2.1 To analyze a system blank, analyze reagent water containing the same amount of reagents used to prepare the calibration standards.

9.4.2.2 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 9 also are met.

9.4.2.3 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 12.3).

9.4.3 Reagent blanks—Reagent 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.

9.4.3.1 Reagent 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 7.6) and 0.2% (v/v) hydroxylamine hydrochloride solution (Section 7.4) must be < 20 pg (0.2 ng/L).

9.4.3.2 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.

9.4.4 Method blanks— Method blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples.

9.4.4.1 A minimum of three method blanks per analytical batch are required for both the bubbler and flow-injection systems.

9.4.4.2 If the result for any method blank containing the nominal amount of reagent used to prepare a sample (Section 11.1.1) 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.

9.4.4.3 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.

9.4.5 Field blanks–Field blanks are used to demonstrate that samples have not been contaminated by the sample collection and transport activities.

9.4.5.1 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.

9.4.5.2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 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 or otherwise used for regulatory compliance purposes.

9.4.5.3 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.

9.4.5.4 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.

9.4.6 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.

9.4.6.1 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.

9.4.6.2 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.

9.4.7 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 6.1.2) 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 9.4.5), the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned.

9.5 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:

9.5.1 Analyze the OPR solution (5 ng/L, Section 7.11) prior to the analysis of each analytical batch according to the procedure beginning in Section 11. An OPR also must be analyzed at the end of an analytical sequence or at the end of each 12-hour shift.

9.5.2 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.

9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 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%.

9.6 Quality control sample (QCS) – The laboratory must obtain a QCS from a source different from the Hg used to produce the standards used routinely in this Method (Sections 7.7–7.10). The QCS should be analyzed as an independent check of system performance.

9.7 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 20%. If the RPD of the field duplicates exceeds 20%, 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.

10.0 Calibration and Standardization

10.1 Calibration and standardization— Separate calibration procedures are provided for a bubbler system (Section 10.2) and flow-injection system (Section 10.3). Both systems are 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.

10.2 Bubbler system calibration

10.2.1 Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak. Further details for operation of the purge-and-trap, desorption, and analysis systems are given in Sections 11.2.1 and 11.2.2.

10.2.2 The calibration must contain a minimum of five non-zero points and the results of analysis of three bubbler blanks. The lowest calibration point must be at the Minimum Level (ML).

NOTE: *The purge efficiency of the bubbler system is 100% and is independent of volume at the volumes used in this Method. Calibration of this system is typically performed using units of mass. For purposes of working in concentration, the volume is assumed to be 100 mL.*

10.2.2.1 Standards are analyzed by the addition of aliquots of Hg working standard A (Section 7.9) and Hg working standard B (Section 7.10) directly into the bubblers. Add 0.50 mL of working standard B and 0.5 mL $SnCl_2$ to the bubbler. Swirl to produce a standard containing 50 pg of Hg (0.5 ng/L). Purge under the optimum operating conditions (Section 10.2.1). Sequentially follow with the addition of aliquots of 0.05, 0.25, 0.50 and 1.0 mL of working standard A to produce standards of 500, 2500, 5000, and 10,000 pg Hg (5.0, 25.0, 50.0 and 100.0 ng/L).

NOTE: *If calibration to the higher levels results in carryover (Section 4.3.8.1), calibrate the system across a narrower range (Section 10.4)*

10.2.2.2 Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the height or area for each peak.

10.2.2.3 Prepare and analyze a minimum of 3 bubbler blanks. If multiple bubblers are used, there must be 1 bubbler blank per bubbler (to a maximum of 4 bubblers). Calculate the mean peak area or height for the bubbler blanks.

10.2.2.4 For each calibration point, subtract the mean peak height or area of the bubbler blanks 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 bubbler-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x) - (\overline{A}_{BB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*

$\overline{A}_{BB}$ = *mean peak height or area for Hg in bubbler blank*

C_x = *mass in standard analyzed (ng)*

10.2.2.5 Calculate the mean calibration factor (CF_m), 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/CF_m.

10.2.2.6 If RSD ≤ 15%, calculate the recovery for the lowest standard using CF_m. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m may be used to calculate the concentration of Hg in samples. 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.

10.2.2.7 Calculate the concentration of Hg in the bubbler blanks (Section 10.2.2.1) using CF_m. The bubbler blanks must meet the criteria in Section 9.4.1; otherwise, mercury in the system must be reduced and the calibration repeated until the bubbler blanks meet the criteria.

10.3 Flow-injection system calibration

10.3.1 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 11.2.1.

10.3.2 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).

10.3.2.1 Place 25-30 mL of reagent water and 250 µL of concentrated BrCl solution (Section 7.6) 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 7.10) 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 7.9) to produce standards of 5.0, 25.0, 50.0 and 100.0 ng/L, respectively. Cap the vials and invert once to mix.

10.3.2.2 Immediately prior to analysis, remove the caps and add 125 µL of NH_2OH solution (Section 7.4). 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.

10.3.2.3 Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the height or area for the Hg peak.

10.3.2.4 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.

10.3.2.5 For each calibration point, subtract the mean peak height or area of the system blanks (Section 9.4.2) 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:

$$CF_x = \frac{(A_x) - (\bar{A}_{SB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*
$\bar{A}_{SB}$ = *mean peak height or area for Hg in calibration blanks*
C_x = *concentration of standard analyzed (ng/L)*

10.3.2.6 Calculate the mean calibration factor (CF_m), 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/CF_m.

10.3.2.7 If RSD ≤ 15%, calculate the recovery for the lowest standard (0.5 ng/L) using CF_m. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m 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.

10.3.2.8 Calculate the concentration of Hg in the system blanks (Section 9.4.2) using CF_m. The system blanks must meet the criteria in Section 9.4.2; otherwise, mercury in the system must be reduced and the calibration repeated until the system blanks meet the criteria.

10.4 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

11.0 Procedure

NOTE: *The following procedures for analysis of samples are provided as guidelines. Laboratories may find it necessary to optimize the procedures, such as drying time or potential applied to the Nichrome wires, for the laboratory's specific instrument set-up.*

11.1 Sample Preparation

11.1.1 Pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle. If BrCl was not added as a preservative (Section 8.5), add the amount of BrCl solution (Section 7.6) given below, cap the bottle, and digest at room temperature for a 12 h minimum.

11.1.1.1 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.

11.1.1.2 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.

11.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour 2 additional 100-mL aliquots from a selected sample (see Section 9.3), spike at the level specified in Section 9.3, and process in the same manner as the samples. There must be a minimum of 2 MS/MSD pairs for each analytical batch of 20 samples.

11.2 Hg reduction and purging—Separate procedures are provided for the bubbler system (Section 11.2.1) and flow-injection (Section 11.2.2).

11.2.1 Hg reduction and purging for the bubbler system

11.2.1.1 Add 0.2-0.25 mL of NH_2OH solution to the BrCl-oxidized sample in the 125-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 min 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.*

11.2.1.2 Connect a fresh trap to the bubbler, pour the reduced sample into the bubbler, add 0.5 mL of $SnCl_2$ solution, and purge the sample onto a gold trap with N_2 at 350 ± 50 mL/min for 20 min.

11.2.1.3 When analyzing Hg samples, the recovery is quantitative, and organic interferents are destroyed. Thus, standards, bubbler blanks, and small amounts of high-level samples may be run directly in previously purged water. After very high samples (Section 4.3.8.1), a small degree of carryover (<0.01%) may occur. Bubblers that contain such samples must be demonstrated to be clean prior to proceeding with low level samples. Samples run immediately following a sample that has been determined to result in carryover must be reanalyzed using a bubbler that is demonstrated to be clean as per Section 4.3.8.1.

11.2.2 Hg reduction and purging for the flow-injection system

11.2.2.1 Add 0.2-0.25 mL of NH_2OH solution (Section 7.4) to the BrCl-oxidized sample in the 125-mL sample bottle or in the autosampler tube (the amount of NH_2OH required will be approximately 30 percent of the BrCl volume). 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.*

11.2.2.2 Pour the sample solution into an autosampler vial and place the vial in the rack.

11.2.2.3 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 4.3.8.1) must be reanalyzed using a system demonstrated to be clean as per Section 4.3.8.1.

11.3 Desorption of Hg from the gold trap

11.3.1 Remove the sample trap from the bubbler, place the Nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 2).

11.3.2 Pass argon through the sample and analytical traps at a flow rate of approximately 30 mL/min for approximately 2 min to drive off condensed water vapor.

11.3.3 Apply power to the coil around the sample trap for 3 minutes to thermally desorb the Hg (as Hg(0)) from the sample trap onto the analytical trap.

11.3.4 After the 3-min desorption time, turn off the power to the Nichrome coil, and cool the sample trap using the cooling fan.

11.3.5 Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the Nichrome wire coil around the analytical trap. Heat the analytical trap for 3 min (1 min beyond the point at which the peak returns to baseline).

11.3.6 Stop data collection, turn off the power to the Nichrome coil, and cool the analytical trap to room temperature using the cooling fan.

11.3.7 Place the next sample trap in line and proceed with analysis of the next sample.

NOTE: *Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing through the analytical trap.*

11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds.

11.4.1 Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapor on the trap(s), or an analytical trap damaged by chemical fumes or overheating.

11.4.2 Damage to an analytical trap is also indicated by a sharp peak, followed by a small, broad peak.

11.4.3 If the analytical trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces.

11.4.4 Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

12.0 Data Analysis and Calculations

12.1 Separate procedures are provided for calculation of sample results using the bubbler system (Section 12.2) and the flow-injection system (Section 12.3), and for method blanks (Section 12.4).

12.2 Calculations for the bubbler system

12.2.1 Calculate the mean peak height or area for Hg in the bubbler blanks measured during system calibration or with the analytical batch (A_{BB}; n = 3 minimum).

12.2.2 Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

$$[Hg]\ (ng/L) = \frac{A_s - \overline{A}_{BB}}{CF_m \times V}$$

where:
A_s = *peak height (or area) for Hg in sample*
$\overline{A}_{BB}$ = *peak height (or area) for Hg in bubbler blank*
CF_m = *mean calibration factor (Section 10.2.2.5)*
V = *Volume of sample (L)*

12.3 Calculations for the flow-injection system

12.3.1 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)

12.3.2 Calculate the concentration of Hg in ng/L in each sample according to the following equation:

$$[Hg]\ (ng/L) = \frac{(A_s - \overline{A}_{SB})}{CF_m} \times \frac{V_{std}}{V_{sample}}$$

where:
A_s = *peak height (or area) for Hg in sample*
$\overline{A}_{SB}$ = *mean peak height (or area) for Hg in system blanks*
CF_m = *mean calibration factor (Section 10.3.2.6)*
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*

12.4 Calculations for concentration of Hg in method blanks, field blanks, and reagent blanks.

12.4.1 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 12.2.2 (if bubbler system is used) or Section 12.3.2 (if flow injection system is used) and substituting the peak height or area resulting from the method blank, field blank, or reagent blank for A_s.

12.4.2 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 9.4.4.3). The concentration of Hg in the corresponding method blank may be subtracted from the concentration of Hg in the sample per Section 12.5.2.

12.5 Reporting

12.5.1 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.

12.5.2 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.

12.5.3 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, but do not relieve a discharger or permittee of reporting timely results.

13.0 Method Performance

13.1 This Method was tested in 12 laboratories using reagent water, freshwater, marine water and effluent (Reference 16.19). The quality control acceptance criteria listed in Table 2 were verified by data gathered in the interlaboratory study, and the method detection limit (MDL) given in Section 1.5 was verified in all 12 laboratories. In addition, the techniques in this Method have been compared with other techniques for low-level mercury determination in water in a variety of studies, including ICES-5 (Reference 16.20) and the International Mercury Speciation Intercomparison Exercise (Reference 16.21).

13.2 Precision and recovery data for reagent water, freshwater, marine water, and secondary effluent are given in Table 3.

14.0 Pollution Prevention

14.1 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.

14.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

15.0 Waste Management

15.1 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).

15.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

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

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17.0 Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

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

17.2 **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).

17.3 **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.

17.4 **Bubbler Blank**—For this Method, the bubbler blank is specific to the bubbler system and is used to determine that the analytical system is free from contamination. After analysis of a standard, blank, or sample, the solution in the bubbler is purged and analyzed. A minimum of three bubbler blanks is required for system calibration.

17.5 **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.

17.6 **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.

17.7 **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.

17.8 **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.

17.9 **May**—This action, activity, or procedural step is allowed but not required.

17.10 **May not**—This action, activity, or procedural step is prohibited.

17.11 **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.

17.12 **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 10^n, where n is an integer (See Section 1.5).

17.13 **Must**—This action, activity, or procedural step is required.

17.14 **Quality Control Sample (QCS)**—A sample containing Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.

17.15 **Reagent blank**—Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, $NH_2OH{\cdot}HCl$, and $SnCl_2$) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.

17.16 **Reagent Water**—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MΩ 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.

17.17 **Regulatory Compliance Limit**—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.

17.18 **Shall**—This action, activity, or procedure is required.

17.19 **Should**—This action, activity, or procedure is suggested, but not required.

17.20 **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.

17.21 **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.

17.22 **Ultraclean Handling**— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

18.0 Tables and Figures

Table 1

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 2

Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery (IPR)	9.2.2	
Precision (RSD)	9.2.2.3	21
Recovery (X)	9.2.2.3	79-121
Ongoing Precision and Recovery (OPR)	9.5.2	77-123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

Table 3

Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water Using Method 1631

Matrix	***Mean Recovery (%)**	***Precision (% RSD)**
Reagent Water	98.0	5.6
Fresh Water (Filtered)	90.4	8.3
Marine Water (Filtered)	92.3	4.7
Marine Water (Unfiltered)	88.9	5.0
Secondary Effluent (Filtered)	90.7	3.0
Secondary Effluent (Unfiltered)	92.8	4.5

*****Mean percent recoveries and RSDs are based on expected Hg concentrations.

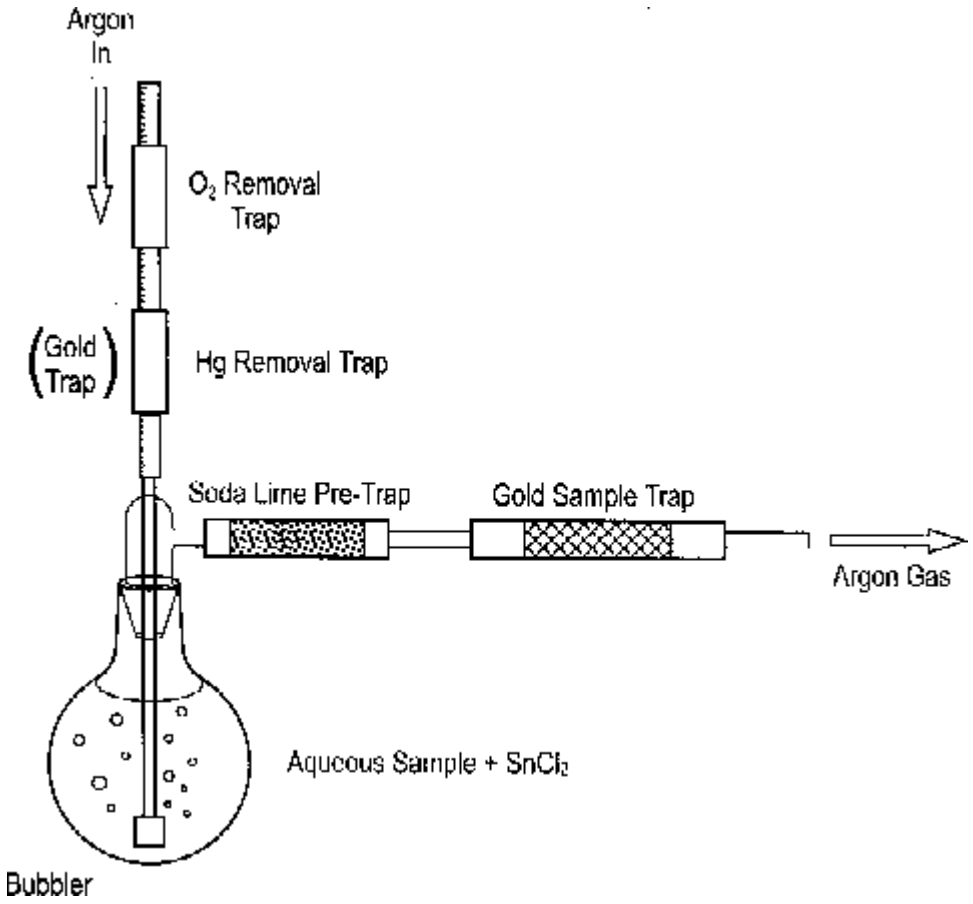

Figure 1. Schematic Diagram of Bubbler Setup

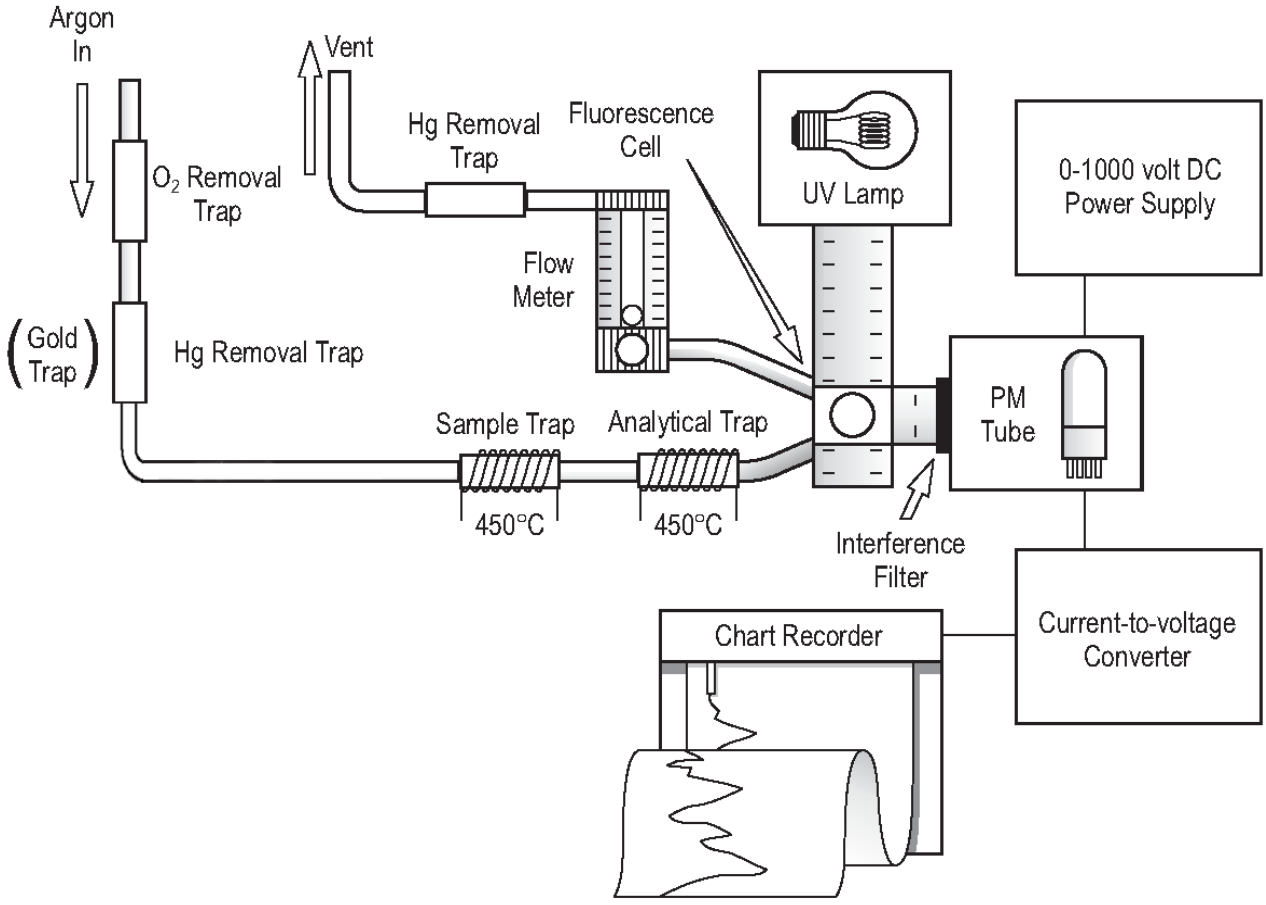

Figure 2. Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

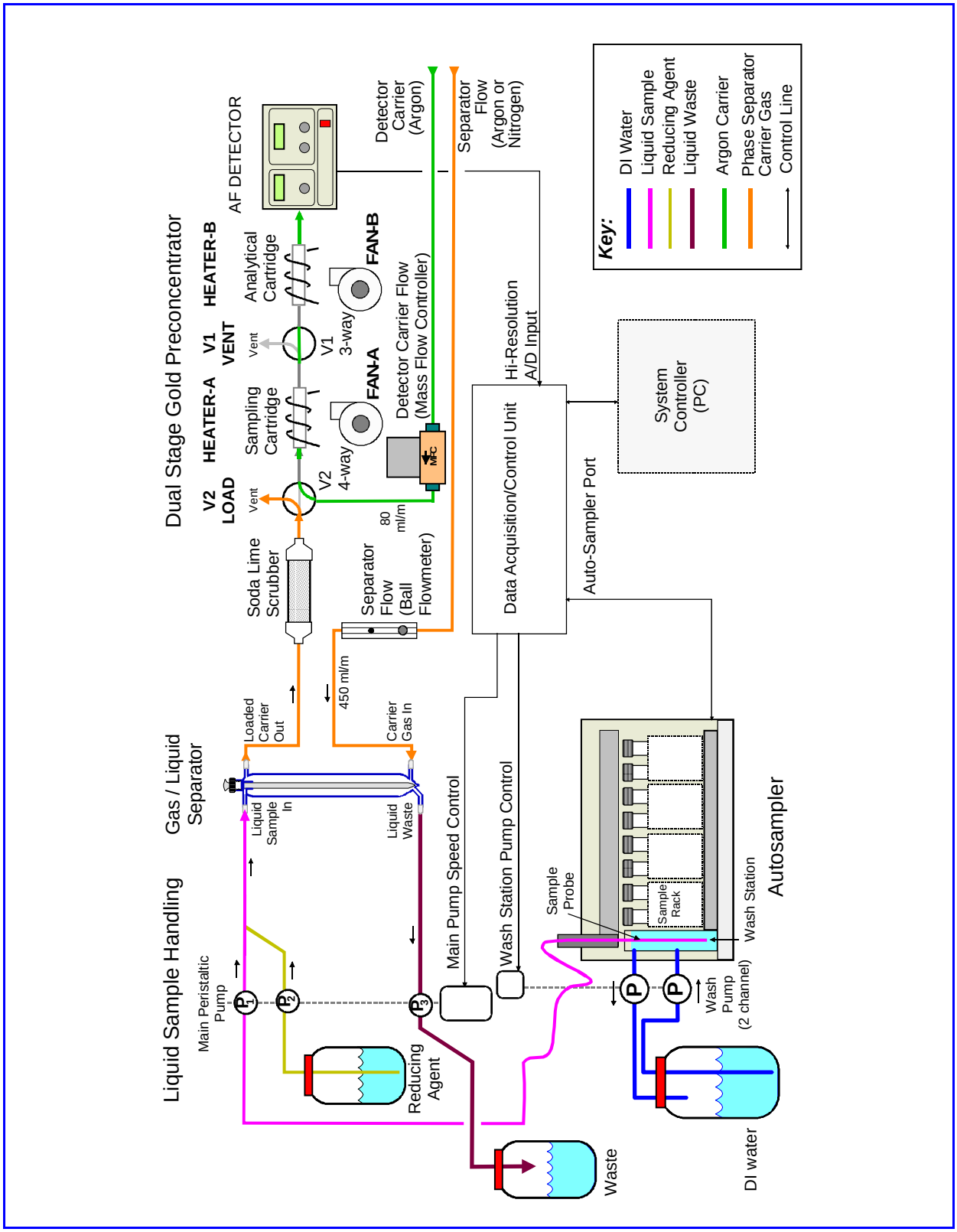

Figure 3. Schematic Diagram of the Flow-Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

Standard Operating Procedure (SOP)

Determination of Reactive Mercury in Surface Water by Direct Tin-Reduction of Inorganic Hg(II), Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

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Introduction: This Standard Operating Procedure (SOP) is modified from that for the analysis of total Hg in water, as developed by M. Olson and J. DeWild (Olson and Dewild, 1999).

1.0 Scope and Application:

1.1 Applicable Matrices: This method may be used to determine reactive mercury ($Hg(II)_R$) in filtered or non-filtered surface water, stormwater runoff or precipitation (rain or snow) samples.

1.2 Minimum Reporting Limit: The minimum reporting limit for this method is approximately 0.03 ng (absolute Hg concentration). Since the typical range of aqueous phase assayed is 100 ml, the resulting minimum reporting range is approximately 0.3 ng/L. However, this could be extended by assaying even larger sample volumes.

2.0 Summary of Method:

This method combines the concept of chemical extraction techniques with standard mercury determination technique of stannous Chloride ($SnCl_2$) reduction to operationally determine the amount of readily reducible Hg(II) in aqueous samples. The biggest difference with this approach and that for quantifying total-mercury, is that there is no BrCl oxidation step to remove organic constituents. This operationally defined 'reactive' divalent inorganic mercury ($Hg(II)_R$) parameter is used as a surrogate for labile mercury species that may be available to microbes for Hg(II)-methylation.

Freshly collected (within 7 days) aqueous phase samples (filtered or non-filtered) are subsampled (100 ml) into a trace-metal clean 200 ml gas-purging vessel (bubbler). Acidic tin chloride ($SnCl_2$) solution is added and the mixture is allowed to react (reducing labile Hg(II) to gaseous Hg^0 while purging with an inert gas for a defined time period (15 minutes). The gaseous Hg^0 is purged onto gold-coated sand traps (sample). The trapped Hg^0 is subsequently thermally desorbed onto a second gold trap (analytical), and from that detected by cold vapor atomic fluorescence spectrometry (CVAFS). A parallel set of samples can be similarly processed, without the addition of $SnCl_2$, to assess the concentration of dissolved gaseous Hg^0 in the original aqueous sample (which is often minor compared to the labile Hg(II) fraction), an subsequently subtracted from its $SnCl_2$ amended counterpart to calculate $Hg(II)_R$.

3.0 Safety Issues: Before beginning any of the procedures involved in this method, each individual must read and sign the Chemical Hygiene Plan developed for the lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets for that chemical – all of which are located in the laboratory. Two extremely important areas for this method are addressed below.

3.1 Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Due to the toxicological and physical properties of Hg, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of gloves and high flow volume hoods when preparing standards.

3.2 Strong acid solutions are employed in the cleaning of equipment, preparation of reagents and in sample preservation. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant clothing and the utilization of high volume fume hoods.

4.0 Sample Containers, Preservation and Holding Times:

4.1 Aqueous samples are initially collected in trace-metal cleaned containers (e.g. glass, Teflon, or PETG plastic). Unless containers are proven to be effectively trace-metal clean directly out of the box (e.g. certified I-Chem vials, some brands of PETG plastic bottle), appropriate cleaning methods must be employed. These include the prescribed cleaning approach for Teflon or glass as detailed in EPA Method 1631 Section 6.1.2.1 (EPA, 2002). Container cleaning will consist of: a) soaking vials for 24 hours in dilute Micro solution, b) rinsing 3X with Milli-Q water, c) soaking in 5% HCl bath for 24 hours, d) rinsing 3X with Milli-Q water, e) drying vials in Laminar flow hood, f) storing vials in a double zip locked bag until further use. Glass may also be combusted (500˚C) for 4 hrs in a muffle furnace to volatilize trace amounts of Hg contamination.

4.2 Aqueous handling protocols are designed to minimize the contact of the sample, with the standard 'clean hands / dirty hands' approach (USEPA, 1996) being used in the field and/or laboratory to collect the sample and transfer it to the appropriate container. Field samples are stored chilled in the dark and transferred to a refrigerator upon return to the laboratory. Freezing is not recommended as it can have variable effect on dissolved organic matter in solution (precipitating it out in some cases) and can facilitate Hg(II) adhering to the walls of the sample vessel. Apart from refrigeration, no other preservation (e.g. acidification) is used for samples to be run for $Hg(II)_R$.

4.3 If the dissolved fraction is to be targeted, sample filtration should occur within 24 hrs of collection. All filtration equipment must be rigorously cleaned as per section 4.1, and pre-combusted glass fiber filters should be used.

4.4 Sample holding times should not exceed 7 days post-collection.

5.0 Reagents and Standards:

5.1 Reagents: All reagents and/or dry chemicals used to make reagents must be of the highest purity available from the vendor and shown to be low in mercury. Upon receipt at the laboratory, containers will be marked with the date of receipt and stored in the appropriate areas. When reagents are mixed for use in this method, the person who mixes them will initial and date the reagent container.

5.1.1 Reagent water: Ultra pure reagent grade water shown to be > 18 MΩ starting from pre-purified source (distilled, RO, etc.). The water is delivered through a 0.2 uM filter. All water is obtained from a Millipore Academic water purification system.

5.1.2 Hydrochloric Acid: Trace metal grade HCl (containing less than 5 ng/L Hg) .

5.1.3 Stannous chloride ($SnCl_2$). In a 100 mL acid-cleaned beaker, add 10 mL concentrated HCl flushed with N2 gas. After 30 mins add 20 g $SnCl_2$ and stir to dissolve the SnCl2. Bring the total volume to 100ml and purge for 1 hour with Hg-free N_2 at 300 mL/min. Dispense into clean serum vials, and purge the head space. Cover vials with aluminum foil to prevent oxidation. Cloudiness can occur. Discard solution if solution is cloudy or yellow upon preparation.

5.1.4 Nitrogen (N_2) or Helium (He). Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

5.1.5 Argon (Ar). Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

5.2 Standards: Upon receipt at the laboratory or on the day of preparation, containers should be labeled with the date received or made and the initials of the person preparing them. The stock and substock standards should by stored outside of the clean laboratory to prevent contamination of the entire lab.

5.2.1 Stock standard (1000 mg/L): Commercially available Hg standard verified against a NIST standard reference material. All subsequent standards are prepared using the stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.

5.2.2 Substock standard (1000 ng/mL): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette 100 µL of the stock standard (1000 mg/L) and bring to volume with reagent water. To clean the volumetric flask, fill to approximately 80 % total volume with 30% HCl, place the ground glass stopper on its side over the opening to

prevent pressure buildup, and heat to near boiling on a hotplate for 8 hours.

5.2.3 Working standard (1 ng/mL): Dispense approximately 50 mL of reagent grade water and 1 mL of BrCl into a 100 mL mercury clean (sec. 5.2.2) class A volumetric flask. Pipette 100 µL of the substock standard (1000 ng/mL) and bring to volume with reagent water. This working standard must be compared to the previous working standard and agree within ± 5%. Prepare fresh every 6 months.

6.0 Quality Control: Each analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This includes the ability to reproduce standards, establish acceptable daily detection limits (DDL), produce acceptable relative percent differences between replicates, and produce spike recoveries that meet acceptance criteria.

6.1 Bubbler blanks: A bubbler blank is prepared by adding 0.5 ml of $SnCl_2$ to a bubbler containing approximately 50 mL of Milli-Q water and 250 µl of concentrated HCl. Blanks are critical to the reliable determination of Hg at low levels. Frequent analysis of bubbler blanks is required to demonstrate freedom of system contamination and the absence of carry over from one sample or standard to the next.

6.1.1 Acceptance criteria: No bubbler blank (BB) must contain more than 25 pg of Hg. A daily detection limit (DDL) is calculated each day prior to analysis of samples. The DDL is computed using the following formula:

$$DDL = 3 \times \sigma_{BB}$$

σ_{BB} *= is the standard deviation (*σ*, n=4 bubblers) of the peak areas. The DDL units are (ng), in absolute terms.*

The acceptable value for the DDL must be 0.1 ng or less.

6.1.2 Corrective Actions:

6.1.2.1 If a bubbler blank is found to contain more than 25 pg Hg, at the beginning of the day, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is accurate. If this second set blanks is also out of compliance the analyst must isolate and correct the problem before continuing.

6.1.2.2 If a bubbler blank is found to contain more than 25 pg Hg, during the course of the day's analyses, the system is out of QA compliance and data produced on that bubbler should be rerun or carefully evaluated and flagged as being suspect.

6.1.2.3 If the DDL exceeds 0.1 ng, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is accurate. If this second set of blanks is also out of QA compliance, the analyst must isolate and correct the problem before continuing.

6.2 Standards: A standard is prepared by adding a known volume of working $HgCl_2$ standard solution (1 ng/ml) and 0.5 ml of $SnCl_2$ to a bubbler containing approximately 50 mL of Milli-Q water. The water in the bubbler must first be reduced with $SnCl_2$ and purged for 20 minutes to remove all Hg, prior to analysis of standards.

6.2.1 Acceptance criteria: A mean response factor (RF_m) is calculated at the beginning of the day from the ratio of mass to peak area (ng/PA) for 4 standards of different concentrations (sec. 7.6.11). The RSD among the ng/PA ratios of the standards must ≤10%.

$$RSD\ (\%) = (\sigma / mean) \times 100$$

σ = standard deviation among four standards

6.2.2 Corrective action: If the RSD of the standards fails to meet acceptance criteria, an additional set of standards must be run to ensure no operator error exists. If the second set of standards still does not meet acceptance criteria, the analyst must isolate and correct the problem before continuing.

6.3 Certified Reference Material (CRM) sample: No certified value for reactive Hg(II) has been established in any known CRM.

6.4 Duplicates: All samples are run in duplicate if the sample lot is sufficiently small. If the batch is larger than 10 samples, then one of every ten samples analyzed must be analytical duplicates, and one of every 20 must be a field duplicate.

6.4.1 Acceptance criteria:

6.4.1.1 The acceptance criteria is a relative percent difference (RPD) of ≤ 10%.

$$RPD\ (\%) = ((|X_1 - X_2|) / Mean) \times 100$$

X1 = Measured value of first replicate

X2 = Measured value of second replicate

6.4.2 Corrective action:

6.4.2.1 If the RPD between the two replicates is greater than 10%, the sample is analyzed a third time.

6.4.2.2 If the relative standard deviation (RSD) between the three replicates is greater than 10 %, the sample is flagged and/or analyzed a fourth time.

$$RSD\ (\%) = (\sigma / mean) \times 100$$

σ = standard deviation among three replicates

6.5 Matrix spike: The performance of a matrix spike has been deemed to have little or no value to this analysis as added mercury partitions into native dissolved organic matter to varying degrees, depending on the aqueous sample composition (e.g. organic content, solid phase mineralogy, redox conditions, etc…). Thus, low recoveries could not be distinguished from particularly strong partitioning.

7.0 Procedure

7.1 Comments: The samples are collected and prepared using ultra clean sampling techniques.

7.1.1 Interferences:

7.1.1.1 Free halogens: The destruction of the gold traps exists if they are exposed to free halogens resulting in low mercury values. This can be avoided with the addition of a soda lime trap directly upstream of the sample traps during purging. Traps should be changed every 2-3 days.

7.1.1.2 Water vapor: Water vapor may collect on the gold traps during the purging step. If water vapor is present on the traps this will give a false peak during analysis. This can be avoided with the addition of a soda lime directly upstream of the sample traps during purging.

7.1.1.3 Carrier gas: The fluorescent intensity of the detector is strongly dependent on the inertness of the carrier gas. The dual amalgamation step virtually eliminates quenching due to impurities in the carrier gas, but it is the analyst's responsibility to ensure high purity inert carrier gas and a leak free analytical train.

7.1.2 Helpful hints:

7.1.2.1 Working with detection limits in the parts per trillion range, protecting these samples from contamination cannot be over emphasized. The greatest difficulty in low level mercury analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout the preparation, collection and analysis procedures to avoid contamination.

7.1.2.2 It is very important that the laboratory air be low in both particulate and gaseous Hg. The mercury in the air can be reduced with the use of gold-coated cloth at the intakes of the laminar flow hoods.

7.1.2.3 If cloudy residue becomes apparent on the inside of the bubblers, dissolve approximately 2 grams of Potassium Hydroxide in 250 mL of reagent water and allow bubblers to soak for 1 hr.

7.1.2.3 If the peak area for Hg on a trap exceeds 3 ng, reburn the trap. If the peak exceeds 5 pg, reburn the trap, if a peak is still present, discard the trap and incorporate a new trap in its place.

7.2 General Description: Refer to section 2 of this procedure for a summary of this method.

7.3 Labware:

7.3.1 All-plastic pneumatic fixed-volume and variable pipettors in the range of 5 µL to 10 mL.

7.3.2 Analytical balance capable of measuring to the nearest 0.0001 g.

7.4 Sample preparation

7.4.1 Prepare samples according to section 4.3

7.5 Instrumentation:

7.5.1 Regulator capable of supplying 30 psi of pressure.

7.5.2 Teflon tubing (sizes: 1/8" – ¼" i.d.) is use for all transfer lines between bubblers, soda lime traps, and gold traps on the bubbling rig; and between the gold traps on the CVAFS dual amalgam flushing train.

7.5.3 C-Flex tubing (sizes: 1/8" – ¼" i.d.) is used for connecting teflon tubing and glass gold traps and glass bubblers.

7.5.4 Shrink-wrap tubing is used for connecting teflon tubing and glass gold traps.

7.5.5 Heat gun to seal shrink wrap tubing around glass fittings.

7.5.6 Flow meter(s) capable of measuring a N_2, He, or Ar flow of up to 300-400 mL/min.

7.5.7 Needle valve to shut off and control N_2 flow to bubblers.

7.5.8 Gold coated sand (or glass bead) traps: The gold coated glass bead traps are constructed of a 7 mm quartz tube, 8 cm long and with a constriction at 1 ¼" from the outlet end. A quartz plug is placed into the inlet end, about 0.7 g (3.5 cm in the tube) of gold coated beads are added and the inlet end is plugged with another piece of quartz wool. Female fittings for gold traps are made from small pieces of 6 mm i.d. monobarb Teflon tubing. Heating ¼" Teflon tubing and sealing one end by pinching with pliers until cool creates end plugs.

7.5.9 Teflon plugs (solid and single holed) to cap the ends of the sample traps, and to use as connectors between teflon tubing and analytical traps.

7.5.10 Bubblers Rig: The bubblers are 200 mL borosilicate glass flasks with the standard 24/40 tapered neck. The sparging stopper has a coarse glass frit that extends to the bottom of the flask. Bubbling rig consists of (in order) a He or N_2 gas source, a needle valve gas-shut off, a gold-pretrap, a single line split into 4 lines (using plastic or Teflon "T"'s), a flowmeter on each of these lines leading to a single bubbler, a soda lime trap (7.5.11) connected to the outlet of each bubbler, a sample gold trap after each soda lime trap. Teflon tubing is used to connect all parts, and C-flex tubing, shrink tubing and one-holed Teflon plugs are used to connect lines to bubblers, soda-lime and gold traps.

7.5.11 Soda lime traps: The soda lime traps are constructed of a 10 mm i.d. x 7 cm length Teflon tube. The traps are filled with 4-8 mesh soda lime with salinized glass wool plugs at either end to hold the soda lime in place. The traps are pre-purged for 20 min before collection of a sample onto a gold trap. Soda lime traps should be repacked every 2-3 days.

7.6 Desorption and analysis:

7.6.1 Analytical train: The sample train consists of (in order) an Ar gas source, a gas flow shut-off valve, a gold pre-trap, a sample gold trap, an analytical gold trap, the CVAFS unit (Brooks Rand Model III), a rotometer to control gas flow at the end of the train. All pieces are connected with lengths of Teflon tubing, attached with C-flex and shrink tubing, as needed. Once a sample trap is prepared, it is placed on the analytical train, and the Ar gas flow is set at 35 ml/min. A variable AC transformer, with two alligator clips at the output, connects to Nichrome coils that are wrapped around the pre-trap, sample traps and the analytical trap. The alligator clips are first placed on the Nichrome wire of the sample trap, which is heated to 425^{o}C (12 V) for 2 minutes. This desorbs the Hg^0 from the sample trap and places on the analytical trap. The sample trap is then cooled for 2 minutes by an electric fan. The clips are then moved to the analytical trap, which is then similarly heated for 2 minutes. As the Hg^0 desorbs from the analytical trap it passes through the CVAFS detector and up an exhaust hood. The signal from the detector is sent to an integrator, which records the sample peak area and retention time.

7.6.2 Integrator: Peak Simple digital signal integration software (run on a PC) is used to integrate the signal coming out of the Brooks Rand Mercury analyzer.

7.7 Initial start-up, calibration and sample analysis:

7.7.1 Check pressure in Argon tank to verify adequate volume for the day's analyses.

7.7.2 Adjust the rotometer at detector outlet to 35 mL/min.

7.7.3 Check baseline at the integrator (Attenuation = 4, Area reject = 1000, Peak Threshold = 5), after pre-burning the pre-trap and analytical trap. The baseline should be flat.

7.7.4 Start by pre-burning the set of eight sample traps. While these traps are being burned proceed with step **7.7.5**.

7.7.4.1 Remove the plugs from the ends of the first trap and place it into the analytical train by threading it, with the id number downstream, through the center of the Nichrome wire coil. Center the Nichrome wire over the gold sand. Heat as per **7.6.1**. Repeat for each of the remaining sample traps. Similarly heat the analytical trap after all the sample traps are burned, to clean it, prior to running actual samples.

7.7.4.2 You need to have 4 traps burned before step **7. 7.5** is complete. You have 8 traps and four bubblers. The bubbling of samples takes 15 minutes and the burning of 4 traps approximately 36 minutes. You will be bubbling a round of samples while burning (analyzing) the previous round. This is the cycle you will follow throughout the day.

7.7.5 Set-up bubbler rig (as per **7.5.10**) with thoroughly cleaned bubblers containing 50 mL of reagent grade Milli-Q water and 250 µL 12N HCl. Add 500 µL of $SnCl_2$ solution. Attach a clean gold trap to the end of the soda lime trap and proceed purging as in **7.6.7**. Begin purging bubblers at 250 - 300 mL/min with N_2 or He for 15 minutes. This represents the bubbler blank set.

7.7.5.1 Note: Time course studies have revealed that in many samples the rate of reduction by $SnCl_2$ is very high within the first 5 minutes and then reaches a minimum at 15 minutes. After 15 minutes, the rates gradually increase, suggesting that Hg(II) may be released from other components (e.g. strongly bound to DOC or suspended particulates). The pool that is reduced within the first 15 minutes is therefore the operationally defined $Hg(II)_R$ pool.

7.7.6 When the 15-minute purging cycle for the bubbler blanks has elapsed, remove the gold traps from the end of the soda lime traps, cap both ends of the gold traps with solid Teflon plugs, and shut-off the gas flow to the bubblers.

7.7.7 Analyze the gold traps as in **7.6.1**. While these traps are being burned proceed with step **7.7.8**.

7.7.8 Pipette 0.1, 0.3, 0.6, and 1.0 mL of the working standard (1 ng/ml) into bubblers 1, 2, 3, and 4, respectively. Attach a clean gold trap to the end of the soda lime trap and proceed as in **7.6.7**. This represents your first standard set.

7.7.9 Analyze the gold traps as in **7.6.1**. While these traps are being burned proceed with step **7.7.10**

7.7.10 Empty contents of the bubbler, and rinse thoroughly with MQ water. Add 100 mL of environmental sample followed by 500 ul of $SnCl_2$ solution. Purge sample at 250 - 300 mL/min with N_2 or He for 15 minutes.. This represents your first sample set.

7.7.11 Analyze the gold traps from **7.7.10** as in **7.6.1**. While these traps are being burned proceed with the next round of samples as per the chart below.

7.7.12 In between sample sets, the bubblers should be rinsed thoroughly. Pour the contents of the bubbler into a waste container. Detach bubbler from gas lines. Fill the bubbler with DI water and shake vigorously. Lodge a 1000 µL pipette tip into the end of a DI line, creating a high-pressure stream. Use this stream to clear the glass frits of any particulates. Once clear, rinse the bubbler with 1M KOH. Remove the KOH and rinse the bubbler completely, using the high pressure DI stream to rinse flush the inside of the glass fritted tube. Use a clean source of air to flush any water vapor out of the bubbler inlet or outlet before attaching to soda lie trap.

Round	BUBBLER 1	Bubbler 2	Bubbler 3	Bubbler 4
Blanks	BB1	BB2	BB3	BB4
Standards	0.1 ng	0.3 ng	0.6 ng	1.00 ng
Sample set	S1	S1	S2	S2
Sample set	S3	S3	S4	S4
Sample set	S5	S5	S6	S6
Sample set	S7	S7	S8	S8
OOPS	OOPS	OOPS	OOPS	OOPS

BB = bubbler blank

SX = sample

OOPS = sample whose replicates do not meet acceptance criteria

7.7.13 All samples need to be bracketed by standards, if the sample peak area is greater than the highest standard, either a higher standard is analyzed or the sample is analyzed using a smaller sample volume.

7.8 Calibration and performance documentation: During the analysis run, the analyst must evaluate the calibration data, bubbler blank values, and RPDs for duplicate analyses to ensure acceptance criteria (sec. 6.0) are being met. The following information must be recorded on the daily datasheet.

7.8.1 Date of analysis.

7.8.2 Type and date prepared for reagents and standards used.

7.8.3 Name of analyst.

7.8.4 Identification of bubbler contents, volume analyzed, instrument response, and sample trap identification for each analysis performed.

7.8.5 Comments pertaining to special samples run, problem samples, corrective actions taken, and results of any calculations performed to ensure acceptance criteria are being met.

7.8.6 Project that the samples are being run for.

7.9 Shut-down:

7.9.1 After the last sample has been purged, the following steps must be performed to properly store the bubblers until the next analysis run.

7.9.1.1 Shut off N_2 flow at the needle valve and at the tank regulator.

7.9.1.2 Remove the N_2 line from the inlet and the soda lime trap from the outlet of the bubblers.

7.9.1.3 Thoroughly rinse the bubblers and the sparging stoppers with copius amounts of reagent grade water.

7.9.1.4 Fill the bubblers to approximately 95% volume with 3M KOH.

7.8.1.5 Carefully replace the sparging stopper, cap the inlet and outlet of the bubbler and return to the hood.

7.9.2 After the last sample trap has been burned, leave the trap in the analytical train to avoid contamination from room air.

7.9.3 Shut off all gasses, CVAFS detector, and variable AC transformer.

7.10 Maintenance, maintenance records and Responsibilities

7.10.1 Gold traps attached to regulators on the N_2 and Ar tanks should be burned clean at the beginning of every run.

7.10.2 Nichrome wire temperature should be checked quarterly.

7.10.3 Detector lamp driver voltage should be checked quarterly. If voltage exceeds 12.5, the lamp should be adjusted or replaced according to manufacturers guidelines.

7.11 Calculations

7.11.1 The following formula is used to calculate $Hg(II)_R$ concentration for environmental and QC samples.

$$C = ((PA_s - BB_m) \times RF_m) / V_s * 1000$$

C = concentration in ng/L

PA_s = peak area of sample, in PA units

BB_m = mean bubbler blank, in PA units (sec. 6.1)

RF_m = mean response factor, in ng/PA unit (sec. 6.2)

V_s = volume of sample assayed, in ml

7.12 Data validation and evaluation: After the data has been entered into the EXCEL spreadsheet, someone other than the analyst must verify that no values have been incorrectly entered in either the log book or the spreadsheet. The data is then evaluated carefully by the QC officer to ensure all data quality objectives have been met for the run and that the data seem reasonable. Data is evaluated as to reasonability if historical data from a site exists.

7.13 Reporting:

7.13.1 Reporting units: Total mercury as ng/L.

7.13.2 Reporting levels and significant figures:

7.13.2.1 Report to the nearest 0.1 ng/L for values less than 10 ng/L.

7.13.2.2 Report to three significant figures for values exceeding 10 ng/L.

8.0 Archiving: All raw data produced in the laboratory is archived in a filing cabinet located in the clean room. Hard copies of the data report sheets are archived in the appropriate project 3-ringed binder. All electronic data is archived on the laboratory manager's computer, which is backed up daily.

9.0 References

EPA, 2002, Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: U.S. Environmental Protection Agency, Office of Water EPA-821-R-02-019, 46 p., On-Line: http://www.epa.gov/waterscience/methods/method/mercury/1631.pdf

Olson, M.L., and Dewild, J.F., 1999, Techniques for the collection and species-specific analysis of low levels of mercury in water.: U. S. Geological Survey - Toxic Substance Hydrology Program. 99-4018B, 191-199 p. [Water-Resources Investigation Reports], On-Line:

USEPA, 1996, Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels: U.S. Environmental Protection Agency, Office of Water Engineering and Analysis Division, 37 p., On-Line:

Standard Operating Procedure (SOP)

Determination of Reactive Mercury in Surface Water by Direct Tin-Reduction of Inorganic Hg(II), Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

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Introduction: This Standard Operating Procedure (SOP) is modified from that for the analysis of total Hg in water, as developed by M. Olson and J. DeWild (Olson and Dewild, 1999).

1.0 Scope and Application:

1.1 Applicable Matrices: This method may be used to determine reactive mercury ($Hg(II)_R$) in filtered or non-filtered surface water, stormwater runoff or precipitation (rain or snow) samples.

1.2 Minimum Reporting Limit: The minimum reporting limit for this method is approximately 0.03 ng (absolute Hg concentration). Since the typical range of aqueous phase assayed is 100 ml, the resulting minimum reporting range is approximately 0.3 ng/L. However, this could be extended by assaying even larger sample volumes.

2.0 Summary of Method:

This method combines the concept of chemical extraction techniques with standard mercury determination technique of stannous Chloride ($SnCl_2$) reduction to operationally determine the amount of readily reducible Hg(II) in aqueous samples. The biggest difference with this approach and that for quantifying total-mercury, is that there is no BrCl oxidation step to remove organic constituents. This operationally defined 'reactive' divalent inorganic mercury ($Hg(II)_R$) parameter is used as a surrogate for labile mercury species that may be available to microbes for Hg(II)-methylation.

Freshly collected (within 7 days) aqueous phase samples (filtered or non-filtered) are subsampled (100 ml) into a trace-metal clean 200 ml gas-purging vessel (bubbler). Acidic tin chloride ($SnCl_2$) solution is added and the mixture is allowed to react (reducing labile Hg(II) to gaseous Hg^0 while purging with an inert gas for a defined time period (15 minutes). The gaseous Hg^0 is purged onto gold-coated sand traps (sample). The trapped Hg^0 is subsequently thermally desorbed onto a second gold trap (analytical), and from that detected by cold vapor atomic fluorescence spectrometry (CVAFS). A parallel set of samples can be similarly processed, without the addition of $SnCl_2$, to assess the concentration of dissolved gaseous Hg^0 in the original aqueous sample (which is often minor compared to the labile Hg(II) fraction), an subsequently subtracted from its $SnCl_2$ amended counterpart to calculate $Hg(II)_R$.

3.0 Safety Issues: Before beginning any of the procedures involved in this method, each individual must read and sign the Chemical Hygiene Plan developed for the lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets for that chemical – all of which are located in the laboratory. Two extremely important areas for this method are addressed below.

3.1 Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Due to the toxicological and physical properties of Hg, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of gloves and high flow volume hoods when preparing standards.

3.2 Strong acid solutions are employed in the cleaning of equipment, preparation of reagents and in sample preservation. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant clothing and the utilization of high volume fume hoods.

4.0 Sample Containers, Preservation and Holding Times:

4.1 Aqueous samples are initially collected in trace-metal cleaned containers (e.g. glass, Teflon, or PETG plastic). Unless containers are proven to be effectively trace-metal clean directly out of the box (e.g. certified I-Chem vials, some brands of PETG plastic bottle), appropriate cleaning methods must be employed. These include the prescribed cleaning approach for Teflon or glass as detailed in EPA Method 1631 Section 6.1.2.1 (EPA, 2002). Container cleaning will consist of: a) soaking vials for 24 hours in dilute Micro solution, b) rinsing 3X with Milli-Q water, c) soaking in 5% HCl bath for 24 hours, d) rinsing 3X with Milli-Q water, e) drying vials in Laminar flow hood, f) storing vials in a double zip locked bag until further use. Glass may also be combusted (500˚C) for 4 hrs in a muffle furnace to volatilize trace amounts of Hg contamination.

4.2 Aqueous handling protocols are designed to minimize the contact of the sample, with the standard 'clean hands / dirty hands' approach (USEPA, 1996) being used in the field and/or laboratory to collect the sample and transfer it to the appropriate container. Field samples are stored chilled in the dark and transferred to a refrigerator upon return to the laboratory. Freezing is not recommended as it can have variable effect on dissolved organic matter in solution (precipitating it out in some cases) and can facilitate Hg(II) adhering to the walls of the sample vessel. Apart from refrigeration, no other preservation (e.g. acidification) is used for samples to be run for $Hg(II)_R$.

4.3 If the dissolved fraction is to be targeted, sample filtration should occur within 24 hrs of collection. All filtration equipment must be rigorously cleaned as per section 4.1, and pre-combusted glass fiber filters should be used.

4.4 Sample holding times should not exceed 7 days post-collection.

5.0 Reagents and Standards:

5.1 Reagents: All reagents and/or dry chemicals used to make reagents must be of the highest purity available from the vendor and shown to be low in mercury. Upon receipt at the laboratory, containers will be marked with the date of receipt and stored in the appropriate areas. When reagents are mixed for use in this method, the person who mixes them will initial and date the reagent container.

5.1.1 Reagent water: Ultra pure reagent grade water shown to be > 18 MΩ starting from pre-purified source (distilled, RO, etc.). The water is delivered through a 0.2 uM filter. All water is obtained from a Millipore Academic water purification system.

5.1.2 Hydrochloric Acid: Trace metal grade HCl (containing less than 5 ng/L Hg) .

5.1.3 Stannous chloride ($SnCl_2$). In a 100 mL acid-cleaned beaker, add 10 mL concentrated HCl flushed with N2 gas. After 30 mins add 20 g $SnCl_2$ and stir to dissolve the SnCl2. Bring the total volume to 100ml and purge for 1 hour with Hg-free N_2 at 300 mL/min. Dispense into clean serum vials, and purge the head space. Cover vials with aluminum foil to prevent oxidation. Cloudiness can occur. Discard solution if solution is cloudy or yellow upon preparation.

5.1.4 Nitrogen (N_2) or Helium (He). Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

5.1.5 Argon (Ar). Grade 5.0 (ultra high purity) that is passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

5.2 Standards: Upon receipt at the laboratory or on the day of preparation, containers should be labeled with the date received or made and the initials of the person preparing them. The stock and substock standards should by stored outside of the clean laboratory to prevent contamination of the entire lab.

5.2.1 Stock standard (1000 mg/L): Commercially available Hg standard verified against a NIST standard reference material. All subsequent standards are prepared using the stock standard. Before preparing other standards, ensure the expiration date of the stock standard has not been exceeded.

5.2.2 Substock standard (1000 ng/mL): Dispense approximately 50 mL of reagent grade water and 5 mL of BrCl into a 100 mL mercury clean class A volumetric flask. Pipette 100 µL of the stock standard (1000 mg/L) and bring to volume with reagent water. To clean the volumetric flask, fill to approximately 80 % total volume with 30% HCl, place the ground glass stopper on its side over the opening to

prevent pressure buildup, and heat to near boiling on a hotplate for 8 hours.

5.2.3 Working standard (1 ng/mL): Dispense approximately 50 mL of reagent grade water and 1 mL of BrCl into a 100 mL mercury clean (sec. 5.2.2) class A volumetric flask. Pipette 100 µL of the substock standard (1000 ng/mL) and bring to volume with reagent water. This working standard must be compared to the previous working standard and agree within ± 5%. Prepare fresh every 6 months.

6.0 Quality Control: Each analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This includes the ability to reproduce standards, establish acceptable daily detection limits (DDL), produce acceptable relative percent differences between replicates, and produce spike recoveries that meet acceptance criteria.

6.1 Bubbler blanks: A bubbler blank is prepared by adding 0.5 ml of $SnCl_2$ to a bubbler containing approximately 50 mL of Milli-Q water and 250 µl of concentrated HCl. Blanks are critical to the reliable determination of Hg at low levels. Frequent analysis of bubbler blanks is required to demonstrate freedom of system contamination and the absence of carry over from one sample or standard to the next.

6.1.1 Acceptance criteria: No bubbler blank (BB) must contain more than 25 pg of Hg. A daily detection limit (DDL) is calculated each day prior to analysis of samples. The DDL is computed using the following formula:

$$DDL = 3 \times \sigma_{BB}$$

σ_{BB} *= is the standard deviation (*σ*, n=4 bubblers) of the peak areas. The DDL units are (ng), in absolute terms.*

The acceptable value for the DDL must be 0.1 ng or less.

6.1.2 Corrective Actions:

6.1.2.1 If a bubbler blank is found to contain more than 25 pg Hg, at the beginning of the day, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is accurate. If this second set blanks is also out of compliance the analyst must isolate and correct the problem before continuing.

6.1.2.2 If a bubbler blank is found to contain more than 25 pg Hg, during the course of the day's analyses, the system is out of QA compliance and data produced on that bubbler should be rerun or carefully evaluated and flagged as being suspect.

6.1.2.3 If the DDL exceeds 0.1 ng, another set of bubbler blanks should be run to ensure the entire system has been purged and that the value is accurate. If this second set of blanks is also out of QA compliance, the analyst must isolate and correct the problem before continuing.

6.2 Standards: A standard is prepared by adding a known volume of working $HgCl_2$ standard solution (1 ng/ml) and 0.5 ml of $SnCl_2$ to a bubbler containing approximately 50 mL of Milli-Q water. The water in the bubbler must first be reduced with $SnCl_2$ and purged for 20 minutes to remove all Hg, prior to analysis of standards.

6.2.1 Acceptance criteria: A mean response factor (RF_m) is calculated at the beginning of the day from the ratio of mass to peak area (ng/PA) for 4 standards of different concentrations (sec. 7.6.11). The RSD among the ng/PA ratios of the standards must ≤10%.

$$RSD\ (\%) = (\sigma / mean) \times 100$$

σ = standard deviation among four standards

6.2.2 Corrective action: If the RSD of the standards fails to meet acceptance criteria, an additional set of standards must be run to ensure no operator error exists. If the second set of standards still does not meet acceptance criteria, the analyst must isolate and correct the problem before continuing.

6.3 Certified Reference Material (CRM) sample: No certified value for reactive Hg(II) has been established in any known CRM.

6.4 Duplicates: All samples are run in duplicate if the sample lot is sufficiently small. If the batch is larger than 10 samples, then one of every ten samples analyzed must be analytical duplicates, and one of every 20 must be a field duplicate.

6.4.1 Acceptance criteria:

6.4.1.1 The acceptance criteria is a relative percent difference (RPD) of ≤ 10%.

$$RPD\ (\%) = ((|X_1 - X_2|) / Mean) \times 100$$

X1 = Measured value of first replicate

X2 = Measured value of second replicate

6.4.2 Corrective action:

6.4.2.1 If the RPD between the two replicates is greater than 10%, the sample is analyzed a third time.

6.4.2.2 If the relative standard deviation (RSD) between the three replicates is greater than 10 %, the sample is flagged and/or analyzed a fourth time.

$$RSD\ (\%) = (\sigma / mean) \times 100$$

σ = standard deviation among three replicates

6.5 Matrix spike: The performance of a matrix spike has been deemed to have little or no value to this analysis as added mercury partitions into native dissolved organic matter to varying degrees, depending on the aqueous sample composition (e.g. organic content, solid phase mineralogy, redox conditions, etc…). Thus, low recoveries could not be distinguished from particularly strong partitioning.

7.0 Procedure

7.1 Comments: The samples are collected and prepared using ultra clean sampling techniques.

7.1.1 Interferences:

7.1.1.1 Free halogens: The destruction of the gold traps exists if they are exposed to free halogens resulting in low mercury values. This can be avoided with the addition of a soda lime trap directly upstream of the sample traps during purging. Traps should be changed every 2-3 days.

7.1.1.2 Water vapor: Water vapor may collect on the gold traps during the purging step. If water vapor is present on the traps this will give a false peak during analysis. This can be avoided with the addition of a soda lime directly upstream of the sample traps during purging.

7.1.1.3 Carrier gas: The fluorescent intensity of the detector is strongly dependent on the inertness of the carrier gas. The dual amalgamation step virtually eliminates quenching due to impurities in the carrier gas, but it is the analyst's responsibility to ensure high purity inert carrier gas and a leak free analytical train.

7.1.2 Helpful hints:

7.1.2.1 Working with detection limits in the parts per trillion range, protecting these samples from contamination cannot be over emphasized. The greatest difficulty in low level mercury analysis is preventing the samples from becoming contaminated. Extreme caution must be used throughout the preparation, collection and analysis procedures to avoid contamination.

7.1.2.2 It is very important that the laboratory air be low in both particulate and gaseous Hg. The mercury in the air can be reduced with the use of gold-coated cloth at the intakes of the laminar flow hoods.

7.1.2.3 If cloudy residue becomes apparent on the inside of the bubblers, dissolve approximately 2 grams of Potassium Hydroxide in 250 mL of reagent water and allow bubblers to soak for 1 hr.

7.1.2.3 If the peak area for Hg on a trap exceeds 3 ng, reburn the trap. If the peak exceeds 5 pg, reburn the trap, if a peak is still present, discard the trap and incorporate a new trap in its place.

7.2 General Description: Refer to section 2 of this procedure for a summary of this method.

7.3 Labware:

7.3.1 All-plastic pneumatic fixed-volume and variable pipettors in the range of 5 µL to 10 mL.

7.3.2 Analytical balance capable of measuring to the nearest 0.0001 g.

7.4 Sample preparation

7.4.1 Prepare samples according to section 4.3

7.5 Instrumentation:

7.5.1 Regulator capable of supplying 30 psi of pressure.

7.5.2 Teflon tubing (sizes: 1/8" – ¼" i.d.) is use for all transfer lines between bubblers, soda lime traps, and gold traps on the bubbling rig; and between the gold traps on the CVAFS dual amalgam flushing train.

7.5.3 C-Flex tubing (sizes: 1/8" – ¼" i.d.) is used for connecting teflon tubing and glass gold traps and glass bubblers.

7.5.4 Shrink-wrap tubing is used for connecting teflon tubing and glass gold traps.

7.5.5 Heat gun to seal shrink wrap tubing around glass fittings.

7.5.6 Flow meter(s) capable of measuring a N_2, He, or Ar flow of up to 300-400 mL/min.

7.5.7 Needle valve to shut off and control N_2 flow to bubblers.

7.5.8 Gold coated sand (or glass bead) traps: The gold coated glass bead traps are constructed of a 7 mm quartz tube, 8 cm long and with a constriction at 1 ¼" from the outlet end. A quartz plug is placed into the inlet end, about 0.7 g (3.5 cm in the tube) of gold coated beads are added and the inlet end is plugged with another piece of quartz wool. Female fittings for gold traps are made from small pieces of 6 mm i.d. monobarb Teflon tubing. Heating ¼" Teflon tubing and sealing one end by pinching with pliers until cool creates end plugs.

7.5.9 Teflon plugs (solid and single holed) to cap the ends of the sample traps, and to use as connectors between teflon tubing and analytical traps.

7.5.10 Bubblers Rig: The bubblers are 200 mL borosilicate glass flasks with the standard 24/40 tapered neck. The sparging stopper has a coarse glass frit that extends to the bottom of the flask. Bubbling rig consists of (in order) a He or N_2 gas source, a needle valve gas-shut off, a gold-pretrap, a single line split into 4 lines (using plastic or Teflon "T"'s), a flowmeter on each of these lines leading to a single bubbler, a soda lime trap (7.5.11) connected to the outlet of each bubbler, a sample gold trap after each soda lime trap. Teflon tubing is used to connect all parts, and C-flex tubing, shrink tubing and one-holed Teflon plugs are used to connect lines to bubblers, soda-lime and gold traps.

7.5.11 Soda lime traps: The soda lime traps are constructed of a 10 mm i.d. x 7 cm length Teflon tube. The traps are filled with 4-8 mesh soda lime with salinized glass wool plugs at either end to hold the soda lime in place. The traps are pre-purged for 20 min before collection of a sample onto a gold trap. Soda lime traps should be repacked every 2-3 days.

7.6 Desorption and analysis:

7.6.1 Analytical train: The sample train consists of (in order) an Ar gas source, a gas flow shut-off valve, a gold pre-trap, a sample gold trap, an analytical gold trap, the CVAFS unit (Brooks Rand Model III), a rotometer to control gas flow at the end of the train. All pieces are connected with lengths of Teflon tubing, attached with C-flex and shrink tubing, as needed. Once a sample trap is prepared, it is placed on the analytical train, and the Ar gas flow is set at 35 ml/min. A variable AC transformer, with two alligator clips at the output, connects to Nichrome coils that are wrapped around the pre-trap, sample traps and the analytical trap. The alligator clips are first placed on the Nichrome wire of the sample trap, which is heated to 425^{o}C (12 V) for 2 minutes. This desorbs the Hg^0 from the sample trap and places on the analytical trap. The sample trap is then cooled for 2 minutes by an electric fan. The clips are then moved to the analytical trap, which is then similarly heated for 2 minutes. As the Hg^0 desorbs from the analytical trap it passes through the CVAFS detector and up an exhaust hood. The signal from the detector is sent to an integrator, which records the sample peak area and retention time.

7.6.2 Integrator: Peak Simple digital signal integration software (run on a PC) is used to integrate the signal coming out of the Brooks Rand Mercury analyzer.

7.7 Initial start-up, calibration and sample analysis:

7.7.1 Check pressure in Argon tank to verify adequate volume for the day's analyses.

7.7.2 Adjust the rotometer at detector outlet to 35 mL/min.

7.7.3 Check baseline at the integrator (Attenuation = 4, Area reject = 1000, Peak Threshold = 5), after pre-burning the pre-trap and analytical trap. The baseline should be flat.

7.7.4 Start by pre-burning the set of eight sample traps. While these traps are being burned proceed with step **7.7.5**.

7.7.4.1 Remove the plugs from the ends of the first trap and place it into the analytical train by threading it, with the id number downstream, through the center of the Nichrome wire coil. Center the Nichrome wire over the gold sand. Heat as per **7.6.1**. Repeat for each of the remaining sample traps. Similarly heat the analytical trap after all the sample traps are burned, to clean it, prior to running actual samples.

7.7.4.2 You need to have 4 traps burned before step **7. 7.5** is complete. You have 8 traps and four bubblers. The bubbling of samples takes 15 minutes and the burning of 4 traps approximately 36 minutes. You will be bubbling a round of samples while burning (analyzing) the previous round. This is the cycle you will follow throughout the day.

7.7.5 Set-up bubbler rig (as per **7.5.10**) with thoroughly cleaned bubblers containing 50 mL of reagent grade Milli-Q water and 250 µL 12N HCl. Add 500 µL of $SnCl_2$ solution. Attach a clean gold trap to the end of the soda lime trap and proceed purging as in **7.6.7**. Begin purging bubblers at 250 - 300 mL/min with N_2 or He for 15 minutes. This represents the bubbler blank set.

7.7.5.1 Note: Time course studies have revealed that in many samples the rate of reduction by $SnCl_2$ is very high within the first 5 minutes and then reaches a minimum at 15 minutes. After 15 minutes, the rates gradually increase, suggesting that Hg(II) may be released from other components (e.g. strongly bound to DOC or suspended particulates). The pool that is reduced within the first 15 minutes is therefore the operationally defined $Hg(II)_R$ pool.

7.7.6 When the 15-minute purging cycle for the bubbler blanks has elapsed, remove the gold traps from the end of the soda lime traps, cap both ends of the gold traps with solid Teflon plugs, and shut-off the gas flow to the bubblers.

7.7.7 Analyze the gold traps as in **7.6.1**. While these traps are being burned proceed with step **7.7.8**.

7.7.8 Pipette 0.1, 0.3, 0.6, and 1.0 mL of the working standard (1 ng/ml) into bubblers 1, 2, 3, and 4, respectively. Attach a clean gold trap to the end of the soda lime trap and proceed as in **7.6.7**. This represents your first standard set.

7.7.9 Analyze the gold traps as in **7.6.1**. While these traps are being burned proceed with step **7.7.10**

7.7.10 Empty contents of the bubbler, and rinse thoroughly with MQ water. Add 100 mL of environmental sample followed by 500 ul of $SnCl_2$ solution. Purge sample at 250 - 300 mL/min with N_2 or He for 15 minutes.. This represents your first sample set.

7.7.11 Analyze the gold traps from **7.7.10** as in **7.6.1**. While these traps are being burned proceed with the next round of samples as per the chart below.

7.7.12 In between sample sets, the bubblers should be rinsed thoroughly. Pour the contents of the bubbler into a waste container. Detach bubbler from gas lines. Fill the bubbler with DI water and shake vigorously. Lodge a 1000 µL pipette tip into the end of a DI line, creating a high-pressure stream. Use this stream to clear the glass frits of any particulates. Once clear, rinse the bubbler with 1M KOH. Remove the KOH and rinse the bubbler completely, using the high pressure DI stream to rinse flush the inside of the glass fritted tube. Use a clean source of air to flush any water vapor out of the bubbler inlet or outlet before attaching to soda lie trap.

Round	BUBBLER 1	Bubbler 2	Bubbler 3	Bubbler 4
Blanks	BB1	BB2	BB3	BB4
Standards	0.1 ng	0.3 ng	0.6 ng	1.00 ng
Sample set	S1	S1	S2	S2
Sample set	S3	S3	S4	S4
Sample set	S5	S5	S6	S6
Sample set	S7	S7	S8	S8
OOPS	OOPS	OOPS	OOPS	OOPS

BB = bubbler blank

SX = sample

OOPS = sample whose replicates do not meet acceptance criteria

7.7.13 All samples need to be bracketed by standards, if the sample peak area is greater than the highest standard, either a higher standard is analyzed or the sample is analyzed using a smaller sample volume.

7.8 Calibration and performance documentation: During the analysis run, the analyst must evaluate the calibration data, bubbler blank values, and RPDs for duplicate analyses to ensure acceptance criteria (sec. 6.0) are being met. The following information must be recorded on the daily datasheet.

7.8.1 Date of analysis.

7.8.2 Type and date prepared for reagents and standards used.

7.8.3 Name of analyst.

7.8.4 Identification of bubbler contents, volume analyzed, instrument response, and sample trap identification for each analysis performed.

7.8.5 Comments pertaining to special samples run, problem samples, corrective actions taken, and results of any calculations performed to ensure acceptance criteria are being met.

7.8.6 Project that the samples are being run for.

7.9 Shut-down:

7.9.1 After the last sample has been purged, the following steps must be performed to properly store the bubblers until the next analysis run.

7.9.1.1 Shut off N_2 flow at the needle valve and at the tank regulator.

7.9.1.2 Remove the N_2 line from the inlet and the soda lime trap from the outlet of the bubblers.

7.9.1.3 Thoroughly rinse the bubblers and the sparging stoppers with copius amounts of reagent grade water.

7.9.1.4 Fill the bubblers to approximately 95% volume with 3M KOH.

7.8.1.5 Carefully replace the sparging stopper, cap the inlet and outlet of the bubbler and return to the hood.

7.9.2 After the last sample trap has been burned, leave the trap in the analytical train to avoid contamination from room air.

7.9.3 Shut off all gasses, CVAFS detector, and variable AC transformer.

7.10 Maintenance, maintenance records and Responsibilities

7.10.1 Gold traps attached to regulators on the N_2 and Ar tanks should be burned clean at the beginning of every run.

7.10.2 Nichrome wire temperature should be checked quarterly.

7.10.3 Detector lamp driver voltage should be checked quarterly. If voltage exceeds 12.5, the lamp should be adjusted or replaced according to manufacturers guidelines.

7.11 Calculations

7.11.1 The following formula is used to calculate $Hg(II)_R$ concentration for environmental and QC samples.

$$C = ((PA_s - BB_m) \times RF_m) / V_s * 1000$$

C = concentration in ng/L

PA_s = peak area of sample, in PA units

BB_m = mean bubbler blank, in PA units (sec. 6.1)

RF_m = mean response factor, in ng/PA unit (sec. 6.2)

V_s = volume of sample assayed, in ml

7.12 Data validation and evaluation: After the data has been entered into the EXCEL spreadsheet, someone other than the analyst must verify that no values have been incorrectly entered in either the log book or the spreadsheet. The data is then evaluated carefully by the QC officer to ensure all data quality objectives have been met for the run and that the data seem reasonable. Data is evaluated as to reasonability if historical data from a site exists.

7.13 Reporting:

7.13.1 Reporting units: Total mercury as ng/L.

7.13.2 Reporting levels and significant figures:

7.13.2.1 Report to the nearest 0.1 ng/L for values less than 10 ng/L.

7.13.2.2 Report to three significant figures for values exceeding 10 ng/L.

8.0 Archiving: All raw data produced in the laboratory is archived in a filing cabinet located in the clean room. Hard copies of the data report sheets are archived in the appropriate project 3-ringed binder. All electronic data is archived on the laboratory manager's computer, which is backed up daily.

9.0 References

EPA, 2002, Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: U.S. Environmental Protection Agency, Office of Water EPA-821-R-02-019, 46 p., On-Line: http://www.epa.gov/waterscience/methods/method/mercury/1631.pdf

Olson, M.L., and Dewild, J.F., 1999, Techniques for the collection and species-specific analysis of low levels of mercury in water.: U. S. Geological Survey - Toxic Substance Hydrology Program. 99-4018B, 191-199 p. [Water-Resources Investigation Reports], On-Line:

USEPA, 1996, Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels: U.S. Environmental Protection Agency, Office of Water Engineering and Analysis Division, 37 p., On-Line:

Total Suspended Solids Procedure, Mass Balance (Dried at 103-105^{O}C)

1.0 Summary of Method

A well-mixed sample is filtered through a standard GF/F glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105^{O}C.

2.0 Definitions

Total Suspended Solids is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105^{O}C.

3.0 Sample Handling and Preservation

3.1 Non-representative particulates such as leaves, sticks, and paint chips should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

3.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4^{O}C, to minimize microbiological decomposition of solids, is required. The maximum holding time for sample is 7 days.

4.0 Interferences

4.1 Filtration apparatus, filter material, prewashing, postwashing, and drying temperature are specified because these variables have been shown to affect the results.

5.0 Apparatus

5.1.1 Glass microfiber filters discs, 47 mm, without organic binder, Whatman type GF/F (0.7 m).

5.1.2 Disposable aluminum dishes

5.1.3 Tweezers

5.1.4 Suction flask, 1000 mL

5.1.5 47 mm glass microanalysis filter holder (funnel, clamp, and base)

5.1.6 Magnetic stir plate with stir bar and stir bar retriever

5.1.7 Drying oven for operation at 103-105^{O}C

5.1.8 Desiccator

5.1.9 Analytical balance, capable of weighing to 0.1 mg

5.1.10 Milli-Q reagent grade water (ASTM Type I water), Millipore Corp, Bedford, MA

6.0 Procedure for Total Suspended Solids

6.1 Preparation of the glass fiber filter disk: Insert the filter disk onto the base and clamp on funnel. While vacuum is applied, wash the disk with three successive 20 mL volumes of Milli-Q water. Remove all traces of water by continuing to apply vacuum after water has passed through. Dry in a oven at 103-105^{O}C for one hour in aluminum dish. When needed, remove dish from the oven, desiccate, and weigh in dish.

6.2 Re-dry and re-weigh filter until weight change is less than 4% of previous weight or 0.5 mg.

6.3 Select a sample volume (max. of 200 mL) that will yield no more than 200 mg of total suspended solids.

6.4 Place the filter on the base and clamp on funnel and apply vacuum. Wet the filter with a small volume of Milli-Q water to seal the filter against the base.

6.5 Stir sample continuously while sub-sampling and quantitatively transfer the sample to the filter using a 100 mL graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

6.6 Rinse the graduated cylinder onto the filter with 3, 20 mL portions of Milli-Q water. Remove all traces of water by continuing to apply vacuum after water has passed through.

6.7 Carefully remove the filter from the base. Dry at least one hour at 103-105^{O}C. Cool in a desiccator and weigh.

6.8 Re-dry and re-weigh filter until weight change is less than 4% of previous weight or 0.5 mg.

7.0 Calculation of Total Suspended Solids

Calculate Total Suspended Solids as follows:

Total Suspended Solids, mg/L = (A-B) x 1,000/C

Where: A = weight of filter and dish + residue in mg
B = weight of filter and dish in mg
C = volume of sample filtered in mL

8.0 Quality Assurance/ Quality Control

8.1 Glassware Cleaning Procedure
All glassware will be cleaned in an Alconox solution, triple rinsed with both tap water and Milli-Q water, dried in a 100^{O}F oven, then wrapped in aluminum foil.

8.2 One laboratory blank will be analyzed with each storm event. Follow the TSS procedure substituting MQ water for the "sample" when filtering.

8.3 In order to determine an appropriate sample size that will yield at least 2 mg of TSS residue, 100-200 mL will be tested prior to splitting each sample. If 2 mg are not captured using that maximum volume of 200 mL, there is not sufficient TSS in the runoff and the sample will not be processed for data.

8.4 Each one liter sample will be split into 4-5 smaller samples for quality assurance/ quality control purposes in the laboratory. Each split sample will be analyzed following the TSS procedure.

8.5 One duplicate sample will be collected per storm event and analyzed following the TSS procedure.

8.6 A balance check will be performed prior to beginning the TSS procedure . Known weights will be used to verify the balance is working properly.

9.0 Data Calculations and Reporting Units

9.1 Calculate the sample results according to Section 7 of this method.

9.2 Report sample results in concentration units of milligram per liter (mg/L) as total suspended solids. Report TSS concentrations that are less than 100 mg/L to 2 significant figures, and TSS concentrations that are greater than or equal to 100 mg/L to 3 significant figures.

10.0 References

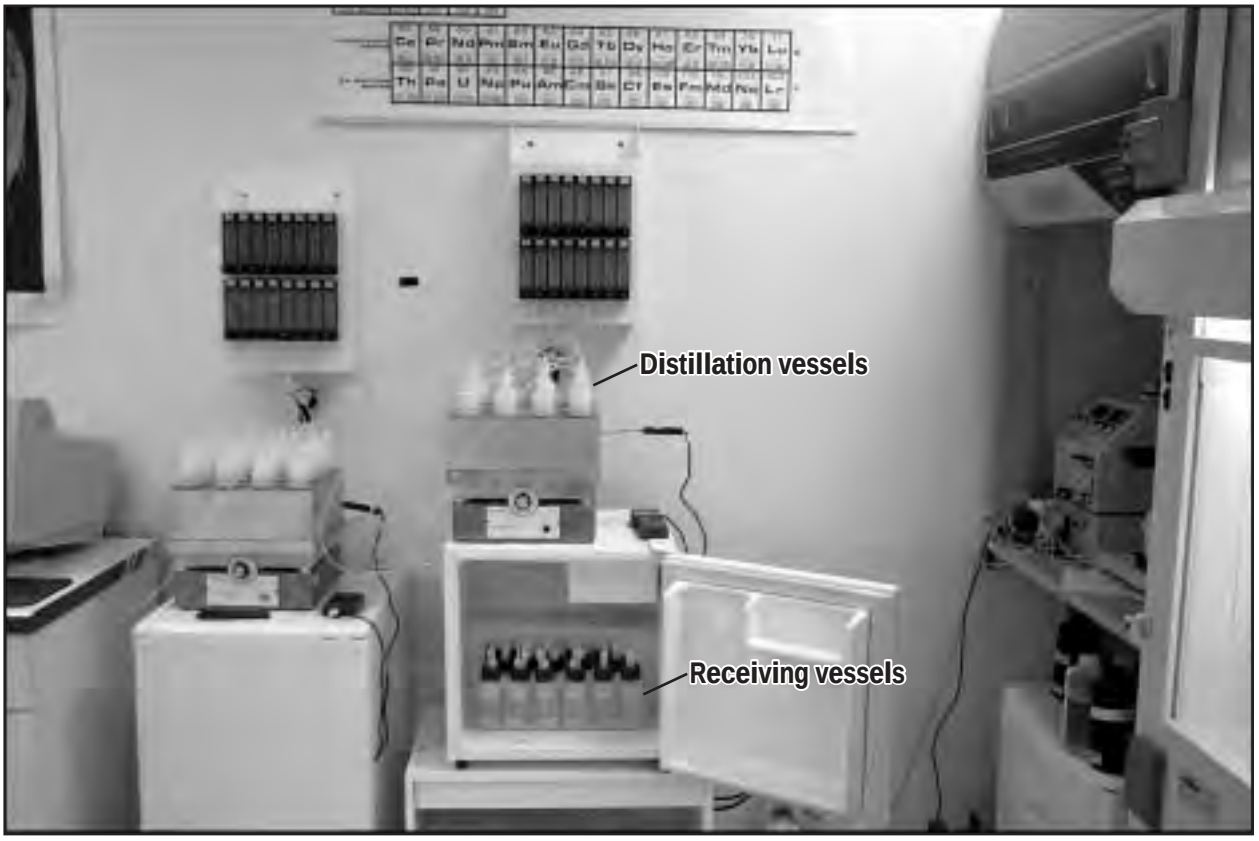
10.1 Methods for the Chemical Analysis of Water and Wastewater, U.S. Environmental Protection Agency, EPA 600/4-79-020, p. 160.2, (1979).

10.2 Standard Methods for the Examination of Water and Wastewater, 16^{th} Edition, p. 96, Method 209C. (1985).

U.S. Department of the Interior
U.S. Geological Survey

Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

Open-File Report 01–445



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Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

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ABBREVIATED WATER-QUALITY UNITS

Abbreviated water-quality units used in this report: Chemical concentration is given in milligrams per liter (mg/L), micrograms per liter (µg/L) or nanograms per liter (ng/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. One thousand nanograms per liter is equal to one microgram per liter.

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8\ (°C) + 32.$$

Other Abbreviations Used in this Report:

ng/L	nanograms per liter (parts per trillion)
ng/mL	nanograms per milliliter (parts per billion)
mg/L	milligrams per liter
µg/g	micrograms per gram (parts per million)
g	gram
mg	milligram (10^{-3} grams)
µg	microgram (10^{-6} grams)
ng	nanograms (10^{-9} grams)
pg	picogram (10^{-12} grams)
N	normality (the number of equivalents per liter of solution)
M	molarity (the number of moles of solute per liter of solution)
MΩ	microMohs
cm	centimeters (10^{-2} meters)
mm	millimeters (10^{-3} meters)
µM	micron (10^{-3} millimeters)
L	liters
mL	milliliters (10^{-3} liters)
µL	microliters (10^{-6} liters)
mL/min	milliliters per minute
in	inches

Determination of Methyl Mercury by Aqueous Phase Ethylation, Followed by Gas Chromatographic Separation with Cold Vapor Atomic Fluorescence Detection

by John F. De Wild, Mark L. Olson, and Shane D. Olund

Abstract

A recent national sampling of streams in the United States revealed low methyl mercury concentrations in surface waters. The resulting median and mean concentrations, calculated from 104 samples, were 0.06 nanograms per liter (ng/L) and 0.15 ng/L, respectively. This level of methyl mercury in surface water in the United States has created a need for analytical techniques capable of detecting sub-nanogram per liter concentrations. In an attempt to create a U.S. Geological Survey approved method, the Wisconsin District Mercury Laboratory has adapted a distillation/ethylation/gas-phase separation method with cold vapor atomic fluorescence spectroscopy detection for the determination of methyl mercury in filtered and unfiltered waters. This method is described in this report. Based on multiple analyses of surface-water and ground-water samples, a method detection limit of 0.04 ng/L was established. Precision and accuracy were evaluated for the method using both spiked and unspiked ground-water and surface-water samples. The percent relative standard deviations ranged from 10.2 to 15.6 for all analyses at all concentrations. Average recoveries obtained for the spiked matrices ranged from 88.8 to 117 percent. The precision and accuracy ranges are within the acceptable method-performance limits. Considering the demonstrated detection limit, precision, and accuracy, the method is an effective means to quantify methyl mercury in waters at or below environmentally relevant concentrations.

INTRODUCTION

Presently (2002), 41 States in the Nation have issued fish consumption advisories because of the high levels of mercury (Hg) in fish (U.S. Environmental Protection Agency, 2001a). Over the past 15 years, scientists have revealed that methyl mercury (CH_3Hg^+) is the specific form of mercury that bioaccumulates most readily in mammals (Bloom, 1992), is the most toxic, and where research priorities are needed to better understand and respond appropriately to this widespread contamination problem. Within the U.S. Geological Survey (USGS), the importance of Hg as a contaminant is demonstrated in that it has been selected as one of five priority issues to be addressed over the next 10 years as part of the National Water-Quality Assessment (NAWQA) program. Because of the increased awareness of environmental Hg contamination, and the understanding that the production and bioaccumulation of CH_3Hg^+ drives the contamination problem, the need for a reliable analytical method for CH_3Hg^+ has increased. Horvat and others (1993) were the first to describe a distillation/ethylation/gas-phase separation method for CH_3Hg^+, which greatly reduces matrix-interference problems, and that largely has been adopted worldwide by Hg research laboratories. Since the start up of the USGS Wisconsin District Mercury Laboratory (WDML) in 1995, an adaptation of this method has been the operational method for CH_3Hg^+ determinations. The purpose of this report is to document the method and describe the results of a methodological test of the WDML's ability to provide quality data at ng/L concentrations for CH_3Hg^+ in water samples.

SUMMARY OF METHOD

Water samples are distilled to remove potential matrix interferences. The pH of the distillate is adjusted to 4.9 (to maximize ethylation potential) using acetate

buffer. The distillate then is ethylated using sodium tetraethyl borate ($NaBEt_4$) and allowed to react for 15 minutes. After reaction with $NaBEt_4$, the distillate is purged with nitrogen gas (N_2) for 20 minutes and the ethylated mercury species are collected on a sample trap containing Carbotrap. These ethylated mercury species are desorbed thermally from the sample trap, separated using a gas chromatographic (GC) column, reduced using a pyrolytic column, and detected using a cold vapor atomic fluorescence spectrometry (CVAFS) detector.

This method may be used to determine CH_3Hg^+ concentrations in filtered or unfiltered water samples in the range of 0.040–5 ng/L. The upper range may be extended to higher concentrations by distilling smaller sample volumes or ethylating less of the distillate.

It should be noted that repeated attempts to analyze reagent grade water spiked with CH_3Hg^+ resulted in low recoveries (40–60 percent). The reasons for these low recoveries have not been resolved; however, other mercury research laboratories also obtain similar recoveries (J. Hurley, University of Wisconsin; C. Gilmour, Academy of Natural Sciences, oral commun., 2001). Therefore, reagent water is not an appropriate water source for spiked standard solutions and should not be used for quality-assurance or quality-control purposes.

Contamination

Methyl mercury analysis, as with all trace metal analysis, is extremely sensitive to contamination. Extreme care must be taken to avoid contamination in the collection and analysis steps of this method. All of the sample collection and analytical equipment that comes in contact with samples must be Teflon or glass and vigorously cleaned prior to and between uses. New Teflon equipment is rinsed with tap water, and cleaned by immersing in a 4 N hydrochloric acid (HCl) bath heated to 65°C for at least 48 hours. Immediately following removal from the bath, the equipment is immersed in fresh reagent grade water and rinsed at least three times with reagent grade water. Following the rinsing step, each sample bottle is filled to 25 percent full volume with 0.12 N HCl and capped. The exterior of the bottles and all other equipment is allowed to air dry on a Hg-clean bench under a laminar flow hood equipped with a High Efficiency Particulate Air (HEPA) filter which is 99.99 percent efficient on particles less than 0.3 microns in diameter. Dry equipment is double bagged in new zip-type bags. After the initial 48 hour cleaning, equipment needs to be immersed in the hot acid for only 24 hours.

Sample Preservation

Samples are acidified with 6N HCl to 1 percent, volume to volume (v/v), and kept in the dark to prevent photodegradation (Krabbenhoft and others, 2001) of CH_3Hg^+. Samples preserved in this manner can be held for up to 6 months before analysis (Bloom, 1995).

Method Detection Limit

The U.S. Environmental Protection Agency (USEPA) has established a fish tissue methyl mercury enforcement standard of 0.3 µg/g (U.S. Environmental Protection Agency, 2001b). A water column concentration of 0.058 ng/L was determined to correspond with a 0.3 µg/g fillet concentration for age-3 largemouth bass (Brumbaugh and others, 2001). To demonstrate that the WDML can accurately quantify methyl mercury in water samples at or below this environmentally important level, a method detection limit study was performed. A method detection limit of 0.04 ng/L was determined from multiple analyses of an unspiked surface-water sample and a spiked ground-water sample (table 1) according to USEPA protocol (U.S. Environmental Protection Agency, 1990). The ground-water sample was collected from a residential well in a 1L Teflon bottle; 0.1 ng of CH_3Hg^+ standard was added to the sample at the lab and the sample was then acidified with 12N HCl to 1 percent (v/v). Each of these samples was distilled in seven separate distillation batches and analyzed over five days.

Table 1. Results from multiple analyses of surface water and ground water for detection limit assay
[All concentrations in nanograms per liter (ng/L)]

	Unspiked surface water	Spiked ground water
	0.134	0.093
	.095	.078
	.123	.095
	.102	.090
	.101	.064
	.116	.090
	.115	.099
	.095	.085
Average	.110	.087
Standard deviation	.014	.011
Percent relative standard deviation	12.9	12.9
Detection limit (standard deviation x 2.998)	.042	.033

Reagents

All reagents and/or dry chemicals used to make reagents must be of high purity and low in Hg.

A. Reagent water: Ultra pure reagent grade water shown to be greater than 18 MΩ starting from a pre-purified source (distilled, RO, and others) and found to be less than 0.1 ng/L Hg. The water is delivered through a 0.2 µM filter, as obtained from a Millipore Academic water-purification system or equivalent.

B. Copper sulfate: 1M $CuSO_4$ in reagent water.

C. Hydrochloric acid: Concentrated HCl found to be less than 0.5 ng/L Hg (EM Science Omni Trace or equivalent).

D. Acetate buffer: 11.8 mL of glacial acetic acid and 27.2 g reagent grade sodium acetate trihydrate diluted to 100 mL with reagent water.

E. Ethylating Reagent: 1 g of Sodium Tetraethyl Borate ($NaBEt_4$; Strem 11-0575) dissolved in 100 mL of 2 percent Potassium Hydroxide (KOH), weight to weight (w/w), solution that has been chilled to form slush. The $NaBEt_4$ solution is divided equally among 9 clean 15 mL Teflon vials that then are capped and frozen. This solution should be kept frozen and made fresh every 2 weeks. Never use $NaBEt_4$ solid or solutions that are yellow in color. *Note: $NaBEt_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaBEt_4$ use should take place in a high-volume fume hood. To discard unused portions of ethylating reagent, empty bottles into a large beaker of 6N hydrochloric acid (HCl) inside a high-volume fume hood. Place beaker on a hotplate and boil down to half-volume, then discard the remaining solution as an acid waste. Triethylboron will boil off into the air where it is oxidized to harmless boric acid.*

F. Nitrogen (N_2). Ultra high purity grade 5.0 N_2 passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

G. Argon (Ar). Ultra high purity grade 5.0 Ar passed through a gold bead trap attached to the outlet of the tank to remove any Hg.

Standards

Upon receipt at the laboratory or on the day of preparation, reagent containers should be labeled with the date received or made and the initials of the person preparing them. The stock and substock standards should be stored outside of the Hg-clean analytical laboratory to prevent contamination of the laboratory.

A. CH_3Hg^+ stock solution (1,000 mg/L CH_3Hg^+ as Hg): 1.252 g of reagent grade methyl Hg chloride (Strem 80-2250) is dissolved in 1L of 2 percent glacial acetic acid, 0.2 percent HCl v/v.

B. CH_3Hg^+ substock solution (1 mg/L CH_3Hg^+ as Hg): Dilute 100 µL of CH_3Hg^+ stock solution to 100 mL with 2 percent glacial acetic acid, 0.2 percent HCl v/v.

C. CH_3Hg^+ working standard (1 ng/mL CH_3Hg^+ as Hg): Dilute 100 µL of CH_3Hg^+ substock solution to 100 mL with 2 percent glacial acetic acid, 0.2 percent HCl v/v. Because measurement errors are present in laboratory processes the exact concentration of the working standard must be determined analytically. The following procedure is used to determine the exact concentration of the working standard.

1. Add 8.0 mL of reagent grade water; 1.0 mL of the CH_3Hg^+ working standard and 1.0 mL of bromine monochloride (BrCl) to four 15 mL Teflon vials.
2. Add 9.0 mL of reagent grade water and 1.0 mL of BrCl to four 15 mL Teflon vials.
3. Double bag and place the eight vials described in steps 1 and 2 into an oven at 50°C overnight and analyze each aliquot for total Hg by USEPA method 1631.
4. Analyze four separate 1.0 mL aliquots of the CH_3Hg^+ working standard for inorganic Hg (Hg(II); readily reducible with $SnCl_2$) using USEPA method 1631 without the BrCl oxidation step.
5. Subtract the average blank concentration determined from analyses of solutions in step 2 from the average concentration determined from analyses of the solutions in step 1 to determine the reagent blank corrected concentration of the working standard.

6. Subtract the average concentration of the Hg(II) in the CH_3Hg^+ working standard, determined in step 4, from the reagent blank corrected value determined in step 5 to determine the actual working-standard concentration.

ANALYTICAL METHOD

Sample Preparation

Samples must be distilled prior to analysis to remove potential matrix interferences such as reduced sulfur containing compounds, calcium, and humic acids associated with dissolved organic carbon (Horvat and others, 1993).

Distillation Equipment

The distillation system (fig. 1a) consists of a solid aluminum heating block, a small refrigerator, Teflon distillation and receiving vessels, and Teflon transfer lines.

A. A custom fabricated aluminum block (fig. 1b) is heated with a Thermolyne type 2200 (or equivalent) hot plate during the distillation step. A temperature probe placed in the center of the block monitors block temperature.

B. A small commercially available refrigerator is used to hold the receiving vials, aid in condensation, maintain distillate at 4°C and protect the distillate from exposure to light. Small holes are drilled in the side of the refrigerator to accommodate the transfer lines.

C. The distillation and receiving vessels are 125 mL Teflon bottles (Nalgene catalogue number 1630-0004 or equivalent). The distillation vessel caps (fig. 1c) and receiving vessel caps (fig. 1d) consists of a Teflon insert (Savillex part number 0738-4-2 or equivalent) molded integrally with two transfer ports equipped with compression fittings for 1/4-in. (6.4 mm) outside diameter (O.D.) tubing. A length of 1/4-in. O.D. tubing is inserted into one of the ports so that it will extend to within 2 mm of the bottom of the distillation and receiving vessels to insure complete sample purging and recondensation, respectively. A short length of 1/4-in. O.D. tubing also must be inserted flush with the lower side of the insert in the remaining port to accommodate the transfer line. The Teflon bottle caps must be machined to accommodate the insert and form an airtight seal for the distillation vessels, whereas the green polypropylene cap included with the insert can be used for the receiving vessels. Teflon transfer lines of 1/8-in. (3.2 mm) O.D. are connected by friction fit from the outlet tubing of the distillation vessel to the inlet tubing of the receiving vessel.

D. Flowmeters capable of maintaining a flow of 60 mL/min of N_2 are placed immediately upstream of the distillation vials to maintain constant and equal flow to all distillation vials. Gas is supplied through 1/8-in. O.D. Teflon line inserted into the inlet tubing of the distillation vessel.

Distillation Procedure

A WDML distillation batch consists of 11 environmental samples, 3 method blanks, a matrix spike, and a matrix spike duplicate. Distillation blanks are reagent grade water acidified with 12N HCl to 1 percent (v/v). The matrix spike and matrix-spike duplicates are prepared by adding a known amount of working standard to two of three bottles containing similar volumes of the same sample.

A. Dispense approximately 60 mL of water (sample or reagent water) into each distillation vessel and add 1 mL of 1M $CuSO_4$ (to bind sulfide–Olson and others, 1997) to each of the bottles in the batch. Record the bottle identifier, tare weight and full weight of each vessel. Cap each of the vials with the distillation cap corresponding to the block position to be occupied by that vial.

B. Dispense approximately 40 mL of reagent water to each of the receiving vessels. Record the bottle identifier, tare weight and bottle plus reagent water weight of each. Cap each of the vials with the receiving cap corresponding to the block position occupied by the matching distillation vessel.

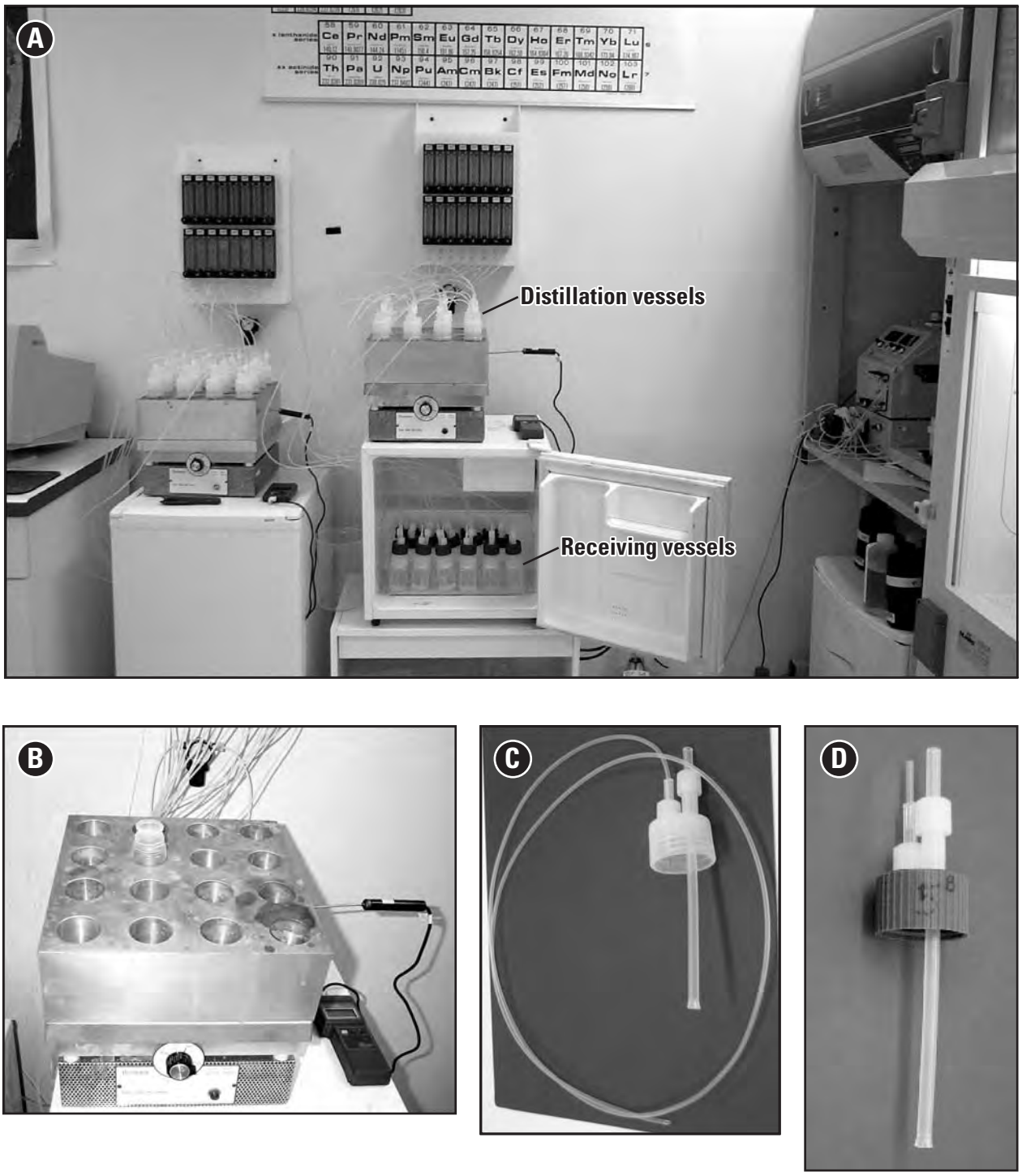

Figure 1. Methyl mercury distillation system: (A) entire system, (B) distillation, (C) distillation vessel cap, and (D) receiving vessel cap.

C. Place the distillation vials in their respective positions in the distillation block and thread the transfer lines through the numbered holes in the refrigerator.
D. Turn on the N_2 flow to the flowmeters and connect the gas lines to the inlet ports of the distillation caps.
E. Place the receiving vial tray in the refrigerator and begin placing the receiving vials into the tray. As the receiving vials are placed into the tray, connect the transfer lines to the inlet ports of the receiving caps. Check for bubbling in the reagent water. This checking verifies a leak-free system.
F. Adjust the flow on the flowmeters to 60 mL/min. Adjust the hot plate temperature to maintain a block temperature of 120 +/- 5°C. This temperature should result in a distillation rate of 6–8 mL per hour but adjustments may need to be made for individual systems.
G. Check the receiving vials to ensure unrestricted flow, the distillation vials to ensure no leakage, and the block temperature for stability periodically throughout the distillation.
H. Remove the transfer lines from the receiving vessels and the distillation vessels from the block when approximately 20 percent of the volume in the distillation vessel remains. The distillation caps as well as the inside of the transfer lines should be rinsed thoroughly with reagent water.
I. Weigh the receiving vessels and record the weight for later determination of the percent of the original sample that was distilled. Cap the bottles and place in a refrigerator at 4°C until analysis (distillates should be analyzed within 48 hours).

Sample Analysis

After the samples have been distilled, they are ready for analysis and should be analyzed within 48 hours. The analysis is a two-step process consisting of purging the mercury species from the distillate and detecting the mercury species with a cold vapor atomic fluorescence detector.

Analytical Equipment

The analytical portion of the process requires two separate systems; one for loading the traps (fig. 2a) and one for desorbing and detecting the Hg species (fig. 3a). The anlalytical equipement used is listed below.

A. Flow meters equipped with needle valves capable of delivering a N_2 flow of 250 mL/min to the reaction vessels.
B. Reaction vessels (figs. 2c and 2d) are 250 mL Erlenmeyer flask with a standard/taper 24/40 neck and a sparging stopper fitted with a four-way valve (fig. 2b).
C. Sample traps (fig. 3b) are made from 7 mm quartz tubes, 10 cm long with a constriction at 3 cm from the outlet end (the trap identifier is placed at this end); about 0.2 g (3 cm in the tube) of Carbotrap (graphitized carbon black, Supelco 2-0287 or equivalent) is placed in the center and contained by quartz wool plugs at either end. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the sample traps to provide a connection point between the sample trap and the reaction vessel, and to provide connection points in the analytical train.
D. An analytical balance capable of measuring to the nearest 0.1g is used to determine sample volumes to the nearest 0.1mL.
E. Pneumatic fixed-volume and variable pipettes ranging from 5 µL to 5 mL.
F. Hewlett Packard model HP3395 integrator or equivalent, connected to a timer, controls the analytical system. The timer is connected to a transformer that is connected to a Nichrome wire coil wrapped to fit around the sample trap.
G. The gas chromatographic column (fig. 3c) is a 4 mm inside diameter (I.D.), 6 mm O.D., glass column 50 cm long and filled with Chromosorb WAW-DMSC 60/80 mesh (Supelco 2-0152) enclosed in a glass sheath 2 cm in diameter and 25 cm long. This column is housed in a cylindrical oven (figs. 3a and 3c) connected to a transformer, which supplies a constant voltage to maintain a temperature of 95 +/- 5°C. Column

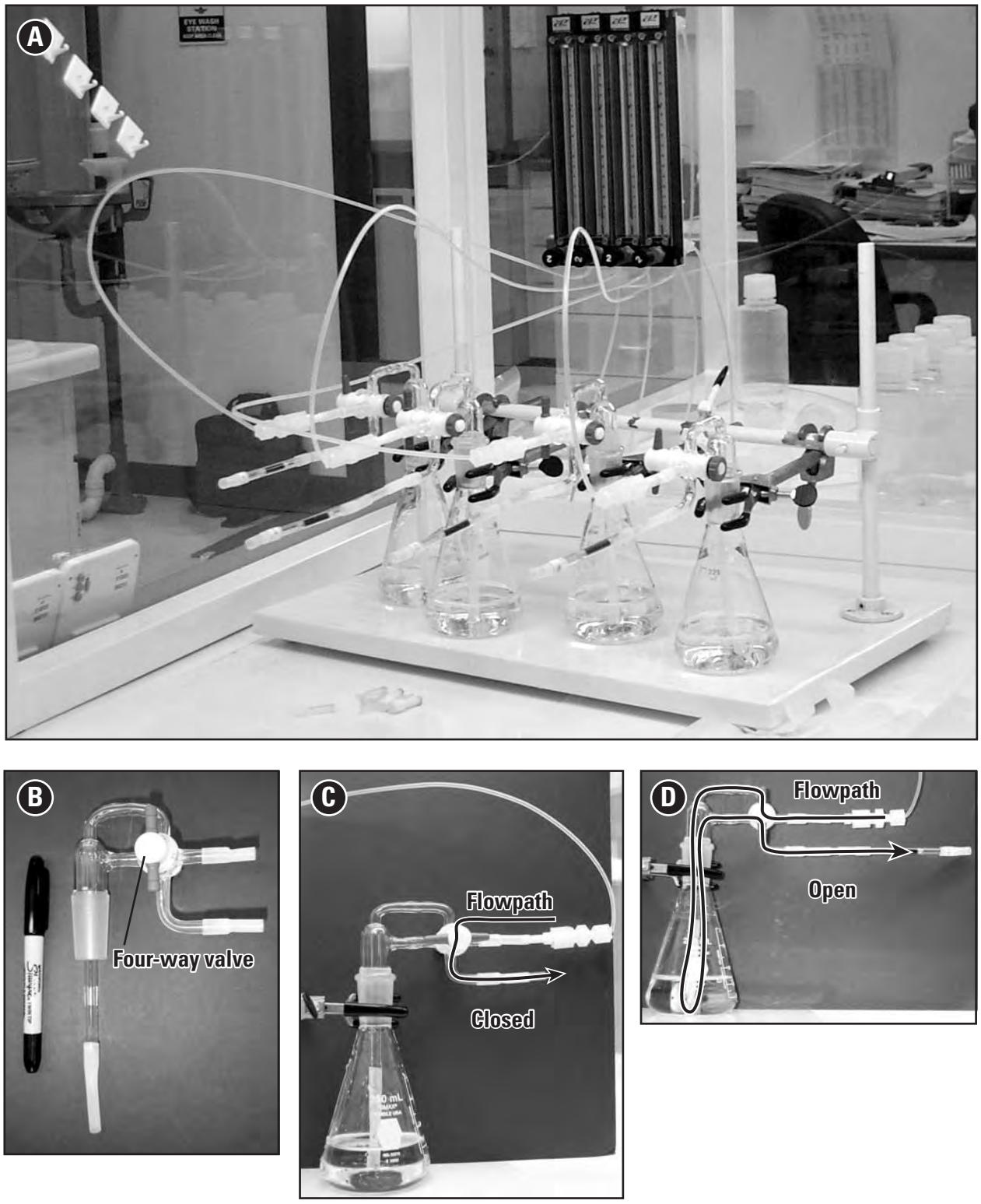

Figure 2. Methyl mercury reaction and purging system: (A) entire system, (B) sparging stopper fitted with a four-way valve, (C) reaction vessel in the closed (reaction) position, and (D) reaction vessel in the open (purging) position.

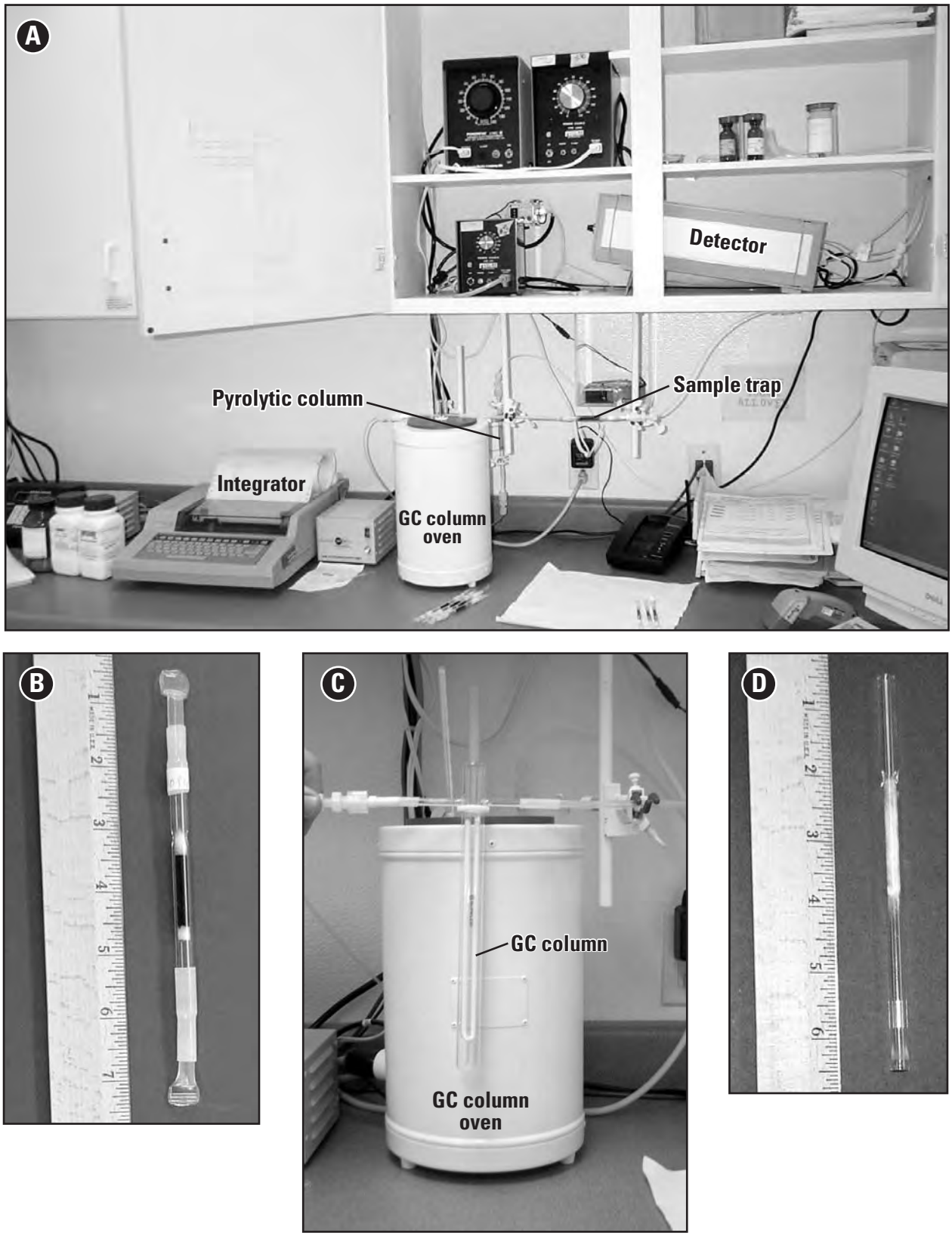

Figure 3. Methyl mercury desorbtion and dectection system: (A) entire system, (B) sample trap, (C) gas chromatographic column, and (D) pyrolytic column.

oven temperature may need to be adjusted on individual systems to insure good peak separation and symmetry.

H. The pyrolytic column (fig. 3d) is a 7 mm quartz tube 15 cm in length with the center 4–5 cm filled with quartz wool. Small pieces of 7 mm Teflon tubing are friction fit to the ends of the pyrolytic column to provide connection points in the analytical train. A length of nichrome wire is wrapped around the tube to cover the length of quartz wool. The wire is connected to a transformer that heats the column to approximately 800°C.

I. The detector is a commercially available Model 2500 CVAFS Mercury Detector from Tekran (Toronto, Ontario) equipped with a mass flow controller capable of maintaining 20 mL/min of Argon flow through the entire analytical train. Detector analog output returns to the HP3395 integrator where the peak areas are recorded.

Analytical Procedure

A WDML analytical batch generally consists of 2 distillation batches, as well as standards and blanks used to evaluate the performance of the analytical train. All chemical additions to the reaction vessels are carried out in a fume hood and then the vessels are transferred to a clean bench below a laminar flow hood equipped with a HEPA filter which is 99.99 percent efficient on particles less than 0.3 microns in diameter.

A. Create a standard curve by adding varying amounts of working standard (typically 100, 50, 25, and 10 µL, but the range needs to cover the expected concentrations in the analytical batch) to approximately 100 mL of reagent water in each of the reaction vessels. Pipette 200 µL of acetate buffer and 100 µL of $NaBEt_4$ to each of the reaction vessels. The $NaBEt_4$ reagent serves to derivatize the two remaining ionic Hg species after the distillation step (inorganic Hg(II) and CH_3Hg^+) to their ethylated forms (diethyl Hg and methylethyl Hg, respectively). Elemental Hg does not react with the $NaBEt_4$. *Note: The $NaBEt_4$ needs to remain near 0°C. It should be removed from the freezer approximately 3 minutes before being added to the reaction vessels and placed in a dark place to partially thaw. A new vial of $NaBEt_4$ should be used each day.*

B. Tighten the sparging stoppers, ensure the four-way valve is in the closed position (fig. 2c), gently swirl the reaction vessels, and allow the reaction to proceed for 15 minutes. After the reaction time has elapsed, remove the plugs from the ends of the sample traps. Place the sample traps onto the outlet of the reaction vessels, with the identification number downstream, turn the four-way valve to the open position (fig. 2d), and allow grade 5 N_2 to purge the vessel at a rate of 250 mL/min for 20 minutes.

C. After the samples have been purged, turn the four-way valve to the closed position and remove the sample trap from the reaction vessel outlet. Remove the N_2 line from the inlet of the four-way valve and place the sample trap on the end of the N_2 line. Allow the N_2 to flow through the sample traps at 250 mL/min for 7 minutes to remove any water vapor that has collected on the sample trap.

D. Four ethylation blanks are prepared by adding approximately 100 mL of reagent grade water, 200 µL of acetate buffer, and 100 µL of $NaBEt_4$ to separate reaction vessels. Then proceed as in step B.

E. While one set of reaction vessels and sample traps are being used to collect the purged sample, the other set can be desorbed and analyzed. Remove the sample traps from the N_2 lines, attach the N_2 lines to the inlets of the four-way valves, and cap both ends of the sample traps.

F. To desorb and analyze the traps, remove the plugs from the ends of the first trap and place it into the analytical train (fig. 3a) by threading it, with the identification number upstream, through the center of the nichrome wire coil. Center the nichrome wire over the Carbotrap, allow the flow to stabilize for approximately 30 seconds, and press start on the integrator. The nichrome wire will heat to 250°C with a ramp time of 30 seconds to desorb the Hg from the sample trap. As the Hg is desorbed from the sample trap it is carried by the Ar carrier gas at a flow of 20 mL/min into the GC column where the elemental Hg, methylethyl Hg and the diethyl Hg are separated. Following separation, the individual Hg species are carried into the pyrolytic column where the methylethyl and diethyl Hg species are reduced thermally to elemental Hg.

G. The CVAFS detector can only detect elemental mercury. The detector then outputs a millivolt signal to the integrator resulting in three distinct peaks (fig. 4).

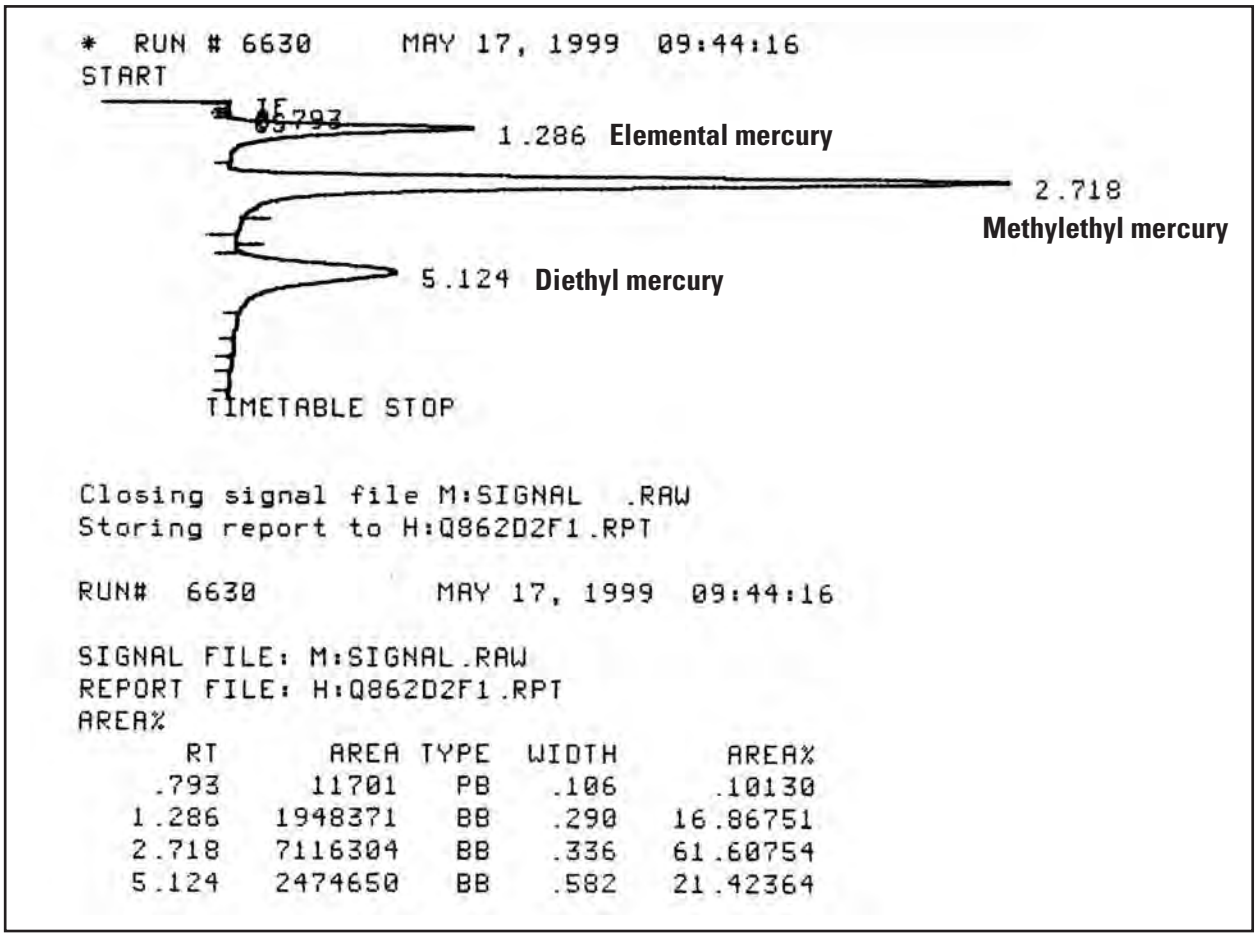

Figure 4. Example of methyl mercury detection chromatograph with peak identities.

H. After the standard curve and the ethylation blanks have been analyzed, and found to meet the daily quality objectives (DQO), the distillates from the batch can be analyzed. The procedure for analyzing the method blanks, environmental samples, matrix spikes and matrix-spike duplicates are identical to the procedure used for the standards and ethylation blanks. Simply dispense an appropriate amount of distillate into the reaction vessel, add the acetate buffer and the $NaBEt_4$ and proceed as in step B. An appropriate amount of sample would be an amount that produces a CH_3Hg^+ peak with an area that falls within the calibration range (for most water samples this amount is the entire distillate volume).

Data Interpretation

The integrator output should show three distinct peaks for a given sample (fig. 4). A peak for the elemental Hg appears at approximately 1 minute and 30 seconds, the methylethyl Hg peak at 2 minutes and 40 seconds, and the diethyl Hg peak appears at 4 minutes and 40 seconds. The methylethyl Hg peak is the peak of interest and the area under its curve is used to calculate concentration of CH_3Hg^+ in the original sample.

Peak areas obtained for the standards during the calibration are corrected for CH_3Hg^+ in the acetate buffer and the $NaBEt_4$ by subtracting the average peak area of the ethylation blanks (DQO is absolute mass less than or equal to 2 pg). Simple linear regression, forcing zero intercept, is applied to the peak area/mass combinations to determine the best-fit line (DQO is a correlation coefficient equal to or greater than 0.995) and establish the equation used to determine the mass of the sample aliquot from its resulting peak area. Each distillation batch contains three method blanks (DQO is an absolute mass less than or equal to 5 pg) to evaluate the contribution of CH_3Hg^+ from the distillation process and reagents. The average mass found in these blanks is subtracted from the mass in the sample dis-

tillates. After correcting for the method blanks, the final sample concentrations are corrected for the fraction distilled (because the fraction of methyl mercury distilled is equal to the fraction of the sample volume distilled), and the difference between the volume of the distillate ethylated and the total volume of distillate recovered. The following series of formulas are used to calculate final concentration.

SAMPLE VOLUME:

$V_s = W_{F1} - W_T$,

where

V_s = sample volume

W_{F1} = weight of reaction vessel with sample

W_T = weight of reaction vessel

FRACTION DISTILLED:

$D = V_S/(W_{F2} - W_W)$,

where

D = fraction distilled

V_S = sample volume

W_{F2} = weight of receiving vessel after distillation

W_W = weight of receiving vessel with reagent water before distillation

MASS OF Hg IN ALIQUOT ANALYZED

$M_A = (PA/S) - MB_{AVE}$,

where

M_A = mass per aliquot

PA = peak area

S = slope of calibration line

MB_{AVE} = average mass found in method blanks

MASS OF Hg IN ORIGINAL SAMPLE

$M_S = (M_A / D)*((W_{F2} - W_{T2})/(W_{F2} - W_A))$,

where

M_S = mass in original sample

M_A = mass per aliquot

D = fraction distilled

W_{F2} = weight of receiving vessel after distillation

W_{T2} = weight of receiving vessel

W_A = weight of receiving vessel after pouring off aliquot to be ethylated

FINAL CH_3Hg^+ CONCENTRATION

$C = M_S / V_S$,

where

C = concentration

M_S = mass in original sample

V_S = sample volume

Table 2a. Results for the analysis of ground water spiked at two different concentrations
[All concentrations in nanograms per liter (ng/L)]

	Ground water spiked at 0.1 ng/L	Percent recovery	Ground water spiked at 1.0 ng/L	Percent recovery
	0.093	95.2	0.927	92.6
	.078	79.9	1.15	114.3
	.095	97.6	.933	93.1
	.090	91.6	.835	83.4
	.064	62.2	.886	88.5
	.090	91.8	1.088	108.6
	.099	101.6	.995	99.4
	.085	87.0	.843	84.2
	.087	88.8	.956	95.5
Average	.087	88.8	.956	95.5
Standard deviation	.011	11.5	.112	11.21
Percent relative standard deviation	12.9	12.9	11.7	11.7

METHOD PERFORMANCE

Precision and accuracy for this method were evaluated using three water sources at two concentrations and analyzed seven times each (U.S. Geological Survey, Office of Water Quality Technical Memorandum 98.05) over a period of five days using different calibration curves. Memorandum 98.05 recommends the use of surface water, ground water, and reagent water as the three sources; however, multiple analyses of reagent water spiked with CH_3Hg^+ resulted in consistently poor recoveries of CH_3Hg^+ for undetermined reasons and, thus, reagent water was not used to evaluate this method. Instead, ground water from a residential well, surface water from a freshwater lake in Canada, and surface water from the Everglades in southern Florida were used to evaluate method performance. The ground water was found to contain no CH_3Hg^+ on initial analysis; therefore, analyte was spiked into this matrix so that it could be evaluated for precision and accuracy. Both surface-water samples contained CH_3Hg^+ at detectable (greater than 0.04 ng/L) concentrations. The USGS requires that sample matrices be evaluated at two different concentrations; therefore, the ground-water sample was spiked at two different concentrations and the surface-water samples were spiked with analyte so that two different concentrations could be evaluated. The results of the analyses of these matrices are presented in tables 2a–c.

Method precision was evaluated by examining the percent relative standard deviation of the concentrations obtained from all analyses of each matrix at each concentration. The percent relative standard deviations ranged from 10.2 to 15.6. Average recoveries of the added analyte obtained at the different concentrations in the different matrices evaluated ranged from 88.8 to 117 percent, which are considered within acceptable method performance limits for accuracy at laboratories using this analytical method (Nicolas Bloom, Frontier Geosciences, Seattle, Washington, written communication, 1999).

SUMMARY AND CONCLUSIONS

This report documents a method for the analysis of CH_3Hg^+ in water samples, and describes the results of a methodological test of the WDML's ability to provide quality CH_3Hg^+ data at ng/L concentrations. Acceptance of this method by the USGS will help to establish a National database of CH_3Hg^+ concentrations from areas across the nation. The need for a reliable method of CH_3Hg^+ detection was precipitated by the National Water-Quality Assessment program's identification of mercury as one of the top five priority issues over the next 10 years coupled with the fact that CH_3Hg^+ is the species of mercury that most readily bioaccumulates in mammals.

The Wisconsin District Mercury Laboratory has adapted a distillation/ethylation/gas-phase separation

Table 2b. Results for the analysis of spiked and unspiked Canada surface water.
[All concentrations in nanograms per liter (ng/L); --, no sample]

	Surface water unspiked	Surface water spiked at 0.627 ng/L[1]	Percent recovery
	0.134	0.638	101.8
	.095	.571	91.0
	.123	.606	96.6
	.102	.668	106.6
	.101	.573	91.4
	.116	.564	89.9
	.115	.482	76.9
	.095	--	--
Average	.110	.586	93.5
Standard deviation	.014	.060	9.57
Percent relative standard deviation	12.9	10.2	10.2

[1]Concentration calculated by adding average concentration of sample to known spike addition

Table 2c. Results for the analysis of spiked and unspiked Everglades' surface water
[all concentrations in nanograms per liter (ng/L)]

	Everglades water unspiked	Everglades water spiked at 1.25 ng/L[1]	Percent recovery
	0.255	1.51	120.8
	.300	1.63	130.1
	.236	1.02	81.6
	.280	1.48	118.2
	.275	1.47	118.0
	.323	1.64	131.2
Average	.278	1.46	116.6
Standard deviation	.031	0.227	18.2
Percent relative standard deviation	11.1	15.6	15.6

[1]Concentration calculated by adding average concentration of sample to known spike addition.

method with cold vapor atomic fluorescence spectroscopy detection for the determination of methyl mercury in filtered and unfiltered waters. A method detection limit of 0.04 ng/L was proven to be achievable from multiple matrices using this method. The accuracy of this method also was tested using multiple matrices at different concentrations and found to be acceptable based on average spike recoveries ranging from 88.8 to 117 percent.

Reagent water is not an appropriate matrix to evaluate method performance as spiked reagent water consistently results in low recovery. Low ionic strength water samples such as snow have also resulted in low recoveries at the WDML as well as other laboratories using this method. Samples high in dissolved organic carbon (DOC) also can be difficult to evaluate because the spike recoveries can be quite inconsistent. When analyzing these types of water samples with these matrices, professional judgment and caution must be used in evaluating method performance.

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Method 1638

Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry

January 1996

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Disclaimer

This method has been reviewed and approved for publication by the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Introduction

This analytical method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, EPA developed new sampling and analysis methods to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which the new sampling and analysis methods are based. Method 1638 was specifically developed to provide reliable measurements of nine of these metals at EPA WQC levels using inductively coupled plasma-mass spectrometry techniques.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This analytical method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies should be directed to:

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Cincinnati, OH 45242
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Note: This method is intended to be performance-based, and the laboratory is permitted to omit any step or modify any procedure provided that *all* performance requirements set forth in this method are met. The laboratory is *not* allowed to omit any quality control analyses. The terms "must," "may," and "should" are included throughout this method and are intended to illustrate the importance of the procedures in producing verifiable data at water quality criteria levels. The term "must" is used to indicate that researchers in trace metals analysis have found certain procedures essential in successfully analyzing samples and avoiding contamination; however, these procedures can be modified or omitted if the laboratory can demonstrate that data quality is not affected.

Method 1638
Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma — Mass Spectrometry

1.0 Scope and Application

1.1 This method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using inductively coupled plasma-mass spectrometry (ICP-MS). It may also be used for determination of total recoverable element concentrations in these waters. This method was developed by integrating the analytical procedures in EPA Method 200.8 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels. This method contains QC procedures that will assure that contamination will be detected when blanks accompanying samples are analyzed. 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 assure that trace metals determinations will not be compromised by contamination during the sampling process.

1.2 This method is applicable to the following elements:

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Cadmium	(Cd)	7440-43-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

Table 1 lists the EPA WQC levels, the Method Detection Limit (MDL) for each metal, and the minimum level for each metal in this method. Linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.3 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range.

1.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination. These suggestions are given in Section 4.0, "Contamination and Interferences" and are based on findings of researchers performing trace metals analyses (References 1-8).

Additional suggestions for improvement of existing facilities may be found in EPA's *Guidance for Establishing Trace Metals Clean Rooms in Existing Facilities*, which is available from the National Center for Environmental Publications and Information (NCEPI) at the address listed in the introduction to this document.

1.5 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 of their lack of an exact definition. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques (Reference 9).

1.6 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 10).

1.7 This method is "performance-based"; i.e., an alternate procedure or technique may be used, as long as the performance requirements in the method are met. Section 9.1.2 gives details of the tests and documentation required to support and document equivalent performance.

1.8 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in the Sampling Method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in the Sampling Method; procedures for laboratory preservation are provided in this method.

1.9 For the determination of total recoverable analytes in ambient water samples, a digestion/extraction (see Section 12.2) is required before analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids).

1.10 The procedure given in this method for digestion of total recoverable metals is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of samples containing higher concentrations of silver, succeedingly smaller volume, well-mixed sample aliquots must be prepared until the analysis solution contains <0.1 mg/L silver.

1.11 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), including the interpretation of spectral and matrix interferences and procedures for their correction, and this method should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of metals at EPA WQC levels. A minimum of six months experience with commercial instrumentation is recommended.

1.12 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 Monitoring*. Before using this method, data users should state the data quality objectives (DQOs) required for a project.

2.0 Summary of Method

2.1 An aliquot of a well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made to volume, mixed, and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The digested sample is introduced into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio (m/z) by a mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height at m/z 300. Ions transmitted through the mass analyzer are detected by an electron multiplier or Faraday detector and the resulting current is processed by a data handling system (References 11-13).

3.0 Definitions

3.1 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.

3.2 Other definitions of terms are given in Section 18.0 at the end of this method.

4.0 Contamination and Interferences

4.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical 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. More recently, historical trace metals data collected from freshwater rivers and streams have been shown to be similarly biased because of contamination during sampling and analysis (Reference 14). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and 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 that are directly exposed to exhalation (Reference 3).

4.3 Contamination Control

4.3.1 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 metals.

4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for control of sample contamination are given in this method and the Sampling Method.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. Requirements and suggestions for protecting the laboratory are given in this method.

4.3.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this method and the Sampling Method.

4.3.2 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 by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class 100 clean room (Section 6.1.1). If a clean room is not available, all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally, in the clean room.

4.3.4 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.

4.3.5 Clean work surfaces—Before processing a given batch of samples, 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.

4.3.6 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.9.7) 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 handling the Apparatus again. 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.

4.3.7 Use metal-free Apparatus—All Apparatus used for determination of metals at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

4.3.7.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials resulting either in contamination or low-biased results (Reference 3). All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures described in Section 11.0 and must be known to be clean and metal-free before proceeding.

4.3.7.2 The following materials have been found to contain trace metals and should not contact the sample or be used to hold liquids that contact the sample, *unless* these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 15).

4.3.7.3 Serialization—It is recommended that serial numbers 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 labware to injection into the instrument. It may be useful to dedicate separate sets of labware 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 labware can be detected.

4.3.7.4 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.

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

4.3.8.1 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. To reduce carryover, the sample introduction system may be rinsed between samples with dilute acid and reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a laboratory blank to check for carryover. For samples containing high levels of metals, it may be necessary to acid clean or replace the connecting tubing or inlet system to ensure that contamination will not affect subsequent measurements. Samples known or suspected to contain the lowest concentration of metals should be analyzed first followed by samples containing higher levels. For instruments containing autosamplers, the laboratory should keep track of which station is used for a given sample. When an unusually high concentration of a metal is detected in a sample, the station used for that sample should be cleaned more thoroughly to prevent contamination of subsequent samples, and the results for subsequent samples should be checked for evidence of the metal(s) that occurred in high concentration.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of inorganic substances are processed and analyzed. As stated in Section 1.0, this method is not intended for application to these samples, and samples containing high concentrations should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.

4.3.8.3 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 then subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of ambient water samples be cleaned as specified in Section 11.0.

4.3.8.4 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.

4.4 Interferences—Interference sources that may cause inaccuracies in the determination of trace elements by ICP-MS are given below and must be recognized and corrected for. Instrumental drift, as well as suppressions or enhancements of instrument response caused by the sample matrix, should be corrected for by the use of internal standards.

4.4.1 Isobaric elemental interferences—Are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal m/z and that cannot be resolved by the mass spectrometer. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interferences. Of the isotopes recommended for use with this method (Table 5), only selenium-82 (krypton) has an isobaric elemental interference. If an alternative isotope that has a higher natural abundance is selected to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the contribution the isotope of interest based on the relative abundance of the alternate isotope and isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the relative abundance used in the equation for data calculations. Relative abundances should be established before applying any corrections.

4.4.2 Abundance sensitivity—Is a property defining the degree to which the wings of a mass peak contribute to adjacent m/z's. The abundance sensitivity is affected by ion energy and quadruple operating pressure. Wing overlap interferences may result when a small m/z peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.4.3 Isobaric polyatomic ion interferences—Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified (Reference 13), and these are listed in Table 3 together with elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of an alternative m/z, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence because the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common ^{82}Kr interference that affects the determination of both arsenic and selenium can be greatly reduced with the use of high-purity krypton-free argon.

4.4.4 Physical interferences—Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the

extraction cone, skimmer cone, or both, reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended (Reference 13) to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects (Reference 16). Internal standards ideally should have analytical behavior similar to the elements being determined.

4.4.5 Memory interferences—Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.6.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated before analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals below the minimum level (ML) should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period.

5.0 Safety

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

5.1.1 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method (References 17-20). A reference file of material safety data sheets (MSDSs) should also be available to all personnel involved in the chemical analysis. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. The references and bibliography at the end of Reference 20 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.1.2 Concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear protective clothing and safety glasses or a shield for eye protection, and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents.

5.4 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

6.0 Apparatus, Equipment, and Supplies

DISCLAIMER: *The mention of trade names or commercial products in this method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus and materials other than those suggested here. Demonstration of equivalent performance is the responsibility of the laboratory.*

6.1 Facility

6.1.1 Clean room—Class 100, 200 ft^2 minimum, with down-flow, positive-pressure ventilation, air-lock entrances, and pass-through doors.

6.1.1.1 Construction materials—Nonmetallic, preferably plastic sheeting attached without metal fasteners. If painted, paints that do not contain the metal(s) of interest should be used.

6.1.1.2 Adhesive mats—For use at entry points to control dust and dirt from shoes.

6.1.2 Fume hoods—Nonmetallic, two minimum, with one installed internal to the clean room.

6.1.3 Clean benches—Class 100, one installed in the clean room; the other adjacent to the analytical instrument(s) for preparation of samples and standards.

6.2 Inductively Coupled Plasma Mass Spectrometer:

6.2.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

6.2.2 Radio-frequency generator compliant with FCC regulations.

6.2.3 Argon gas supply—High-purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders (Section 4.1.3).

6.2.4 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

6.2.5 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., from polyatomic oxide species).

6.2.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted before analysis.

6.3 Analytical Balance—With capability to measure to 0.1 mg, for use in weighing solids and for preparing standards.

6.4 Temperature Adjustable Hot Plate—Capable of maintaining a temperature of 95°C.

6.5 Centrifuge—With guard bowl, electric timer, and brake (optional).

6.6 Drying Oven—Gravity convection, with thermostatic control capable of maintaining 105°C (±5°C).

6.7 Alkaline Detergent—Liquinox®, Alconox®, or equivalent.

6.8 pH meter or pH paper.

6.9 Labware—For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area should be designated for trace element sample handling. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All labware must be metal-free. Suitable construction materials are fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, and polypropylene. Fluoropolymer should be used when samples are to be analyzed for mercury. All labware should be cleaned according to the procedure in Section 11.4. Gloves, plastic wrap, storage bags, and filters may all be used new without additional cleaning unless results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an alternate supplier must be obtained or the materials must be cleaned.

NOTE: *Chromic acid must not be used for cleaning glassware.*

6.9.1 Volumetric flasks, graduated cylinders, funnels and centrifuge tubes.

6.9.2 Assorted calibrated pipettes.

6.9.3 Beakers—Fluoropolymer (or other suitable material), 250 mL with fluoropolymer covers.

6.9.4 Storage bottles—Narrow-mouth, fluoropolymer with fluoropolymer screw closure, 125-250 mL capacities.

6.9.5 Wash bottle—One-piece stem fluoropolymer, with screw closure, 125 mL capacity.

6.9.6 Tongs—For removal of Apparatus from acid baths. Coated metal tongs may not be used.

6.9.7 Gloves—clean, nontalc polyethylene, latex, or vinyl; various lengths. Heavy gloves should be worn when working in acid baths since baths will contain hot, strong acids.

6.9.8 Buckets or basins—5-50 L capacity, for acid soaking of the Apparatus.

6.9.9 Brushes—Nonmetallic, for scrubbing Apparatus.

6.9.10 Storage bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes) for storage of Apparatus.

6.9.11 Plastic wrap—Clean, colorless polyethylene for storage of Apparatus.

6.10 Sampling Equipment—The sampling team may contract with the laboratory or a cleaning facility that is responsible for cleaning, storing, and shipping all sampling devices, sample bottles, filtration equipment, and all other Apparatus used for the collection of ambient water samples. Before shipping the equipment to the field site, the laboratory or facility must generate an acceptable equipment blank (Section 9.6.3) to demonstrate that the sampling equipment is free from contamination.

6.10.1 Sampling devices—Before ambient water samples are collected, consideration should be given to the type of sample to be collected and the devices to be used (grab, surface, or subsurface samplers). The laboratory or cleaning facility must clean all devices used for sample collection. Various types of samplers are described in the Sampling Method. Cleaned sampling devices should be stored in polyethylene bags or wrap.

6.10.2 Sample bottles—Fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL with lids. Cleaned sample bottles should be filled with 0.1% HCl (v/v) until use.

NOTE: *If mercury is a target analyte, fluoropolymer or glass bottles must be used.*

6.10.3 Filtration apparatus

6.10.3.1 Filter—Gelman Supor 0.45 µm, 15 mm diameter capsule filter (Gelman 12175, or equivalent).

6.10.3.2 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).

6.10.3.3 Tubing for use with peristaltic pump—styrene/ethylene/butylene/silicone (SEBS) resin, approximately 3/8 in i.d. by approx 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 hours, 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.

7.0 Reagents and Standards

Reagents may contain elemental impurities that might affect the integrity of analytical data. Because of the high sensitivity of ICP-MS, high-purity reagents should be used. Each reagent lot should be tested for the metals of interest by diluting and analyzing an aliquot from the lot using the techniques and instrumentation to be used for analysis of samples. The lot will be acceptable if the concentration of the metal of interest is below the MDL listed in this method. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (Table 3); however, hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1 Reagents for cleaning Apparatus, sample bottle storage, and sample preservation.

7.1.1 Nitric acid—Concentrated (sp gr 1.41), Seastar or equivalent.

7.1.2 Nitric acid (1+1)—Add 500 mL conc. nitric acid to 400 mL of regent water and dilute to 1 L.

7.1.3 Nitric acid (1+9)—Add 100 mL conc. nitric acid to 400 mL of reagent water and dilute to 1 L.

7.1.4 Hydrochloric acid—Concentrated (sp gr 1.19).

7.1.5 Hydrochloric acid (1+1)—Add 500 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.6 Hydrochloric acid (1+4)—Add 200 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid (HCl)—1 N trace metal grade.

7.1.8 Hydrochloric acid (HCl)—10% wt, trace metal grade.

7.1.9 Hydrochloric acid (HCl)—1% wt, trace metal grade.

7.1.10 Hydrochloric acid (HCl)—0.5% (v/v), trace metal grade.

7.1.11 Hydrochloric acid (HCl)—0.1% (v/v) ultrapure grade.

7.1.12 Tartaric acid (CASRN 87-69-4).

7.2 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal listed in Table 1. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other technique that removes the metal(s) and potential interferent(s).

7.3 Stock Standard Solutions—Stock standards may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99-99.999% pure). All salts should be dried for one hour at 105°C, unless otherwise specified. Stock solutions should be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of the multielement stock standards can not be verified.

CAUTION: *Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.*

The following procedures may be used for preparing standard stock solutions:

NOTE: *Some metals, particularly those which form surface oxides, require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried, and weighed until the desired weight is achieved.*

7.3.1 Antimony solution, stock 1 mL = 1000 µg Sb—Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL concentrated hydrochloric acid, heating to effect solution. Cool, add 20 mL reagent water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with reagent water.

7.3.2 Beryllium solution, stock 1 mL = 1000 µg Be—Dissolve 1.965 g $BeSO_4 \bullet 4H_2O$ (DO NOT DRY) in 50 mL reagent water. Add 1 mL concentrated nitric acid. Dilute to 100 mL with reagent water.

7.3.3 Bismuth solution, stock 1 mL = 1000 µg Bi—Dissolve 0.1115 g Bi_2O_3 in 5 mL concentrated nitric acid. Heat to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.4 Cadmium solution, stock 1 mL = 1000 µg Cd—Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.5 Cobalt solution, stock 1 mL = 1000 µg Co—Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.6 Copper solution, stock 1 mL = 1000 µg Cu—Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.7 Indium solution, stock 1 mL = 1000 µg In—Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.8 Lead solution, stock 1 mL = 1000 µg Pb—Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent water.

7.3.9 Magnesium solution, stock 1 mL = 1000 µg Mg—Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.10 Nickel solution, stock 1 mL = 1000 µg Ni—Dissolve 0.100 g nickel powder in 5 mL concentrated nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.11 Scandium solution, stock 1 mL = 1000 µg Sc—Dissolve 0.1534 g Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.12 Selenium solution, stock 1 mL = 1000 µg Se—Dissolve 0.1405 g SeO_2 in 20 mL reagent water. Dilute to 100 mL with reagent water.

7.3.13 Silver solution, stock 1 mL = 1000 µg Ag—Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water. Store in dark container.

7.3.14 Terbium solution, stock 1 mL = 1000 µg Tb—Dissolve 0.1176 g Tb_4O_7 in 5 mL concentrated nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.15 Thallium solution, stock 1 mL = 1000 µg Tl—Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL reagent water and 1 mL concentrated nitric acid. Dilute to 100 mL with reagent water.

7.3.16 Yttrium solution, stock 1 mL = 1000 µg Y—Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.3.17 Zinc solution, stock 1 mL = 1000 µg Zn—Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.4 Multielement Stock Standard Solutions—Care must be taken in the preparation of multielement stock standards so that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-

cleaned, not previously used, FEP fluorocarbon bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

Standard Solution A		Standard Solution B
Antimony	Nickel	Silver
Cadmium	Selenium	
Copper	Thallium	
Lead	Zinc	

Except for selenium, multielement stock standard solutions A and B (1 mL = 10 µg) may be prepared by diluting 1.0 mL of each single element stock standard in the combination list to 100 mL with reagent water containing 1% (v/v) nitric acid. For selenium in solution A, an aliquot of 5.0 mL of the stock standard should be diluted to the specified 100 mL (1 ml = 50 µg Se). Replace the multielement stock standards when succeeding dilutions for preparation of the calibration standards cannot be verified with the quality control sample.

7.4.1 Preparation of calibration standards—Fresh multielement calibration standards should be prepared every two weeks or as needed. Dilute each of the stock multielement standard solutions A and B to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. Calibration standards should be prepared at a minimum of three concentrations, one of which must be at the minimum level (Table 1), and another which must be near the upper end of the linear dynamic range. It should be noted the selenium concentration is always a factor of 5 greater than the other analytes. If the direct addition procedure is being used (Method A, Section 10.3), add internal standards (Section 7.5) to the calibration standards and store in fluoropolymer bottles. Calibration standards should be verified initially using a quality control sample (Section 7.8).

7.5 Internal Standard Stock Solution—1 mL = 100 µg. Dilute 10 mL of scandium, yttrium, indium, terbium, and bismuth stock standards (Section 7.3) to 100 mL with reagent water, and store in a FEP bottle. Use this solution concentrate for addition to blanks, calibration standards and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (Method B, Section 10.3).

7.6 Blanks—The laboratory should prepare the following types of blanks. A calibration blank is used to establish the analytical calibration curve; the laboratory (method) blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background; and the rinse blank is used to flush the instrument between samples to reduce memory interferences. In addition to these blanks, the laboratory may be required to analyze field blanks (Section 9.6.2) and equipment blanks (Section 9.6.3).

7.6.1 Calibration blank—Consists of 1% (v/v) nitric acid in reagent water. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards.

7.6.2 Laboratory blank—Must contain all the reagents in the same volumes as used in processing the samples. The laboratory blank must be carried through the same entire preparation scheme as the samples including digestion, when applicable

(Section 9.6.1). If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to the solution after preparation is complete.

7.6.3 Rinse blank—Consists of 2% (v/v) nitric acid in reagent water.

7.7 Tuning Solution—This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium, and lead stock solutions (Section 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 µg/L of each element. Internal standards are not added to this solution. (Depending on the sensitivity of the instrument, this solution may need to be diluted 10 fold.)

7.8 Quality Control Sample (QCS)—The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS, dilute an appropriate aliquot of analytes to a concentration ≤100 µg/L in 1% (v/v) nitric acid. Because of lower sensitivity, selenium may be diluted to a concentration of <500 µg/L. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards after dilution, mix, and store in a FEP bottle. The QCS should be analyzed as needed to meet data quality needs and a fresh solution should be prepared quarterly or more frequently as needed.

7.9 Ongoing Precision and Recovery (OPR) Sample—To an aliquot of reagent water, add aliquots from multielement stock standards A and B (Section 7.4) to prepare the OPR. The OPR must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable (Section 9.7). If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to this solution after preparation has been completed.

8.0 Sample Collection, Filtration, Preservation, and Storage

8.1 Before an aqueous sample is collected, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately before aliquotting for processing or direct analysis to ensure the sample has been properly preserved. If properly acid-preserved, the sample can be held up to six months before analysis.

8.2 Sample Collection—Samples are collected as described in the Sampling Method.

8.3 Sample Filtration—For dissolved metals, samples and field blanks are filtered through a 0.45-µm capsule filter at the field site. Filtering procedures are described in the Sampling Method. For the determination of total recoverable elements, samples are not filtered but should be preserved according to the procedures in Section 8.4.

8.4 Sample Preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field at time of collection or in the laboratory. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within two weeks of collection. Samples and field blanks should be preserved at the laboratory

immediately upon receipt. For all metals, preservation involves the addition of 10% HNO_3 (Section 7.1.3) to bring the sample to pH <2. For samples received at neutral pH, approx 5 mL of 10% HNO_3 per liter will be required.

8.4.1 Wearing clean gloves, remove the cap from the sample bottle, add the volume of reagent grade acid that will bring the pH to <2, and recap the bottle immediately. If the bottle is full, withdraw the necessary volume using a precleaned pipet and then add the acid. Record the volume withdrawn and the amount of acid used.

NOTE: *Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood. See Section 5.2.*

8.4.2 Store the preserved sample for a minimum of 48 hours at 0-4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample pH should be verified as <2 immediately before withdrawing an aliquot for processing or direct analysis. If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to be pH <2. See Section 8.1.

8.4.3 With each sample batch, preserve a method blank and an OPR sample in the same way as the sample(s).

8.4.4 Sample bottles should be stored in polyethylene bags at 0-4°C until analysis.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 21). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine that results of the analysis meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, concentration, and cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in the method is used, that technique must have a specificity equal to or better than the specificity of the techniques in the method for the analytes of interest.

9.1.2.1 Each time the method is modified, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be

affected by the change, the laboratory is required to demonstrate that the MDL (40 *CFR* Part 136, Appendix B) is lower than the MDL for that analyte in this method, or one-third the regulatory compliance level, whichever is higher. If calibration will be affected by the change, the analyst must recalibrate the instrument according to Section 10.0.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A listing of metals measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modification(s).

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration.
(b) Calibration verification.
(c) Initial precision and recovery (Section 9.2).
(d) Analysis of blanks.
(e) Accuracy assessment.

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include, where possible:

(a) Sample numbers and other identifiers.
(b) Digestion/preparation or extraction dates.
(c) Analysis dates and times.
(d) Analysis sequence/run chronology.
(e) Sample weight or volume.
(f) Volume prior to extraction/concentration step.
(g) Volume after each extraction/concentration step.
(h) Final volume prior to analysis.
(i) Injection volume.
(j) Dilution data, differentiating between dilution of a sample or extract.
(k) Instrument and operating conditions (make, model, revision, modifications).
(l) Sample introduction system (ultrasonic nebulizer, flow injection system, etc).
(m) Operating conditions (background corrections, temperature program, flow rates, etc).
(n) Detector (type, operating conditions, etc).

(o) Mass spectra, printer tapes, and other recordings of raw data.

(p) Quantitation reports, data system outputs, and other data to link raw data to results reported.

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The required types, procedures, and criteria for analysis of blanks are described in Section 9.6.

9.1.4 The laboratory shall spike at least 10% of the samples with the metal(s) of interest to monitor method performance. This test is described in Section 9.3 of this method. When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits. If method performance for spikes cannot be brought within the limits given in this method, the result may not be reported for regulatory compliance purposes.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and through analysis of the ongoing precision and recovery aliquot that the analytical system is in control. These procedures are described in Sections 10.2 and 9.7 of this method.

9.1.6 The laboratory shall maintain records to define the quality of data that are generated. Development of accuracy statements is described in Section 9.3.4.

9.2 Initial Demonstration of Laboratory Capability

9.2.1 Method detection limit—To establish the ability to detect the trace metals of interest, the analyst shall determine the MDL for each analyte according to the procedure in 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 Table 1, or one-third the regulatory compliance limit, whichever is greater. MDLs 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 they be redetermined.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.2.1 Analyze four aliquots of reagent water spiked with the metal(s) of interest at two to three times the ML (Table 1), according to the procedures in Section 12.0. All digestion, extraction, and concentration steps, and the containers, labware, and reagents that will be used with samples, must be used in this test.

9.2.2.2 Using results of the set of four analyses, compute the average percent recovery (X) for the metal(s) in each aliquot and the standard deviation of the recovery(ies) for each metal.

9.2.2.3 For each metal, compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X for all metal(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that metal. Correct the problem and repeat the test (Section 9.2.2.1).

9.2.3 Linear calibration ranges—Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper limit must be diluted and reanalyzed. The upper limits should be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.4 Quality control sample (QCS)—When beginning the use of this method, quarterly or as required to meet data quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.8). To verify the calibration standards the determined mean concentration from three analyses of the QCS must be within ±10% of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the calibration standards, acceptable instrument performance, or both cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Method Accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform 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 sample analysis and one MSD sample analysis must be performed for each sample batch (samples collected from the same site at the same time, to a maximum of 10 samples), whichever is more frequent. Blanks (e.g., field blanks) may not be used for MS/MSD analysis.

9.3.1 The concentration of the MS and MSD is determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of a specific metal in the sample is being checked against a regulatory concentration limit, the spike must be at that limit or at one to five times the background concentration, whichever is greater.

9.3.1.2 If the concentration is not being checked against a regulatory limit, the concentration must be at one to five times the background concentration or at one to five times the ML in Table 1, whichever is greater.

9.3.2 Assessing spike recovery

9.3.2.1 Determine the background concentration (B) of each metal by analyzing one sample aliquot according to the procedure in Section 12.0.

9.3.2.2 If necessary, prepare a QC check sample concentrate that will produce the appropriate level (Section 9.3.1) in the sample when the concentrate is added.

9.3.2.3 Spike a second sample aliquot with the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each metal.

9.3.2.4 Calculate each percent recovery (P) as 100(A-B)/T, where T is the known true value of the spike.

9.3.3 Compare the percent recovery (P) for each metal with the corresponding QC acceptance criteria found in Table 2. If any individual P falls outside the designated range for recovery, that metal has failed the acceptance criteria.

9.3.3.1 For a metal that has failed the acceptance criteria, analyze the ongoing precision and recovery standard (Section 9.7). If the OPR is within its respective limit for the metal(s) that failed (Table 2), the analytical system is in control and the problem can be attributed to the sample matrix.

9.3.3.2 For samples that exhibit matrix problems, further isolate the metal(s) from the sample matrix using dilution, chelation, extraction, concentration, hydride generation, or other means, and repeat the accuracy test (Section 9.3.2).

9.3.3.3 If the recovery for the metal remains outside the acceptance criteria, the analytical result for that metal in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

9.3.4 Recovery for samples should be assessed and records maintained.

9.3.4.1 After the analysis of five samples of a given matrix type (river water, lake water, etc.) for which the metal(s) pass the tests in Section 9.3.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (SR) for the metal(s). Express the accuracy assessment as a percent recovery interval from R-2SR to R+2SR for each matrix. For example, if R = 90% and SR = 10% for five analyses of river water, the accuracy interval is expressed as 70-110%.

9.3.4.2 Update the accuracy assessment for each metal in each matrix regularly (e.g., after each 5-10 new measurements).

9.4 Precision of Matrix Spike and Duplicate

9.4.1 Calculate the relative percent difference (RPD) between the MS and MSD per the equation below using the concentrations found in the MS and MSD. Do not use

the recoveries calculated in Section 9.3.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 100 \frac{(|D1-D2|)}{(D1+D2)/2}$$

where,

D1 = Concentration of the analyte in the MS sample.
D2 = Concentration of the analyte in the MSD sample.

9.4.2 The relative percent difference between the matrix spike and the matrix spike duplicate must be less than 20%. If this criterion is not met, the analytical system is judged to be out of control. In this case, correct the problem and reanalyze all samples in the sample batch associated with the MS/MSD which failed the RPD test.

9.5 Internal Standards Responses—The analyst is expected to monitor the responses from the internal standards throughout the sample batch being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards, or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards, and reanalyze. If, after flushing, the responses of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

9.6 Blanks—Blanks are analyzed to demonstrate freedom from contamination.

9.6.1 Laboratory (method) blank

9.6.1.1 Prepare a method blank with each sample batch (samples of the same matrix started through the sample preparation process (Section 12.0) on the same 12-hour shift, to a maximum of 10 samples). Analyze the blank immediately after analysis of the OPR (Section 9.7) to demonstrate freedom from contamination.

9.6.1.2 If the metal of interest or any potentially interfering substance is found in the blank at a concentration equal to or greater than the MDL (Table 1), sample analysis must be halted, the source of the contamination determined, the samples and a new method blank prepared, and the sample batch and fresh method blank reanalyzed.

9.6.1.3 Alternatively, if a sufficient number of blanks (three minimum) are analyzed to characterize the nature of a blank, the average concentration

plus two standard deviations must be less than the regulatory compliance level.

9.6.1.4 If the result for a single blank remains above the MDL or if the result for the average concentration plus two standard deviations of three or more blanks exceeds the regulatory compliance level, results for samples associated with those blanks may not be reported for regulatory compliance purposes. Stated another way, results for all initial precision and recovery tests (Section 9.2) and all samples must be associated with an uncontaminated method blank before these results may be reported for regulatory compliance purposes.

9.6.2 Field blank

9.6.2.1 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.

9.6.2.2 If the metal of interest 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, then results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.6.2.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

9.6.2.4 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 prior to the next sampling event.

9.6.3 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.

9.6.3.1 Bottle blanks—After undergoing appropriate cleaning procedures (Section 11.4), 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 pH<2 and allowed to stand for a minimum of 24 hours. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that 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 recleaned.

9.6.3.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's 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 sampler check blanks at the laboratory or cleaning facility.

9.6.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.2) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method). For 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 sampler into the water and pumping water into a sample container.

9.6.3.2.2 The sampler check blank must be analyzed using the procedures given in this method. If any metal of interest 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 the metal(s) of interest before the equipment may be used in the field.

9.6.3.2.3 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.

9.7 Ongoing Precision and Recovery

9.7.1 Prepare an ongoing precision and recovery sample (laboratory-fortified method blank) identical to the initial precision and recovery aliquots (Section 9.2) with each sample batch (samples of the same matrix started through the sample preparation process (Section 12.0) on the same 12-hour shift, to a maximum of 10 samples) by spiking an aliquot of reagent water with the metal(s) of interest.

9.7.2 Analyze the OPR sample before analyzing the method blank and samples from the same batch.

9.7.3 Compute the percent recovery of each metal in the OPR sample.

9.7.4 For each metal, compare the concentration to the limits for ongoing recovery in Table 2. If all metals meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual recovery falls outside of the range given, the analytical processes are not being performed properly for that metal. In this event, correct the problem, reprepare the sample batch, and repeat the ongoing precision and recovery test (Section 9.7).

9.7.5 Add results that pass the specifications in Section 9.7.4 to initial and previous ongoing data for each metal in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each metal in each matrix type by calculating the average percent recovery (R) and the standard deviation of 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%.

9.8 The specifications contained in this method can be met if the instrument used is calibrated properly and then maintained in a calibrated state. A given instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of metals by this method.

9.9 Depending on specific program requirements, the laboratory may be required to analyze field duplicates collected to determine the precision of the sampling technique. The relative percent difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, 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.

10.0 Calibration and Standardization

10.1 Operating Conditions—Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. The analyst is responsible for verifying that the instrument configuration and operating conditions satisfy the quality control requirements in this method. Table 7 lists instrument operating conditions that may be used as a guide for analysts in determining instrument configuration and operating conditions.

10.2 Precalibration Routine—The following precalibration routine should be completed before calibrating the instrument until it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.

10.2.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 minutes for the instrument to warm up. During this period, conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24, 25, 26. Resolution at high mass is indicated by lead isotopes 206, 207, 208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.2.2 Instrument stability must be demonstrated by running the tuning solution (Section 7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 10%.

10.3 Internal Standardization—Internal standardization must be used in all analyses to correct for instrument drift and physical interferences.

10.3.1 A list of acceptable internal standards is provided in Table 4. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application detail the use of five internal standards: scandium, yttrium, indium, terbium, and bismuth.

10.3.2 Internal standards must be present in all samples, standards, and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank, or sample solution (Method A), or alternatively by mixing with the solution before nebulization using a second channel of the peristaltic pump and a mixing coil (Method B).

10.3.3 The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 1-200 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples, and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

10.4 Calibration—Before initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated at a minimum of three points for each analyte to be determined.

10.4.1 Inject the calibration blank (Section 7.6.1) and calibration standards A and B (Section 7.4.1) prepared at three or more concentrations, one of which must be at the Minimum Level (Table 1), and another that must be near the upper end of the linear dynamic range. A minimum of three replicate integrations is required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

10.4.2 Compute the response factor at each concentration, as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where,

C_s = Concentration of the analyte in the standard or blank solution.
C_{is} = Concentration of the internal standard in the solution.
A_s = Height or area of the response at the m/z for the analyte.
A_{is} = Height or area of the m/z for the internal standard.

10.4.3 Using the individual response factors at each concentration, compute the mean RF for each analyte.

10.4.4 Linearity—If the RF over the calibration range is constant (<20% RSD), the RF can be assumed to be invariant and the mean RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s / A_{is}, vs. RF.

10.5 Calibration Verification—Immediately following calibration, an initial calibration verification should be performed. Adjustment of the instrument is performed until verification criteria are met. Only after these criteria are met may blanks and samples be analyzed.

10.5.1 Analyze the mid-point calibration standard (Section 10.4).

10.5.2 Compute the percent recovery of each metal using the mean RF or calibration curve obtained in the initial calibration.

10.5.3 For each metal, compare the recovery with the corresponding limit for calibration verification in Table 2. If all metals meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue using the response from the initial calibration. If any individual value falls outside the range given, system performance is unacceptable for that compound. In this event, locate and correct the problem and/or prepare a new calibration check standard and repeat the test (Sections 10.5.1 through 10.5.3), or recalibrate the system according to Section 10.4.

10.5.5 Calibration must be verified following every ten samples by analyzing the mid-point calibration standard. If the recovery does not meet the acceptance criteria specified in Table 2, analysis must be halted, the problem corrected, and the instrument recalibrated. All samples after the last acceptable calibration verification must be reanalyzed.

10.6 A calibration blank must be analyzed following every calibration verification to demonstrate that there is no carryover of the analytes of interest and that the analytical system is free from contamination. If the concentration of an analyte in the blank result exceeds the MDL, correct the problem, verify the calibration (Section 10.5), and repeat the analysis of the calibration blank.

11.0 Procedures for Cleaning the Apparatus

11.1 All sampling equipment, sample containers, and labware should be cleaned in a designated cleaning area that has been demonstrated to be free of trace element contaminants. Such areas may include class 100 clean rooms as described by Moody (Reference 22), labware cleaning areas as described by Patterson and Settle (Reference 6), or clean benches.

11.2 Materials, such as gloves (Section 6.9.7), storage bags (Section 6.9.10), and plastic wrap (Section 6.9.11), 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 an alternate supplier must be obtained or the materials must be cleaned.

11.3 Cleaning Procedures—Proper cleaning of the Apparatus is extremely important, because the Apparatus may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the container surface.

NOTE: *If laboratory, field, and equipment blanks (Section 9.6) from the Apparatus cleaned with fewer cleaning steps than those detailed below show no levels of analytes above the MDL, those cleaning steps that do not eliminate these artifacts may be omitted provided all performance criteria outlined in Section 9.0 are met.*

11.3.1 Bottles, labware, and sampling equipment

11.3.1.1 Fill a precleaned basin (Section 6.9.8) with a sufficient quantity of a 0.5% solution of liquid detergent (Section 6.7), and completely immerse each piece of ware. Allow to soak in the detergent for at least 30 minutes.

11.3.1.2 Using a pair of clean gloves (Section 6.9.7) and clean nonmetallic brushes (Section 6.9.9), thoroughly scrub down all materials with the detergent.

11.3.1.3 Place the scrubbed materials in a precleaned basin. Change gloves.

11.3.1.4 Thoroughly rinse the inside and outside of each piece with reagent water until there is no sign of detergent residue (e.g., until all soap bubbles disappear).

11.3.1.5 Change gloves, immerse the rinsed equipment in a hot (50-60°C) bath of concentrated reagent grade HNO_3 (Section 7.1.1) and allow to soak for at least two hours.

11.3.1.6 After soaking, use clean gloves and tongs to remove the Apparatus and thoroughly rinse with distilled, deionized water (Section 7.2).

11.3.1.7 Change gloves and immerse the Apparatus in a hot (50-60°C) bath of 1 N trace metal grade HCl (Section 7.1.7), and allow to soak for at least 48 hours.

11.3.1.8 Thoroughly rinse all equipment and bottles with reagent water. Proceed with Section 11.3.2 for labware and sampling equipment. Proceed with Section 11.3.3 for sample bottles.

11.3.2 Labware and sampling equipment

11.3.2.1 After cleaning, air-dry in a class 100 clean air bench.

11.3.2.2 After drying, wrap each piece of ware and equipment in two layers of polyethylene film.

11.3.3 Fluoropolymer sample bottles—These bottles should be used if mercury is a target analyte.

11.3.3.1 After cleaning, fill sample bottles with 0.1% (v/v) ultrapure HCl (Section 7.1.11) and cap tightly. It may be necessary to use a strap wrench to assure a tight seal.

11.3.3.2 After capping, double-bag each bottle in polyethylene zip-type bags. Store at room temperature until sample collection.

11.3.4 Bottles, labware, and sampling equipment—Polyethylene or material other than fluoropolymer.

11.3.4.1 Apply the steps outlined above in Sections 11.3.1.1 through 11.3.1.8 to all bottles, labware, and sampling equipment. Proceed with Section 11.3.4.2 for bottles or Section 11.3.4.3 for labware and sampling equipment.

11.3.4.2 After cleaning, fill each bottle with 0.1% (v/v) ultrapure HCl (Section 7.1.11). Double-bag each bottle in a polyethylene bag to prevent contamination of the surfaces with dust and dirt. Store at room temperature until sample collection.

11.3.4.3 After rinsing labware and sampling equipment, air-dry in a class 100 clean air bench. After drying, wrap each piece of ware and equipment in two layers of polyethylene film.

NOTE: *Polyethylene bottles cannot be used to collect samples that will be analyzed for mercury at trace (e.g., 0.012 µg/L) levels because of the potential of vapors diffusing through the polyethylene.*

11.3.4.4 Polyethylene bags—If polyethylene bags need to be cleaned, clean according to the following procedure:

11.3.4.4.1 Partially fill with cold, (1+1) HNO_3 (Section 7.1.2) and rinse with distilled deionized water (Section 7.2).

11.3.4.4.2 Dry by hanging upside down from a plastic line with a plastic clip.

11.3.5 Silicone tubing, fluoropolymer tubing, and other sampling apparatus—Clean any silicone, fluoropolymer, or other tubing used to collect samples by rinsing with 10% HCl (Section 7.1.8) and flushing with water from the site before sample collection.

11.3.6 Extension pole—Because of its length, it is impractical to submerse the 2 m polyethylene extension pole (used in with the optional grab sampling device) in acid solutions as described above. If such an extension pole is used, a nonmetallic brush (Section 6.9.9) should be used to scrub the pole with reagent water and the pole wiped down with acids described in Section 11.3.4 above. After cleaning, the pole should be wrapped in polyethylene film.

11.4 Storage—Store each piece or assembly of the Apparatus in a clean, single polyethylene zip-type bag. If shipment is required, place the bagged apparatus in a second polyethylene zip-type bag.

11.5 All cleaning solutions and acid baths should be periodically monitored for accumulation of metals that could lead to contamination. When levels of metals in the solutions become too high, the solutions and baths should be changed and the old solutions neutralized and discarded in compliance with state and federal regulations.

12.0 Procedures for Sample Preparation and Analysis

12.1 Aqueous Sample Preparation—Dissolved analytes.

12.1.1 For determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥20 mL) of the filtered, acid-preserved sample into a clean 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Add the internal standards, cap the tube, and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

12.2 Aqueous Sample Preparation—Total recoverable analytes.

NOTE: *To preclude contamination during sample digestion, it may be necessary to perform the open beaker, total-recoverable digestion procedure described in Sections 12.2.1 through 12.2.7 in a fume hood that is located in a clean room. An alternate digestion procedure is provided in Section 12.2.8; however, this procedure has not undergone interlaboratory testing.*

12.2.1 For the determination of total recoverable analytes in ambient water samples, transfer a 100 mL (±1 mL) aliquot from a well-mixed, acid-preserved sample to a 250 mL Griffin beaker (Section 6.9.3). If appropriate, a smaller sample volume may be used.

12.2.2 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker and place the beaker on the hot plate for digestion. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The beaker should be covered or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

NOTE: *For proper heating, adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass, the temperature of the water will rise to approximately 95°C.)*

12.2.3 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. Do not boil. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

12.2.4 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope.)

12.2.5 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask or 50 mL class A stoppered graduated cylinder, make to volume with reagent water, stopper, and mix.

12.2.6 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If, after centrifuging or standing overnight, the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered to remove the solids before analysis. However, care should be exercised to avoid potential contamination from filtration.)

12.2.7 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 50 mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones.) Add the internal standards and mix. The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

12.2.8 Alternate total recoverable digestion procedure.

12.2.8.1 Open the preserved sample under clean conditions. Add ultrapure nitric and hydrochloric acid at the rate of 10 mL/L and 5 mL/L, respectively. Remove the cap from the original container only long enough to add each aliquot of acid. The sample container should not be filled to the lip by the addition of the acids. However, only minimal headspace is needed to avoid leakage during heating.

12.2.8.2 Tightly recap the container and shake thoroughly. Place the container in an oven preheated to 85°C. The container should be placed on an insulating piece of material such as wood rather than directly on the typical metal grating. After the samples have reached 85°C, heat for two hours. (Total time will be two and one-half to three hours depending on the sample size). Temperature can be monitored using an identical sample container with distilled water and a thermocouple to standardize heating time.

12.2.8.3 Allow the sample to cool. Add the internal standards and mix. The sample is now ready for analysis. Remove aliquots for analysis under clean conditions.

12.3 Sample Analysis

12.3.1 For every new or unusual matrix, it is highly recommended that a semiquantitative analysis be carried out to screen the sample for elements that may be present at high concentration. Information gained from this screening may be used to prevent potential damage to the detector during sample analysis

and to identify elements that may exceed the linear range. Matrix screening may be carried out using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semiquantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards to prevent bias in the calculation of the analytical data.

12.3.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (Section 10.0).

12.3.3 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations is required for data acquisition. Use the average of the integrations for data reporting.

12.3.4 All m/z's that may affect data quality must be monitored during the analytical run. As a minimum, those m/z's prescribed in Table 5 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

12.3.5 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for 30 seconds before data is collected.

12.3.6 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, if quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

13.0 Data Analysis and Calculations

13.1 Table 6 lists elemental equations recommended for sample data calculations. Sample data should be reported in units of µg/L (parts-per-billion; ppb). Report results at or above the ML for metals found in samples and determined in standards. Report all results for metals found in blanks, regardless of level.

13.2 For data values less than the ML, two significant figures should be used for reporting element concentrations. For data values greater than or equal to the ML, three significant figures should be used.

13.3 For aqueous samples prepared by total recoverable procedure (Sections 12.2.1 through 12.2.7), multiply solution concentrations by the dilution factor 1.25. If additional dilutions were made to any samples, the appropriate factor should be applied to the calculated sample concentrations.

13.4 Compute the concentration of each analyte in the sample using the response factor determined from calibration data (Section 10.4) and the following equation:

$$C_s\ (\mu g/L) = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

where,

The terms are as defined in Section 10.4.2.

13.5 Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, because the chloride ion is a common constituent of environmental samples.

13.6 If an element has more than one monitored m/z, examination of the concentration calculated for each m/z, or the relative abundances, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary m/z's in the evaluation of the element concentration. In some cases, the secondary m/z may be less sensitive or more prone to interferences than the primary recommended m/z; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary m/z.

13.7 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.8 Do not perform blank subtraction on the sample results. Report results for samples and accompanying blanks.

14.0 Method Performance

14.1 The method detection limits (MDLs) listed in Table 1 and the quality control acceptance criteria listed in Table 2 were validated in two laboratories (Reference 23) for dissolved analytes.

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The 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 their waste generation. When wastes cannot be feasibly reduced 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 volume of expired standards to be disposed.

15.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *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, 202/872-4477.

16.0 Waste Management

16.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 15.2.

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18.0 Glossary

Many of the terms and definitions listed below are used in the EPA 1600-series methods, but terms have been cross-referenced to terms commonly used in other methods where possible.

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

18.2 Analyte—A metal tested for by the methods referenced in this method. The analytes are listed in Table 1.

18.3 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.

18.4 Calibration Blank—A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument (Section 7.6.1).

18.5 Calibration Standard (CAL)—A solution prepared from a dilute mixed standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

18.6 Dissolved Analyte—The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 8.3).

18.7 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. In addition, equipment blanks should be run on random, representative sets of gloves, storage bags, and plastic wrap for each lot to determine if these materials are free from contamination before use.

18.8 Field Blank—An aliquot of reagent water that 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, storage, preservation, and all analytical procedures, which may include filtration. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

18.9 Field Duplicates (FD1 and FD2)—Two separate samples collected in separate sample bottles at the same time and place under identical circumstances 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.

18.10 Initial Precision and Recovery (IPR)—Four aliquots of the OPR standard analyzed to establish the ability to generate acceptable precision and accuracy. IPRs are performed

before a method is used for the first time and any time the method or instrumentation is modified.

18.11 Instrument Detection Limit (IDL)—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the selected analytical mass(es).

18.12 Internal Standard—Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Sections 7.5 and 9.5).

18.13 Laboratory Blank—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if method analytes or interferences are present in the laboratory environment, the reagents, or the apparatus (Sections 7.6.2 and 9.6.1).

18.14 Laboratory Control Sample (LCS)—See Ongoing Precision and Recovery (OPR) Standard.

18.15 Laboratory Duplicates (LD1 and LD2)—Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

18.16 Laboratory Fortified Blank (LFB)—See Ongoing Precision and Recovery (OPR) Standard.

18.17 Laboratory Fortified Sample Matrix (LFM)—See Matrix Spike (MS) and Matrix Spike duplicate (MSD).

18.18 Laboratory Reagent Blank (LRB)—See Laboratory Blank.

18.19 Linear Dynamic Range (LDR)—The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

18.20 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the method 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 (Section 9.3).

18.21 m/z—Mass-to-charge ratio.

18.22 May—This action, activity, or procedural step is optional.

18.23 May Not—This action, activity, or procedural step is prohibited.

18.24 Method Blank—See Laboratory Blank.

18.25 Method Detection Limit (MDL)—The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Section 9.2.1 and Table 1).

18.26 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 9).

18.27 Must—This action, activity, or procedural step is required.

18.28 Ongoing Precision and Recovery (OPR) Standard—A laboratory blank spiked with known quantities of the method analytes. The OPR is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and to assure that the results produced by the laboratory remain within the method-specified limits for precision and accuracy (Sections 7.9 and 9.7).

18.29 Preparation Blank—See Laboratory Blank.

18.30 Primary Dilution Standard—A solution containing the analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

18.31 Quality Control Sample (QCS)—A sample containing all or a subset of the method analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

18.32 Reagent Water—Water demonstrated to be free from the method analytes and potentially interfering substances at the MDL for that metal in the method.

18.33 Should—This action, activity, or procedural step is suggested but not required.

18.34 Stock Standard Solution—A solution containing one or more method analytes that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

18.35 Total Recoverable Analyte—The concentration of analyte determined by analysis of the solution extract of an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Section 12.2).

18.36 Tuning Solution—A solution which is used to determine acceptable instrument performance before calibration and sample analyses (Section 7.7).

TABLE 1. LIST OF ANALYTES AMENABLE TO ANALYSIS USING METHOD 1638: LOWEST WATER QUALITY CRITERION FOR EACH METAL SPECIES, METHOD DETECTION LIMITS, MINIMUM LEVELS, AND RECOMMENDED ANALYTICAL M/Z's

Metal	Lowest Ambient Water Quality Criterion (µg/L) [1]	Method Detection Limit (MDL) and Minimum Level (ML); µg/L		Recommended Analytical m/z
		MDL [2]	ML [3]	
Antimony	14	0.0097	0.02	123
Cadmium	0.37	0.025	0.1	111
Copper	2.4	0.087	0.2	63
Lead	0.54	0.015	0.05	206, 207, 208
Nickel	8.2	0.33	1	60
Selenium	5	0.45	1	82
Silver	0.32	0.029	0.1	107
Thallium	1.7	0.0079	0.02	205
Zinc	32	0.14	0.5	66

[1] Lowest of the freshwater, marine, or human health WQC promulgated by EPA for 14 states at 40 *CFR* Part 131 (57 *FR* 60848), with hardness-dependent freshwater aquatic life criteria adjusted in accordance with 57 *FR* 60848 to reflect the worst case hardness of 25 mg/L $CaCO_3$ and all aquatic life criteria adjusted in accordance with the 10/1/93 Office of Water guidance to reflect dissolved metals criteria.

[2] Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.

[3] Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, etc. in accordance with procedures used by EAD and described in EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels,* March 22, 1994.

TABLE 2. QUALITY CONTROL ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS IN EPA METHOD 1638[1]

Metal	Initial Precision and Recovery (Section 9.2) s	Initial Precision and Recovery (Section 9.2) X	Calibration Verification (Section 10.5)	Ongoing Precision and Recovery (Section 9.7)	Spike Recovery (Section 9.3)
Antimony	20	81–120	90–111	79–122	79–122
Cadmium	13	85–112	91–105	84–113	84–113
Copper	43	55–141	76–120	51–145	51–145
Lead	30	75–140	91–120	72–143	72–143
Nickel	30	71–131	86–116	68–134	68–134
Selenium	41	63–145	69–127	59–149	59–149
Silver	19	82–120	81–107	74–119	74–119
Thallium	30	66–134	82–118	64–137	64–137
Zinc	43	55–142	76–121	46–146	46–146

[1]All specification expressed as percent.

TABLE 3. COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS		
Molecular Ion	**m/z**	**Element Interference**
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+,ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se

[a]Elements or internal standards affected by the molecular ions.

TABLE 3. COMMON MOLECULAR ION INTERFERENCES IN ICP-MS (Continued)

MATRIX MOLECULAR IONS

BROMIDE (Reference 24)

Molecular Ion	m/z	Element Interference
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	98	Mo
$Ar^{81}Br^+$	121	Sb

CHLORIDE

Molecular Ion	m/z	Element Interference
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se

SULFATE

Molecular Ion	m/z	Element Interference
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V,Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	

PHOSPHATE

Molecular Ion	m/z	Element Interference
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	

TABLE 3. COMMON MOLECULAR ION INTERFERENCES IN ICP-MS (Continued)

GROUP I, II METALS **Molecular Ion**	**m/z**	**Element Interference**
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	
MATRIX OXIDES* **Molecular Ion**	**m/z**	**Element Interference**
TiO	62-66	Ni,Cu,Zn
ZrO	106-112	Ag,Cd
MoO	108-116	Cd

*Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides of which the analyst should be aware are listed.

TABLE 4. INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	**m/z**	**Possible Limitation**
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

[a]May be present in environmental samples.
[b]In some instruments, yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

***NOTE**: Internal standards recommended for use with this method are shown in boldface. Preparation procedures for these are included in Section 7.3.*

TABLE 5. RECOMMENDED ISOTOPES AND ADDITIONAL M/Z'S THAT MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121,123	Antimony
75	Arsenic
135,137	Barium
9	Beryllium
106,108,111,114	Cadmium
52,53	Chromium
59	Cobalt
63,65	Copper
206,207,208	Lead
55	Manganese
95,97,98	Molybdenum
60,62	Nickel
77,82	Selenium
107,109	Silver
203,205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66,67,68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

***NOTE**: Isotopes recommended for analytical determination are underlined.*

TABLE 6. RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Sb	$(1.000)(^{123}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(1)
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(2)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(3)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Zn	$(1.000)(^{66}C)$	

INTERNAL STANDARDS

Element	Elemental Equation	Note
Bi	$(1.000)(^{209}C)$	
In	$(1.000)(^{115}C)-(0.016)(^{118}C)$	(4)
Sc	$(1.000)(^{45}C)$	
Tb	$(1.000)(^{159}C)$	
Y	$(1.000)(^{89}C)$	

C = Counts at specified m/z.

(1) Correction for MoO interference. M/z 106 must be from Cd only, not $Zr^{+}O$. An additional correction should be made if palladium is present.

(2) Allowance for variability of lead isotopes.

(3) Some argon supplies contain krypton as an impurity. Selenium is corrected for ^{82}Kr by background subtraction.

(4) Correction for tin.

TABLE 7. RECOMMENDED INSTRUMENT OPERATING CONDITION

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15°C
Data Acquisition	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8–240 amu
Dwell time	320 µs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 minutes per sample

METHOD 9056A

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of chloride (Cl^-), fluoride (F^-), bromide (Br^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}) anions in aqueous samples, such as drinking water, wastewater, aqueous extracts of solids, and the collection solutions from the bomb combustion of solid waste samples (Method 5050).

1.2 The lower limit of quantitation (LLOQ), the lowest concentration level that can be measured within stated accuracy limits, varies for each individual analyte anion and as a function of sample size.

1.3 Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1. Dilution of samples may allow higher concentration samples to be analyzed.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A small volume of aqueous sample is injected into an ion chromatograph to flush and fill a constant-volume sample loop. The sample is then injected into a flowing stream of carbonate-bicarbonate eluent.

2.2 The sample is pumped through two different ion exchange columns, then a conductivity suppressor device, and into a conductivity detector. The two ion exchange columns, a precolumn or guard column and a separator column, are packed with an anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The conductivity suppressor is an ion exchange-based device that reduces the background conductivity of the eluent to a low or negligible level and simultaneously converts the anions in the sample to their more conductive acid forms. The separated anions in their acid forms are measured using an electrical conductivity cell. Anion identification is based on the comparison of analyte signal peak retention times relative to those of known standards. Quantitation is accomplished by measuring the peak area and comparing it to a calibration curve generated from known standards.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Any species with a retention time similar to that of the desired anion will interfere. Large quantities of ions eluting close to the anion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the method of standard additions can also be used. For example, high levels of organic acids that may interfere with inorganic anion analysis may be present in industrial wastes. Two common species, formate and acetate, elute between fluoride and chloride.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100 times more concentrated than the solution described in Sec. 7.3) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in ion chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks (Sec. 9.3.1). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to Chapter Three for general guidance on the cleaning of glassware.

4.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems. The associated method blanks must also be filtered if any samples or reagents have undergone filtration.

4.5 The acetate, formate, and other monovalent organic acid anion elute early in the chromatographic run and can interfere with fluoride. The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Ion chromatograph -- Capable of delivering 1 to 5 mL of eluent per min at a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa). The chromatograph must be equipped with an injection valve, a 25- to 100-µL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

6.1.1 Precolumn -- A guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents. An example of a suitable column is the Dionex IonPac® AG4A-SC, or equivalent.

6.1.2 Separator (or analytical) column -- A column packed with an anion exchange resin, suitable for resolving F^-, Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}. An example of a suitable column is the Dionex IonPac® AS4A-SC, or equivalent.

6.1.3 Conductivity suppressor -- An ion exchange-based device that is capable of converting the eluent and separated anions to their respective acid forms. Examples of suitable suppressors include the Dionex AMMS-II or ASRS Ultra, or equivalent.

6.1.4 Conductivity detector -- A low-volume, flow-through, temperature-compensated, electrical conductivity cell (approximately 1.25-µL volume), equipped with a meter capable of reading from 0 to 1,000 Siemens/cm on a linear scale. An example of a suitable conductivity detector is the Dionex CD20 or equivalent.

6.1.5 Pump -- Capable of delivering a constant flow of approximately 1 to 5 mL/min throughout the test and tolerating a pressure of 1000 to 4000 psi (6.5 to 27.5 MPa).

6.2 Syringe -- Minimum capacity of 1 mL, equipped with a male pressure fitting.

6.3 Appropriate chromatographic data and control software to acquire data. Dionex PeakNet was used to record and process the chromatogram shown in Figure 2. Alternatively, an integrator or recorder can be used to integrate the area under the chromatographic peaks. If an integrator is used, the maximum area measurement must be within the linear range of the integrator. The recorder should be compatible with the detector output with a full-scale response time of 2 seconds or less.

6.4 Analytical balance -- Capable of weighing to the nearest 0.0001 g.

6.5 Pipets, Class A volumetric flasks, beakers -- Assorted sizes.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- All references to water in this method refer to reagent water, as defined in Chapter One.

7.3 Eluent, 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 -- Dissolve 0.2856 g of sodium bicarbonate (1.7 mM $NaHCO_3$) and 0.3816 g of sodium carbonate (1.8 mM Na_2CO_3) in reagent water and dilute to 2 L with reagent water or follow manufacturer's guidance for the proper eluent for each specific column.

7.4 Conductivity suppressor regenerant solution (25 mM H_2SO_4), if required -- Add 2.8 mL of concentrated sulfuric acid (H_2SO_4) to 4 L of reagent water.

7.5 Stock solutions (1,000 mg/L) -- Certified standards may also be purchased and used as stock solutions. Stock solutions are stable for at least 1 month when stored at #6 EC.

7.5.1 Bromide stock solution (1.00 mL = 1.00 mg of BrG) -- Dry approximately 2 g of sodium bromide (NaBr) for 6 hr at 150 °C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.2 Chloride stock solution (1.00 mL = 1.00 mg of ClG) -- Dry sodium chloride (NaCl) for 1 hr at 600 °C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.3 Fluoride stock solution (1.00 mL = 1.00 mg of FG) -- Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a chemical-resistant glass or polyethylene container.

7.5.4 Nitrate stock solution (1.00 mL = 1.00 mg of NO_3G) -- Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105 °C for 24 hr. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.5 Nitrite stock solution (1.00 mL = 1.00 mg of NO_2G) -- Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hr) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating them for 1 hr at 170 °C in an air oven.

7.5.6 Phosphate stock solution (1.00 mL = 1.00 mg of PO_4^{3}G) -- Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.5.7 Sulfate stock solution (1.00 mL = 1.00 mg of SO_4^{2}G) -- Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water in a Class A volumetric flask.

7.6 Anion calibration standards

Prepare a blank and at least three combination anion calibration standards containing the anions of interest. The combination anion solutions must be prepared in Class A volumetric flasks (see Table 2). Calibration standards should be prepared weekly, except for those that contain nitrite and phosphate, which should be prepared fresh daily. The validity of standards can be confirmed through the analysis of a freshly prepared ICV (Sec. 10.6).

7.6.1 Prepare the high-range calibration standard solution by combining the volumes of each anion stock solution specified in Sec. 7.5 in a Class A volumetric flask and diluting the mixture to 1 L with reagent water.

7.6.2 Prepare the intermediate-range calibration standard solution by diluting 10.0 mL of the high-range calibration standard solution (Sec. 7.6.1) to 100 mL with reagent water.

7.6.3 Prepare the low-range calibration standard solution by diluting 20.0 mL of the intermediate-range calibration standard solution (Sec. 7.6.2) to 100 mL with reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 Preserve samples at #6 EC. If nitrite, nitrate and phosphate are analytes of interest, samples should be analyzed within 48 hr of collection. A longer holding time may be appropriate for chloride, fluoride, sulfate and bromide.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with the sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish an initial demonstration of proficiency.

9.3 Sample quality control for preparation and analysis.

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, the laboratory should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch. Any method blanks, matrix spike samples, replicate samples and LCSs should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch.

9.3.1 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These

blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank. Refer to Chapter One for the proper protocol when analyzing blanks.

9.3.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses, or set by the method quality objectives (MQOs)/data quality objectives (DQOs) of the project. In the absence of historical data or well-defined MQOs/DQOs, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data must be no wider that ± 20%. Consult Method 8000 for further information on developing acceptance criteria for the LCS. When the result of a matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS result is used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS result is not acceptable, then the LCS must be reanalyzed once. If the results are still unacceptable, then all samples analyzed after the last acceptable LCS must be reprepared and reanalyzed.

9.3.3 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

9.3.3.1 At least one matrix spike (MS) sample should be analyzed within each analysis batch for determining method bias and/or sample matrix effects. The MS percent recovery (%R) is calculated as follows:

$$\%R = \frac{\left(MSSR - SR \right)}{SA} \times 100$$

Where:
MSSR = MS Sample Result
SR = Sample Result
SA = Spike Added

When the sample concentration is less than the LLOQ, use SR = 0 for purposes of calculating %R.

9.3.3.2 The method control limits for %R are 80 - 120. Alternate limits may be used provided that they meet the data quality objectives of the specific

project. Failure to meet the MS %R criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem. If %R is outside the control limits and all other QC data is within limits, a matrix effect is suspected. The associated data should be flagged according to project specifications or noted in the comments section of the report.

9.3.3.3 A duplicate or matrix spike duplicate (MSD) should be analyzed within every analytical batch in order to establish the precision of the method. Calculate the relative percent difference (RPD) between the sample and duplicate result as follows.

$$RPD = \frac{|S - D|}{(S - D)/2} \times 100$$

Where:

RPD	=	Relative Percent Difference
S	=	Sample or MS Sample Result
D	=	Duplicate or MSD Result

9.3.3.4 The method control limit for RPD is 15% for all sample concentrations that are near or above the mid-range of the calibration curve. The method control limit for RPD is 50% for sample concentrations that are near the low-range of the calibration curve. Alternate limits may be used provided that they meet the data quality objectives of the specific project. Failure to meet the duplicate RPD criteria indicates potential problems with the analytical system and/or sample matrix effects and corrective action should be taken to investigate and resolve the problem.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1, or as recommended by the manufacturer.

10.2 For each analyte of interest, prepare a blank and calibration standards at a minimum of three concentrations by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. A sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration at or below the laboratory's lower limit of quantitation (LLOQ). The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector.

10.3 The laboratory should establish the LLOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard prepared at the LLOQ concentration levels or use of the LLOQs as the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LLOQ recoveries must be within 50% of the true values to verify the data reporting limit.

10.4 After a stable baseline is obtained (approximately 30 min), begin to inject standards starting with the lowest concentration standard and increasing in concentration to the highest standard. Use a fixed injection volume between 25 and 100 µL (determined by injection loop volume) for each calibration standard. Record the peak area responses and retention times for each analyte.

10.5 Establish the individual analyte calibration curves by plotting the peak area responses for each standard against the corresponding concentrations. Use a least squares-linear regression to calculate the calibration curve formula. The linear correlation coefficient should be equal to or greater than 0.995. A weighted least squares regression may also be performed using 1/concentration or $1/(\text{concentration})^2$ as the weighting factor. The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher. Refer to Method 8000 for additional guidance on calibration procedures.

10.6 Verify the accuracy of the initial calibration curve by analyzing an initial calibration verification (ICV) standard. The ICV standard must be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for the ICV standard must be no greater than ± 10% of its true value. If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed. The analysis data for the ICV must be kept on file with the sample analysis data.

10.7 Verify the accuracy of the working calibration curve on each working day, or whenever the anion eluent composition or strength is changed, and for every batch of 10 or less samples, through the analysis of a continuing calibration verification (CCV) standard. The CCV should be made from the same material as the initial calibration standards at or near mid-range. The acceptance criteria for the CCV standard should be ± 10% of its true value for the calibration to be considered valid. If the CCV standard result does not meet the acceptance criterion, sample analysis must be discontinued, the cause determined, and the instrument recalibrated. All samples analyzed after the last acceptable CCV should be reanalyzed. The analysis data for the CCV should be kept on file with the sample analysis data.

10.8 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading should not exceed approximately 500 ppm total anions when using a 50-µL sample loop and the columns listed in Sec. 6.1.

11.0 PROCEDURE

11.1 Sample preparation

When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. In combustate samples generated by bomb combustion (Method 5050), the water dip should not be observed, since the collecting solution is a concentrated eluent solution that will be equivalent to the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to all samples and standards such that the final sample/standard solution is equivalent to the eluent concentration. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedure follows:

11.1.1 Prepare a 100-mL stock of eluent 100 times a normal concentration by dissolving 1.428 g of $NaHCO_3$ and 1.908 g of Na_2CO_3 in 100 mL of reagent water or use

the manufacturer's specified eluent. Cover or seal the volumetric flask.

11.1.2 Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 mL of the concentrated buffer into the beaker and stir well.

11.1.3 Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

11.2 Sample analysis

11.2.1 Establish ion chromatographic operating parameters exactly equivalent to those used for calibration (Sec. 10.0). Establish a stable baseline. This should take approximately 30 min.

11.2.2 Establish a valid initial calibration or otherwise verify the working calibration curve as outlined in Sec.10.0.

11.2.3 Inject a suitable volume of sample or QC standard into the IC instrument. Use an injection volume that is optimal for the specific analytical column and instrument system. The volume of sample injected must be consistent with that used for calibration (Sec. 10.0). Record the resulting analyte peak sizes in area units as well as the peak retention times.

11.2.4 For each sample or QC standard, identify each analyte by comparing the peak retention time to the established retention time window. The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day, and may include concentrations from both ends of the calibration range. Three times the standard deviation of a retention time may be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.2.5 If the peak area response exceeds the working calibration range, then dilute the sample with an appropriate amount of reagent water or eluent and reanalyze.

11.2.6 If the resulting chromatogram for a particular sample fails to produce adequate resolution such that the identification of the anion of interest is questionable, prepare a new sample spiked with a known amount of the anion under question and reanalyze in order to confirm the presence or absence of analyte.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Using the established calibration curve, compute the concentration of each analyte in each analysis sample or QC standard based on the peak area response. Most chromatography data analysis software systems perform such calculations automatically.

12.2 Calculate the concentration of analyte in the original sample as follows:

$$\text{Final result (mg/L)} = (C)(D)$$

Where:
C = Concentration from calibration curve (mg/L)
D = Dilution factor (if needed)

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Examples of single-operator accuracy and precision values for reagent, drinking, and surface water, and mixed domestic and industrial waste water are listed in Table 3. See EPA Method 300.0 for examples of multiple laboratory determinations of bias for the analytes using an IonPac AS4A column, bicarbonate/carbonate eluent, AMMS suppressor and conductivity detection (see Ref. 1). These data are provided for guidance purposes only.

13.3 Combustate samples

Tables 4 and 5 are based on 41 data points obtained by six laboratories, in which each laboratory analyzed four used crankcase oils and three blends of fuel oil with crankcase oil. Each analysis was performed in duplicate. The oil samples were combusted using Method 5050. Each point represents the duplicate analyses of a sample. One point was judged to be an outlier and was not included in the results. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The 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 their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 The quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions consult *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 St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly

the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA Method 300.0, "Determination of Inorganic Anions by Ion Chromatography," EPA-600/R-93-100, August 1993.

2. Annual Book of ASTM Standards, Volume 11.01 Water, "Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography," D 4327-97, 1998.

3. Standard Methods for the Examination of Water and Wastewater, Method 4110, "Determination of Anions by Ion Chromatography," 18th Edition of Standard Methods, 1992.

4. Dionex, DX-500 System Operation and Maintenance Manual, Dionex Corp., Sunnyvale, CA 94086, 1996.

5. A. Gaskill, E. D. Estes, D. L. Hardison, and L. E. Myers, "Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels," prepared for U.S. Environmental Protection Agency Office of Solid Waste, EPA Contract No. 68-01-7075, WA 80, July 1988.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE CHROMATOGRAPHIC CONDITIONS AND
RETENTION TIMES IN REAGENT WATER

Chromatographic Conditions	
Columns	See Secs. 6.1.1-6.1.2
Conductivity suppressor	See Sec. 6.1.3
Conductivity detector	See Sec. 6.1.4
Eluent	See Sec. 7.3
Sample loop	50 µL
Pump flow rate	2.0 mL/min

Analyte	Concentration of Mixed Standard (mg/L)	Retention Time (min)[a]
Fluoride	2.0	1.2
Chloride	3.0	1.7
Nitrite-N	2.0	2.0
Nitrate-N	5.0	3.2
o-Phosphate-P	2.0	5.4
Sulfate	15.0	6.9

[a]The retention time given for each anion is based on the equipment and analytical conditions described in the method. Use of other analytical columns or different eluent concentrations will affect retention times accordingly.

Data are taken from Ref. 1 and are provided for guidance purposes only.

TABLE 2

EXAMPLE STANDARD SOLUTIONS
FOR INSTRUMENT CALIBRATION

Analyte	Volume of Stock Solution (in mL) used to prepare High-Range Standard[1]	Concentration in mg/L		
		High-Range Standard	Intermediate-Range Standard	Low-Range Standard
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1]Volumes of each stock solution (1.00 mL = 1.00 mg) that are combined in a Class A volumetric flask and diluted to 1 L to prepare the high-range calibration standard (refer to Sec. 7.5). These data are provided for guidance purposes only.

TABLE 3

EXAMPLE SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample Type	Spike (mg/L)	Mean Recovery (%)	Std. Dev. (mg/L)
Chloride	RW	0.050	97.7	0.0047
	DW	10.0	98.2	0.289
	SW	1.0	105.0	0.139
	WW	7.5	82.7	0.445
Fluoride	RW	0.24	103.1	0.0009
	DW	9.3	87.7	0.075
	SW	0.50	74.0	0.0038
	WW	1.0	92.0	0.011
Nitrate-N	RW	0.10	100.9	0.0041
	DW	31.0	100.7	0.356
	SW	0.50	100.0	0.0058
	WW	4.0	94.3	0.058
Nitrite-N	RW	0.10	97.7	0.0014
	DW	19.6	103.3	0.150
	SW	0.51	88.2	0.0053
	WW	0.52	100.0	0.018
o-Phosphate-P	RW	0.50	100.4	0.019
	DE	45.7	102.5	0.386
	SW	0.51	94.1	0.020
	WW	4.0	97.3	0.04
Sulfate	RW	1.02	102.1	0.066
	DW	98.5	104.3	1.475
	SW	10.0	111.6	0.709
	WW	12.5	134.9	0.466

All data are taken from Ref. 1 and are based on the analyses of seven replicates. These data are provided for guidance purposes only.

RW = Reagent water
DW = Drinking water
SW = Surface water
WW = Waste water

TABLE 4

EXAMPLE REPEATABILITY AND REPRODUCIBILITY DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Average Value (µg/g)	Repeatability (µg/g)	Reproducibility (µg/g)
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

Data are taken from Ref. 5 and are provided for guidance purposes only.

TABLE 5

EXAMPLE RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY ANALYSIS

Amount Expected (µg/g)	Amount Found (µg/g)	Bias (µg/g)	Bias (%)
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

Data are taken from Ref. 5 and are provided for guidance purposes only.

FIGURE 1

SCHEMATIC OF ION CHROMATOGRAPHY INSTRUMENTATION

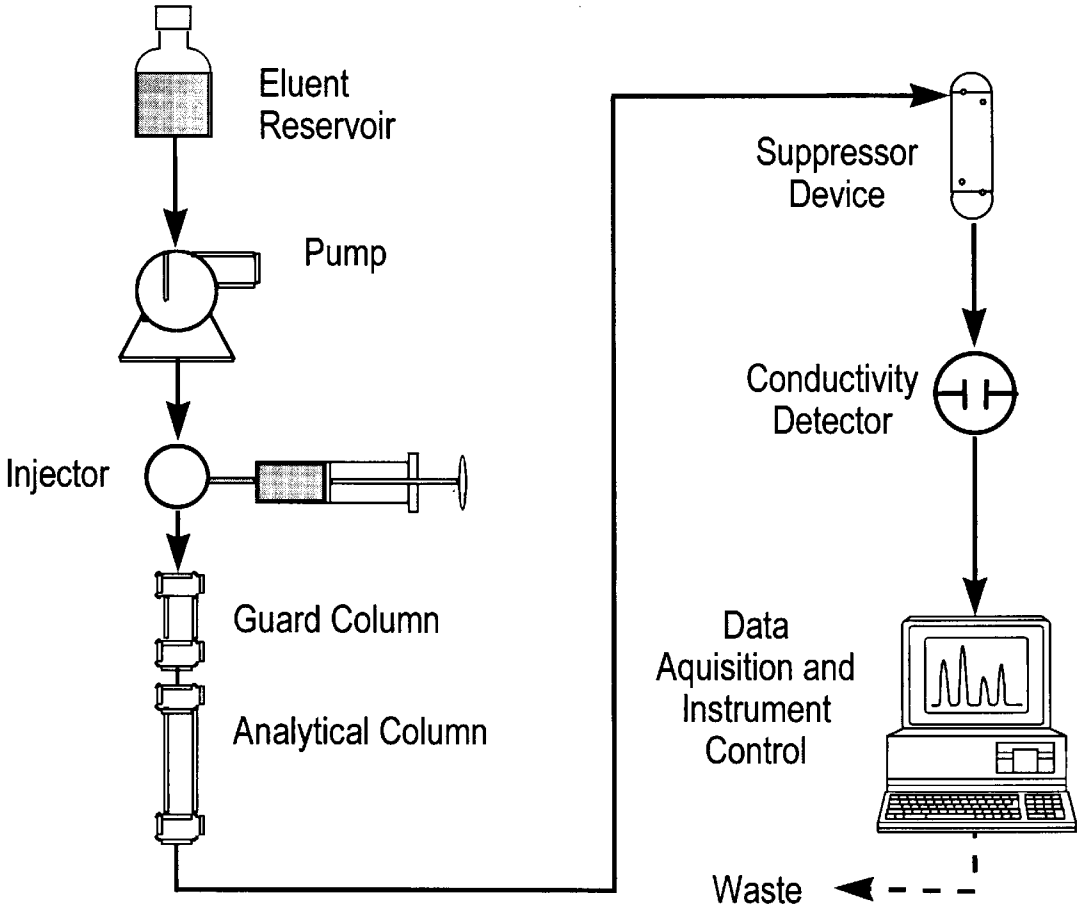
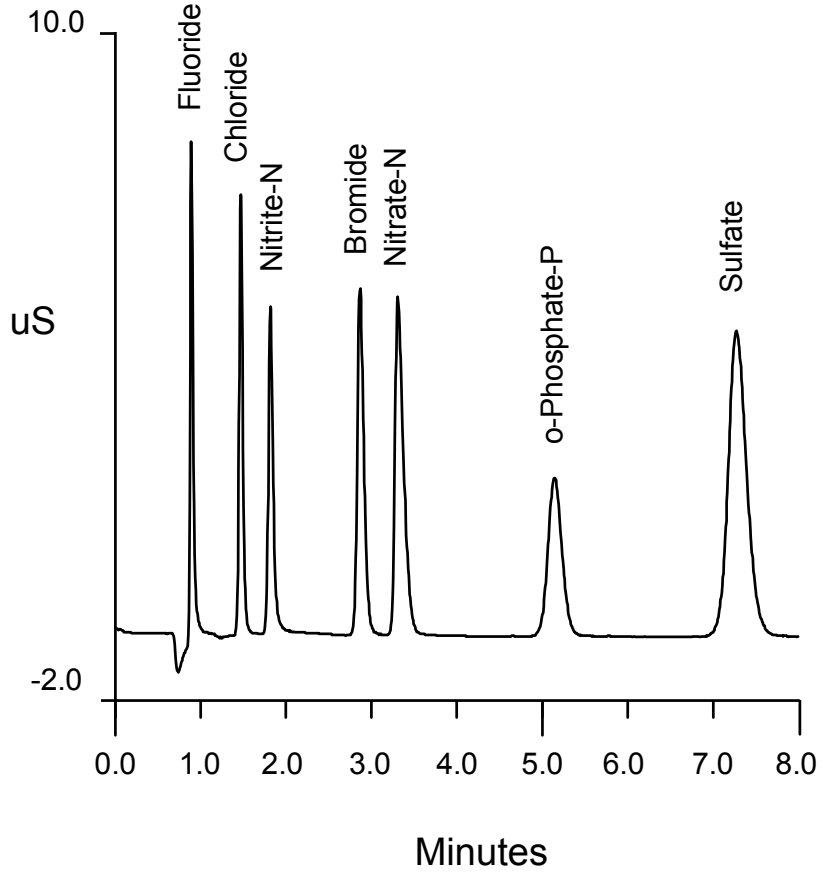


FIGURE 2

EXAMPLE ANION PROFILE



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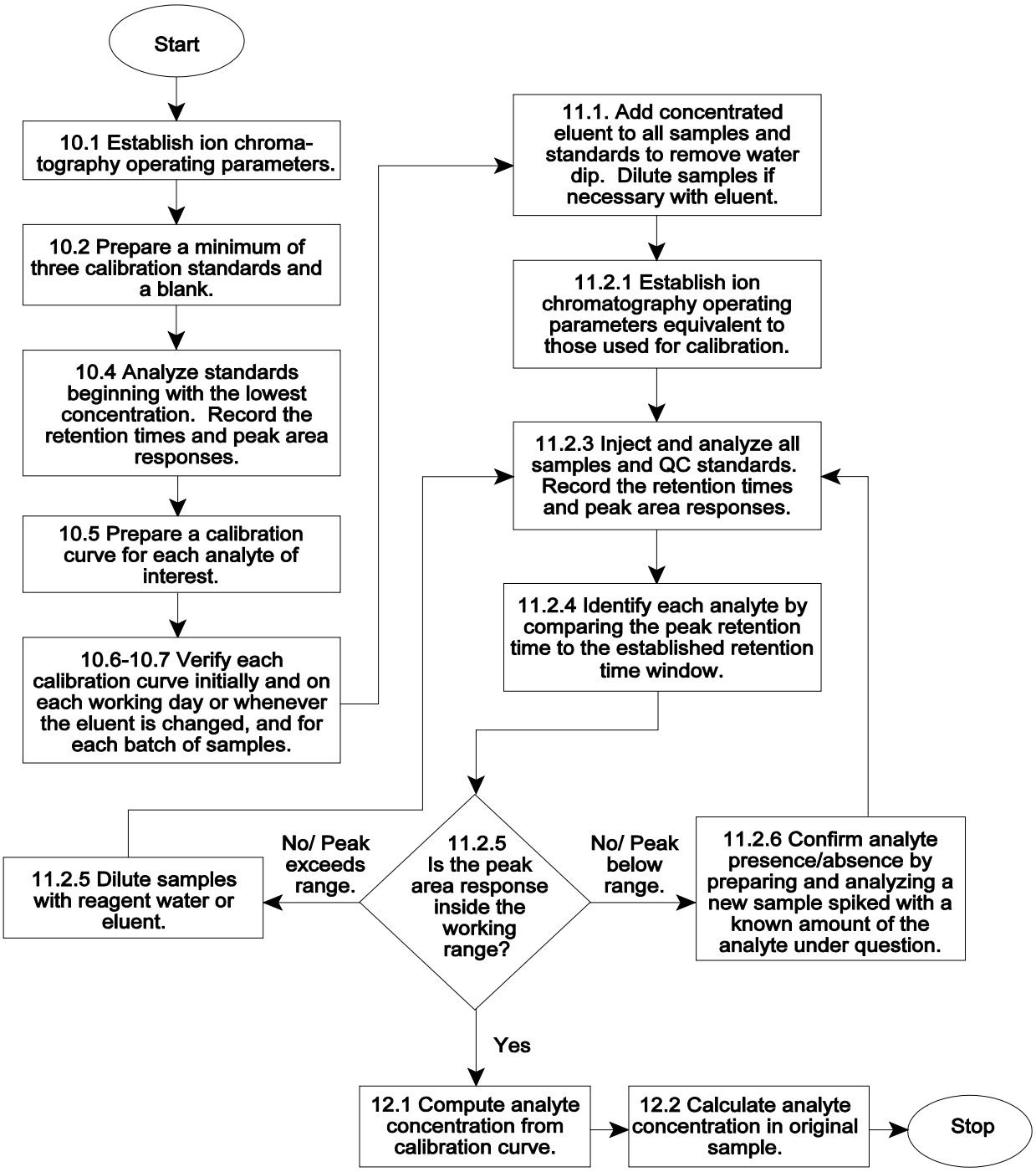
DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY



APPENDIX B

Sacramento Stormwater Urban Runoff Discharge: Sampling and Analysis Plan

OCTOBER 2018 DRAFT

Sacramento Stormwater Quality Partnership

2018/2019 Sacramento Stormwater NPDES Monitoring Urban Runoff Discharge Sampling and Analysis Plan

County of Sacramento

City of Sacramento

City of Citrus Heights

City of Elk Grove

City of Folsom

City of Galt

City of Rancho Cordova

LARRY WALKER ASSOCIATES

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Overview

The Sacramento Stormwater 2018/2019 National Pollutant Discharge Elimination System (NPDES) monitoring program is comprised of several components as required by the Municipal Separate Storm Sewer System (MS4) General Permit (MS4 General Permit, Order No. R5-2016-0040, NPDES No. CAS0085324)[1] which regulates stormwater discharge for municipal and county agencies within the Central Valley, including the County of Sacramento and the cities of Folsom, Galt, Elk Grove, Rancho Cordova, Citrus Heights, and Sacramento (collectively known as the Sacramento Stormwater Quality Partnership). The MS4 General Permit refers to the previous permit's monitoring plan. The Central Valley Regional Water Board approved the 2016-2019 Annual Work Plans, which specify urban runoff discharge monitoring during fiscal year 2018-2019. The monitoring described in this sampling and analysis plan (SAP) will be performed for compliance with the approved proposed 3-year Annual Work Plan.

During the 2018/2019 monitoring season, a Partnership consultant team led by Larry Walker Associates (LWA), Thunder Mountain Enterprises, Inc. (TME), and Pacific EcoRisk (PER) will collect urban discharge monitoring samples at the following three sites: Strong Ranch Slough in Sacramento County as well as the North Natomas Detention Basin No. 4 and Sump 111, both located in the City of Sacramento.
Urban discharge monitoring will occur between October 1, 2018 and June 1, 2019 during three wet weather events and one dry weather event. Monitoring during all four events will include the collection of samples for the complete list of constituents as specified in "Table B" of the NPDES Monitoring and Reporting Program (MRP).

HEALTH AND SAFETY

All LWA employees should review and adhere to the Health and Safety Plan guidelines. Other Sacramento Stormwater Quality Partnership (Partnership) field team consultants should review their own health and safety plans. Field staff should notify the project manager and the consultant health and safety officer of any perceived dangers. Sampling and site visits are not permitted when unsafe conditions occur.

For non-medical incidents, call the police at 916.264.5471 or 916.264.5151 (Emergency number). The following section contains site specific Health and Safety Plan information that should be followed at all times.

SAMPLING SITES

Sampling will be conducted at three urban discharge sites for the 2018/2019 monitoring year. The addresses and coordinates for these sites are shown in **Table 1**, and an overview area map is provided as **Figure 1**. Descriptions of each sampling site are detailed below.

[1] The MS4 General Permit was adopted on June 23, 2016, became effective on October 1, 2016, and will expire on September 30, 2021. The Cities' and County's MS4s are assigned the following General Order Nos.: City of Citrus Heights MS4 (R5-2016-0040-004), City of Elk Grove MS4 (R5-2016-0040-005), City of Folsom MS4 (R5-2016-0040-006), City of Galt MS4 (R5-2016-0040-007), City of Rancho Cordova MS4 (R5-2016-0040-008), City of Sacramento MS4 (R5-2016-0040-009), and County of Sacramento MS4 (R5-2016-0040-010).

Table 1. Monitoring Site Locations

Site	Address	Latitude	Longitude
Strong Ranch Slough (UR2S)	967 Venture Court, Sacramento, CA 95821	38.584985	-121.417627
Sump 111 (UR3)	798 North 5th Street, Sacramento, CA 95835	38.601237	-121.492729
North Natomas Detention Basin No. 4 (UR5)	5151 Crest Dr. Sacramento, CA 95835	38.667779	-121.506603

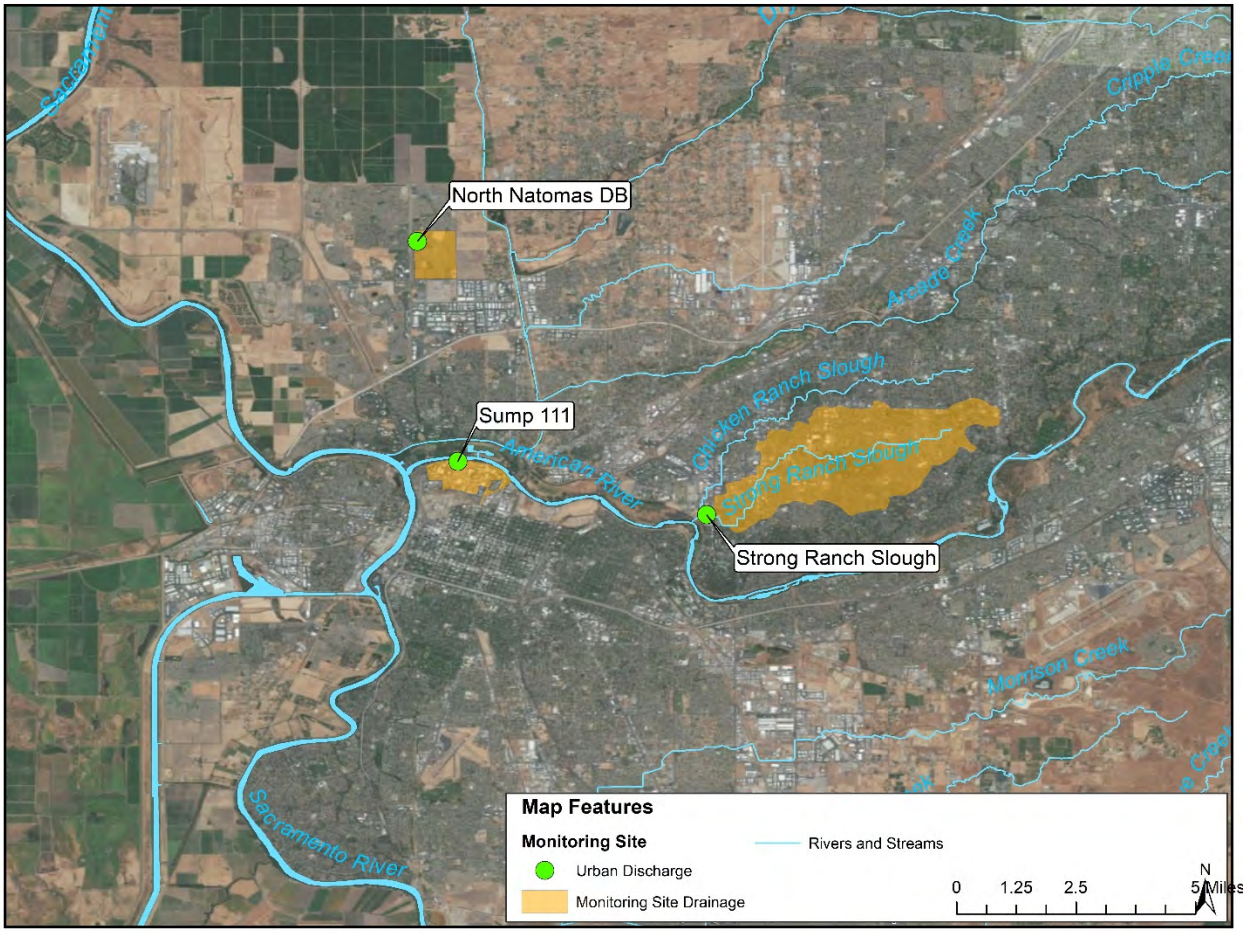

Figure 1. Area Overview and Site Locations

Strong Ranch Slough (Monitoring Site ID: UR2S)

Strong Ranch Slough drains a 4,446 acre mixed-use area of the County of Sacramento. At the sampling point, a trapezoidal channel conveys runoff from Strong Ranch Slough into a holding pond (D5 Basin) before being conveyed to the American River via pump or gravity flow.

Figure 2. Strong Ranch Slough Area Map

Safety

Previously, issues with the transient population and vandalism have occurred at Strong Ranch Slough. If at any point you feel your safety is at risk, leave the area and call the police at 916.874.5115 (Sacramento County Sheriff) or 916.874.5111 (Emergency number). Please be advised of the following:

- Field visits will only occur during the daylight hours.
- Check the immediate area when you arrive at the gate and be aware of your surroundings during sampling.
- Do not enter the channel during storm events.

Access and Notification Requirements

The gate for the Strong Ranch Slough site requires a key. Opening the sampling equipment enclosure also requires the same key. No advance notification is required to access this site.

Sump 111 (Monitoring Site ID: UR3)

Sump 111 is a collection point for stormwater drained from an industrialized 439 acre area of the City of Sacramento. Three storm pumps and one summer pump convey water to the American River.

Figure 3. Sump 111 Area Map

Directions

1. Access to the site is from Richards Boulevard, which can be accessed from I-5 or Highway 160.
2. From either direction, turn north onto North 5th Street.
3. The pump station should be straight ahead, as seen in **Figure 3**.

Safety

For non-medical incidents, call the police at 916.264.5471 (Sacramento Police) or 916.264.5151 (Emergency number). Please be advised of the following:

- Don't fall into the sumps.
- Do not attempt to enter the sumps during a storm for any reason.

- If there is a power failure, stay out of the Motor Control Center (MCC) until after the pumps are restarted. There is a remote possibility of an electrical box explosion when the pumps are started automatically after power is restored.
- You will rarely (if ever) need to enter the MCC in the course of stormwater monitoring. However, if you do need to enter the MCC, there is a light switch located around the corner and to the left as you enter.

In general, be aware of your surroundings, stay together, and keep an eye out for each other.

Access and Notification Requirements

The gate and sampling equipment enclosure for Sump 111 are locked with padlocks. The MCC is locked with a combination lock (combination=0600). Remember to lock the gates behind you when you leave.

Control 12 (916.808.5226) should be notified prior to entering the secured pump station area.

Entering the MCC building will trigger an alarm that notifies police. The need to enter MCC buildings is not anticipated during this stormwater monitoring season. However, in the event that MCC building entry is required, the following notification procedures will be followed:

- During dry weather, Sump 2 shall be notified (916.808.5461) prior to entering and after exiting the MCC building.
- During a storm, Sump 2 shall be notified (916.808.5461) and then Control 12 shall be notified (916.808.5226) prior to entering and after exiting the MCC building.

North Natomas Detention Basin No. 4 (Monitoring Site ID: UR5)

North Natomas Detention Basin No. 4 is a collection point for stormwater drained from a 470 acre area of residential development in North-West Sacramento, before it is pumped into the East Drainage Canal, which is a tributary to the Main Drainage Canal that eventually drains into the Sacramento River.

Figure 4. North Natomas Detention Basin No. 4 Area Map

Directions

Access to the site is from Crest Drive.

1. From I-5, take the Del Paso Road exit and head east.
2. Continue on Del Paso Road until you come to Gateway Park Boulevard and take a left.
3. Take another left on North Bend Drive and then a quick right on Crest Drive.
4. Continue for about a half mile until you see the detention basin on your left (**Figure 4**).
5. Turn left to the access gate and use the City key.
6. At the far end of the access road is the pump station for the detention basin.

Access and Notification Requirements

Control 12 (916.808.5226) should be notified prior to entering the secured pump station area. Access to the fenced City outlet pump area is secured with a combination lock (combination=1514) in addition to other padlocks which require a City master key.

SAMPLE COLLECTION SCHEME

The Partnership consultant field crew team will collect samples during three wet weather storm events and one dry weather event. Events will be numbered chronologically starting with Event 1 and are also assigned an overall program number based on the historical event numbers for the Urban Discharge monitoring program.

During each event and at an individual site, the Partnership field crew consultant team will collect grab samples. Composite samples will be collected by utilizing automatic samplers. The sample collection program for the 2018/2019 monitoring year is outlined in **Table 2**. The water column constituent requirements for the MRP and additional monitoring are shown in **Table 3** (composite samples) and **Table 4** (grab samples). The water column field parameters requirements are shown in **Table 5**.

Composite Sample Collection

To obtain the desired volume, each automatic sampler will be programmed so that the sampler will collect at least 12.0 liters, if the predicted precipitation is delivered by the targeted storm. The standard carboy volume used in the refrigerated samplers is 20 liters. In cases where additional volume is needed for quality assurance/quality control (QA/QC) samples or if runoff predictions underestimate observed conditions, the composite volume will be increased accordingly and bottle changes may be necessary.

Automatic sampling at each of the sites will begin after clean composite bottles are installed by field crews, the sampler has been reset, and pre-specified storm (rainfall and flow) criteria have been met.

Sampling can be terminated when either: (a) 24 hours have passed, or (b) the monitoring manager determines that the storm is finished. At Strong Ranch Slough, sampling can also be terminated automatically if the depth in the channel drops below a pre-specified level.

The Partnership consultant field crew team will collect composite samples according to the methods, bottle types, and sample preservation requirements listed in **Table 3**. The Partnership consultant field crew team will split the composite samples directly into prepared sample bottles (i.e., labeled and containing preservation, if necessary).

Grab Sample Collection

One set of grab samples will be taken at each site during each event. It is desired that these grab samples be collected during peak flow. However, due to the difficulty in predicting the time of peak flow, collecting grab samples during peak flow may be problematic. Therefore, to the greatest extent possible, grab samples will be collected during the first portion of the storm event, at a time when flow rates are increasing and precipitation rates are decreasing.

Single grab samples will be collected according to the methods, bottle types, and sample preservation requirements listed in **Table 4**. Field readings will also be collected at this time, according to **Table 5**.

Table 2. Monitoring and Reporting Program (MRP) Sampling Requirements

Constituent List	Event[1]			
	WW63	WW64	WW65	DW29
Field Measurements (see Table 5)	X	X	X	X
MRP Table B Constituents (see Table 3 and Table 4)	X	X	X	X

[1] WW = wet weather, DW = dry weather.

Table 3. Volumes, Analytical Methods, Type, and Preservation by Sample Bottle for MRP Table B (Composite Samples)

Bottle ID	Bottle Type[1]	Primary Lab	Analysis	Optimum Volume	Method	Preservation
C1	2 X 1 L AG	Caltest	Pyrethroid Pesticides + Chlorpyrifos, Diazinon, and Fipronil	1.00 L	NCI-GCMS-SIM	0-6˚C
C2	2 X 500 mL PE	Caltest	Nitrate + Nitrite	0.15 L	EPA 353.2	0-6˚C, H2SO4 to pH <2
			Total Kjeldahl Nitrogen (TKN)	0.15 L	EPA 351.3	
			Phosphorus, total	0.15 L	EPA 365.2	
			Chemical Oxygen Demand (COD)	0.15 L	Hach 8000	
C3	2 x 1 L PE	Caltest	5-day Biochemical Oxygen Demand (BOD_5)	0.25 L	EPA 405.1	0-6˚C
			Alkalinity	0.25 L	SM 2320 B	
			Total Dissolved Solids (TDS)/Total Suspended Solids (TSS)	0.25 L	EPA 160.1/160.2	
			Turbidity	0.10 L	EPA 180.1	
			Electric Conductivity (EC)	0.10 L	EPA 120.1	
C4	500 mL PE	Caltest	Low Level Metals, total (Cu, Pb, Fe & Zn)	0.25 L	EPA 1638/200.8 ICP/MS	0-6˚C, HNO3
			Total Hardness		EPA130.2/SM2340	
C5	250 mL PE	Caltest	Suspended Sediment Concentration (SSC)	0.25 L	ASTM D 3977-97	0-6˚C
C6	500 mL PE	Caltest	Low Level Metals, dissolved (Cu, Pb, Fe & Zn)	0.25 L	EPA 1638/200.8 ICP/MS	0-6˚C, filter[2], preserve ASAP
C7	2 X 1L AG	PHYSIS	Organophosphate (OP)-Pesticides	2.00 L	EPA 625	0-6˚C
			Polynuclear Aromatic Hydrocarbons (PAHs)			

[1] PE = Polyethylene; AG = Amber Glass; CG = Clear Glass.
[2] Sample will be filtered by the field crew within 15 minutes of collection of composite.

Table 4. Volumes, Analytical Methods, Type, and Preservation by Sample Bottle for MRP Table B (Grab Samples)

Bottle ID	Bottle Type[1]	Primary Lab	Analysis	Optimum Volume	Method	Preservation
G1	500 mL AG	Caltest	Methylmercury	0.30 L	CVAFS	0-6˚C, HCl
G2	500 mL CG	Caltest	Mercury, total	0.30 L	CVAFS	0-6˚C, HCl
G3	3 x 40 mL VOA CG	Caltest	Total Petroleum Hydrocarbons (Gasoline)	0.12 L	EPA 8015M	0-6°C, HCl
C	2 x 1 L AG	Caltest	Total Petroleum Hydrocarbons (Diesel & Motor Oil)	2.00 L	EPA 8015M	0-6°C
F	3 x 40 mL VOA AG	Caltest	Total Organic Carbon (TOC)	0.12 L	EPA 415.1	0-6˚C, HCl to pH <2
G	125 mL AG	Caltest	Dissolved Organic Carbon (DOC)	0.12 L	EPA 415.1	0-6˚C, filter & preserve ASAP
E	100 mL Sterile Plastic	SRCSD	Fecal coliform and *Escherichia coli* (*E.Coli*)	0.375 L	SM 9221 B&E	0-6˚C, $Na_2S_2O_3$

[1] PE = Polyethylene; AG = Amber Glass; CG = Clear Glass.
[2] Sample will be filtered by the field crew within 15 minutes of collection.

Table 5. MRP Required Field Measurements

Water Temperature
pH
Dissolved Oxygen (DO)
Electrical Conductivity (EC)
Air Temperature

Pre-Season Maintenance and Preparation

Prior to the first targeted storm and immediately following each of the subsequent sampling events, the Partnership consultant field team will complete the following monitoring station maintenance and preparation activities.

UPDATE COMMUNICATION PLAN

The project manager should review and update the organizational and communication plan (**Figure 5**) annually and as necessary.

PRE-SEASON SITE ASSESSMENT AND EQUIPMENT INSTALLATION

Before the beginning of the monitoring season, site visits are necessary to prepare for monitoring. The specific purpose of these visits is to prepare the general area of the site to assure safe access, to install protocol-cleaned tubing, to check the function and performance of the samplers, and to take equipment blank samples at the specified site(s).

Site Assessment

Each monitoring site should be inspected for damage, and site access should be cleared by cutting back or removing weed growth around the site. Safety and security should be generally assessed by checking fences for holes and other damage. Locks should be checked for proper functioning. Any concerns should be promptly corrected or relayed to the appropriate agency maintenance department.

Tubing Replacement

At the beginning of each storm sampling season, the suction tubing and Teflon-coated strainer will be removed from automatic samplers, inspected for damage, cleaned, and reinstalled, during a second site visit, using clean techniques. Protocol-cleaned silicone pump tubing will also be installed during the second visit.

Continuous Flow Stage Meters and Multiparameter Sensors

Continuous flow stage meters and multiparameter sensors measuring temperature and turbidity, will be installed at all three sites. Calibrations will be performed to ensure readings are of sufficient accuracy. The data loggers will be programmed to collect measurements every 5 or 15 minutes during storm events and less frequently at other times to conserve battery life.

FIELD EQUIPMENT PREPARATION

Prior to the beginning of the monitoring season, the field crew should take inventory of field equipment (see **Table 6** and **Table 7** for storm kit and storm mobilization equipment checklists, respectively) and replace items as necessary.

Field crews will also order bottles from the laboratories according to **Table 3** (composite samples) and **Table 4** (grab samples).

Table 6. Storm Kit Equipment List

Headlamps/flashlights (2)
Spare batteries (6)
Spare bottle labels
Pencils (2) and waterproof pens/markers (2)
Diagonal clippers
Electrical tape
Cable ties (assorted sizes)
Utility knife
Zip-lock baggies (assorted sizes)
Powder-free nitrile gloves
Rubber bands, heavy duty
Digital Camera
Cellular phone charger (and/or spare batteries)
Duct tape
First Aid kit

Table 7. Storm Mobilization Equipment List

Storm Kit
Sampling and Analysis Plan
Log books/ Field logs
Clipboard
Deionized (D.I.) water squirt bottles
Chain-of-custody forms (specific to each laboratory)
Sample bottles (include spare bottles)
Intermediate containers
Bailers (at least two or three recommended)
Coolers and ice
Bubble wrap
Blank water (for field blanks)
Cellular phone
Personal rain gear and/or Waders
Any necessary safety gear
Heavy anchor or weight, rope and cable ties
Grab pole with bottle holder attachment
Outdoor thermometer (for atmospheric temperature)
Portable field meters for water temperature, pH, DO and EC
Calibration standards (for re-calibration on site, if needed)
Portable peristaltic pump & batteries
Pump (flexible) tubing (40 in.)
Suction (Teflon) tubing (3 lengths; one for each site)
Teflon coated strainer (3)
Vacuum Filters (4)
Personal flotation devices (life jackets)
Umbrella
Paper towels
Trash bags

Storm Tracking, Communication, and Mobilization

DECISION TO SAMPLE AND COMMUNICATION

The decision to sample a storm event will be made by the Partnership in consultation with the LWA monitoring manager and the TME monitoring manager. The Monitoring Program will target the first storm event of the season with a forecasted amount greater than 0.25" of precipitation and two additional storm events during the remaining portion of the storm season.

The communication plan (**Figure 5**) is a schematic of the decision-making process. If a key contact is not available, the decision-making will be performed by the next available staff member on the communication plan contact list or according to a pre-approved event-specific plan. It is the responsibility of each individual included in the communication plan to contact the other individuals they are associated with in the plan, and to report to the monitoring manager if they are unable to establish contact. Monitoring management activities will be located in Sacramento or Yolo County. Contact information is shown in the communication plan.

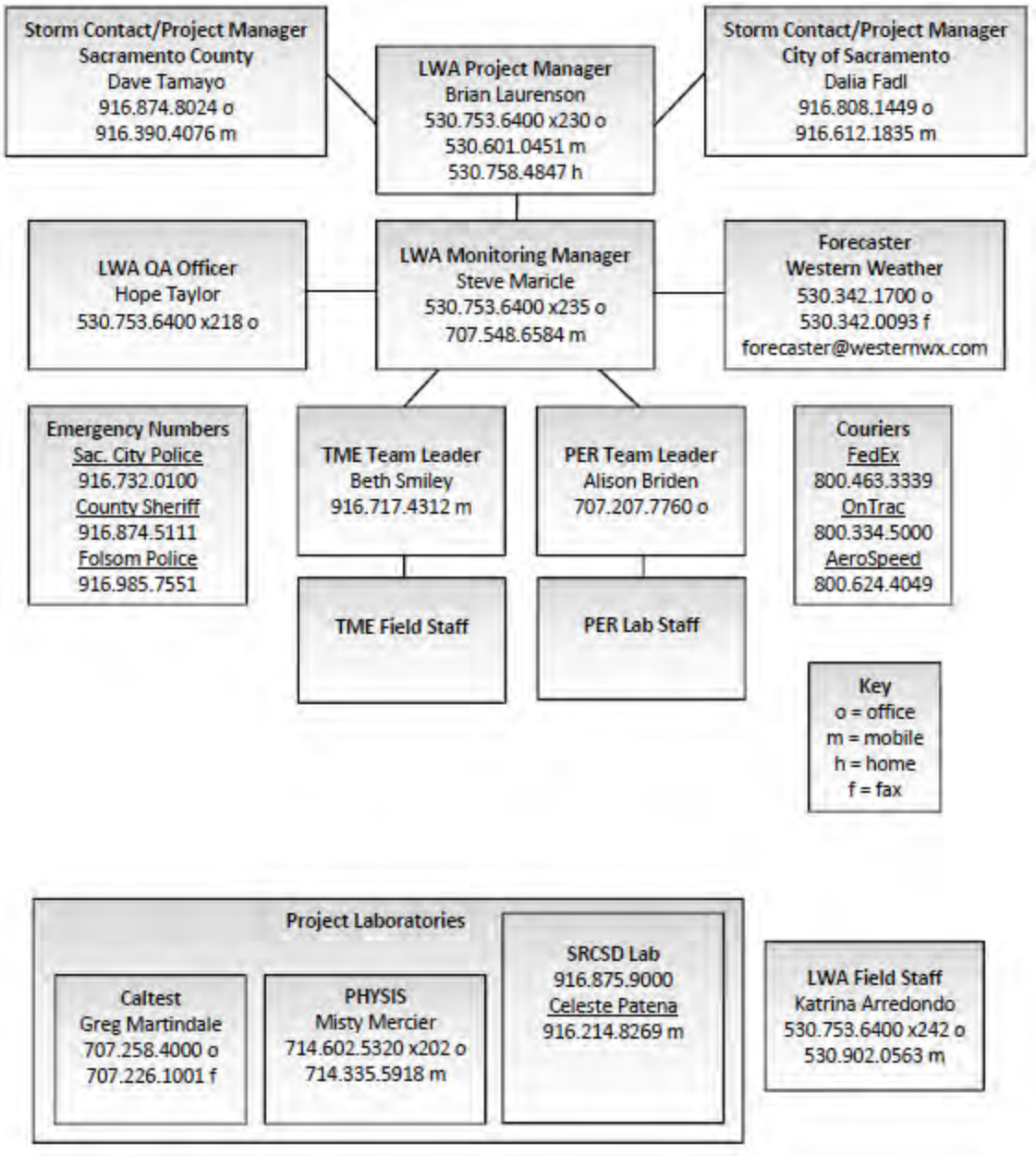

Figure 5. Organization and Communication Plan

STORM ACTION LEVELS

Five action levels are defined for purposes of preparation and mobilization: 1) Chill, 2) Standby, 3) Pre-Alert, 4) Alert, and 5) Go. Two action levels are defined for monitoring shutdown and activity reporting: 1) Cool Down and 2) Post-Alert Email. These action levels and the corresponding conditions and action items are described below and listed in **Table 8**.

Storm Tracking (CHILL and STANDBY)

"CHILL" will be used in email communication when either no storms are expected in the foreseeable future or if a storm does not meet the Partnership's trigger conditions.

"STANDBY" will be used when storms are forecasted in the near future, but at this time they might not be a targetable event. Field crews should continue to monitor the updates by the Monitoring Manager and be prepared if the forecast is upgraded.

Pre-Storm Preparations (PRE-ALERT)

During the "PRE-ALERT" action level, field crews should make sure all equipment, bottles, and vehicles are ready. Each Partnership consultant field team will provide their own vehicles as needed for field crew use during monitoring events.

Storm Sampling Preparation (ALERT)

When the action level changes to "ALERT," the field teams will check each monitoring site for hazardous conditions and issues that would prevent sampling. Crews will clear debris if necessary and alert the monitoring manager to any hazardous conditions that need to be dealt with. Field crews will then install clean or new bottles and replace any tubing that is showing signs of wear. All automatic samplers should be prepped and ready to be initiated.

Mobilization (GO)

The monitoring manager will mobilize the Partnership consultant field teams for coverage of the anticipated monitored storm event and confirm crew status with the TME project manager. Each sampling team will be equipped with one cellular phone or other means of remote communication.

Table 8. Storm Action Levels

Action Level	*Condition*	*Action*
Chill	No targeted storm expected within the foreseeable future	*Monitoring Manager* • Monitor twice-weekly weather reports *Field crew*: • No impact on activities
Standby	Evaluating storm system	*Monitoring Manager*: • Monitor weather reports every 24 hours • Alert field crew regarding change in action level *Field crew*: • Notify *Monitoring Manager* where you will be and how you can be reached if you leave the area for more than one or two days • Arrange for substitute if needed
Pre-Alert	Target storm expected within the next 72 hours	*Monitoring Manager* • Contact County of Sacramento, City of Sacramento & LWA • Monitor weather reports every 6 hours • Alert field crew/laboratories regarding change in action level via communication plan and verify availability/readiness *Field crew*: • Remain in Sacramento area if possible • Verify availability with *Monitoring Manager* • Prepare for sampling effort
Alert	Target storm expected within the next 24 hours	*Monitoring Manager* • Confer with County of Sacramento, City of Sacramento & LWA • Monitor weather reports as needed • Alert field crew regarding change in action level and probable time of storm via communication plan • Alert laboratory regarding potential incoming samples with critical holding times *Field crew*: • Perform on-site station preparation
Go	Precipitation imminent or has begun during targeted storm.	*Monitoring Manager* • Monitor weather reports as needed • Mobilize field crew for sampling • Mobilize standby bacteria lab analyst *Field crew*: • Mobilize to sample collection stations for sampling, or sampling performance checks • Deliver bacteriological samples to laboratories
Cool Down	Precipitation ceased or sampling requirements completed	*Monitoring Manager* • Demobilize field crew *Field Crew*: • Compile bottles, and ship samples to laboratories • Notify laboratories that samples with critical holding times are ready for pick-up or delivery • Complete notes re: problems and solutions • Prepare for next storm (inventory/order/organize equipment) *Laboratories* • Analyze samples
Post-Alert E-mail	Following storms that reach "Alert" status when either monitoring is called off or field crew activities in the "Cool Down" action level are completed	*Monitoring Manager* • Prepare a brief e-mail to the City of Sacramento and the County of Sacramento stating whether or not the event was monitored

Field Monitoring

Field monitoring will consist of physical grab sample collection at both sites, as well as an automated micro-sampler that will collect pumped samples at various times in the hydrograph. This section contains collection methods for the grabs and the micro-sampler as well as general techniques that will be used by the Partnership for this program.

SAMPLING TECHNIQUES

This section contains protocol for specific sampling techniques that need to be adopted by the Partnership, regardless of the site or monitoring program. Along with the following techniques, stormwater samples should be collected while observing the following rules:

1. No smoking;
2. Never sample near a running vehicle, and do not park vehicles in immediate sample collection area (even non-running vehicles);
3. Avoid allowing rainwater to drip from rain gear into sample bottles;
4. Do not eat or drink during sample collection; and
5. Do not breath, sneeze or cough in the direction of an open sample bottle.

GRAB SAMPLE COLLECTION

A two to three person field crew will mobilize to each sampling site to collect grab samples near the peak flow for the storm event. Grab samples will be collected mid-channel with a grab pole and intermediate sample container. The intermediate container should match the material type of the respective sample container. Please be advised of the following:

- Non-preserved/preserved containers:
    - Any non-preserved container should be **rinsed three times** with sample water before collecting the sample.
    - Samples with preservative will be **filled directly** by the intermediate sample container so as not to lose any of the preservative.
- Gloves will be worn at all times and samples should be carefully collected to minimize potential for contamination.
- Total mercury and methylmercury samples will be collected according to the "clean sample handling" techniques outlined in the section blow.
- Dissolved metals will be field filtered within 15 minutes of sample collection, according to the protocol in the section below.

COMPOSITE SAMPLE COLLECTION

Composite samples will be collected using an automatic sampler as described in the Sample Collection Scheme section.

Clean Sample Handling

"Clean sampling" techniques are required to collect and handle water samples, pump tubing and strainers in a way that results in neither contamination, loss, or change in the chemical form of the analytes of interest. Samples are collected using protocols based on EPA Method 1669, as summarized below:

1. Samples are collected only into pre-cleaned sample bottles;
2. At least two persons, wearing clean, powder-free nitrile gloves at all times, are required on a sampling crew;
3. One person ("dirty hands") touches and opens only the outer bag of all double bagged items (such as sample bottles, tubing, strainers and lids), avoiding touching the inside of the bag;
4. The other person ("clean hands") reaches into the outer bag, opens the inner bag, and removes the clean item (sample bottle, tubing, lid, strainer, etc.);
5. After a grab sample is collected, or when a clean item must be re-bagged, it is done in the opposite order from which it was removed;
6. Clean, powder-free nitrile gloves are changed whenever something not known to be clean has been touched; and
7. For this program, clean techniques must be employed whenever handling the suction tubing, strainers, double bagged aliquot bottles, or mercury and bacteriological grab sample bottles. During sample splitting, the metals bottles are also handled using clean techniques.

Sample Filtration

Metals samples are field filtered immediately after collection. The recommend type of vacuum filter has an intake reservoir (500 mL), an applied vacuum attachment, a permeable membrane (0.45 µm) and a filtrate receiver reservoir. The recommended filtration procedure is as follows, however, based on results of filter blanks, the procedure can be modified to ensure that contamination is negligible (<10% of environmental concentration).

1. The sample is directly poured or pumped into the intake reservoir;
2. The "discharge" end of sample collection pump apparatus pump (flexible) tubing is attached to the filter vacuum valve and the pump is reversed to apply vacuum suction on the filter apparatus. A hand pump can also be used in place of a peristaltic pump;
3. After sufficient filtrate (>300 mL) is collected in the receiver reservoir, the vacuum suction is removed;
4. The receiver reservoir is removed and the filtrate is transferred to the laboratory-provided bottle; and
5. The chain of custody should clearly indicate that the sample was field filtered in the notes and the sample ID so that it can be distinguished from the total recoverable metals sample.

FIELD MEASUREMENTS

Field meters will be maintained throughout the monitoring season and calibrated **within 24 hours** of any potential event. Calibrations results will be logged in a calibration log and included with the event summary.

Field measurements for conductivity, turbidity, dissolved oxygen, temperature, and pH shall be taken at each sampling station, each time the station is sampled. Field measurements shall be made after water quality samples have been collected, using the following procedures:

- The required field measurements shall be taken one time at each sampling station at approximately mid-depth, at a location of significant flow (where feasible).

- Field measurements shall be made from a stable, unobstructed area by attaching the probe to an expandable pole and reaching out if needed.
- The probe shall be lowered to approximately mid-depth, readings stored, then recorded on the field log (see **Appendix A**) prior to leaving the sampling station.

Once field measurements are obtained, the Field Crew Lead will compare the results to water quality objectives (WQOs) provided in **Table 9**. If field readings do not meet these WQOs, the field crew will calibrate the instrument and resample. Both of the results will be logged in the field sheet and the calibration log sheet will be attached.

If at any time the collection of field measurements appears unsafe, DO NOT attempt to sample. Refer to the Health and Safety Plan.

Table 9. Water Quality Objectives for Field Parameters

Constituent	Water Quality Objective
Dissolved Oxygen	>7.0 mg/L
Electrical Conductivity	<700 µS/cm
pH	6.5-8.5 std. units

PRIOR TO LEAVING THE SITE

1. Add ice to all collected sample coolers/carrying buckets;
2. Physically inspect monitoring equipment (tubing, stream gauges, etc.);
3. Rinse and purge sample collection tubing/strainer and store in a clean double-bagged plastic garbage bag;
4. Fill out log sheet;
5. Secure the site; and
6. Contact monitoring manager to report site status.

Quality Control Samples

Quality control samples will be collected during each monitoring event according to the schedule presented in **Table 11**. Rinsate blanks, lab/field duplicate, and matrix spike/matrix spike duplicate analyses for the Monitoring Program will rely on the QA/QC activities described below. Quality control sample results will be used for data evaluation and interpretation. Note that the wet and dry weather monitoring events are combined in **Table 11**.

PRE-STORM BOTTLE AND EQUIPMENT BLANKS

All bottles and lids will be cleaned according to specified procedures.

Rinsate Blanks

Prior to the first monitoring event, equipment rinse blanks will be analyzed for TOC, total recoverable metals, total mercury and methylmercury.

MONITORING EVENT QUALITY CONTROL SAMPLES

The following quality control samples will be analyzed during each monitoring event, and a summary is presented in **Table 10**.

- Field Blank: total recoverable metals, dissolved metals, pesticides, PAHs, TOC, bacteriological, total mercury, and methylmercury analyses.
- Field or Laboratory Duplicate: all MRP constituents.
- Matrix Spike/Matrix Spike Duplicate (MS/MSD): total recoverable metals, dissolved metals, total mercury, methylmercury, PAHs, and pesticides.

Table 10. Quality Control Samples

	Rinsate Blank	Field Duplicate	Field Blank	MS/MSD
Pyrethroid Pesticides		X	X	X
OP-Pesticides		X	X	X
PAHs		X	X	X
Petroleum Hydrocarbons		X		
TOC	X	X	X	
DOC		X		
Nutrients		X		
Total Metals	X	X	X	X
Total Hardness		X		
Dissolved Metals (Filter Blank)		X	X	X
Methylmercury	X	X	X	X
Total Mercury	X	X	X	X
Conventionals		X		
Fecal coliform and *Escherichia coli*		X	X	

QC SAMPLE COLLECTION SCHEDULE

Field-generated quality control samples (field duplicates and field blanks) will be submitted "blind" to the laboratory. Quality control samples will be collected according to the schedule shown in **Table 11**.

COLLECTION METHODS

Specific collection methods for each quality control sample type are described below.

Field Blank

Grab sample field blanks will be collected immediately prior to the collection of environmental grab samples. The field crew will use the blank water provided by the laboratory and will fill each grab sample container according to standard procedures.

Filter blanks will be collected for dissolved metals. Field crews will pour laboratory supplied blank water into the filter chamber and collect the sample in the same manner as the environmental sample.

Field blanks will be submitted "blind" to the laboratory using the "***Clear Creek***" site name pseudonym. The date and time of sampling should be noted on the log sheet.

Field blanks will be collected at one site for each event.

Field and Laboratory Duplicate

Grab sample field duplicates will be collected immediately following, and in the same manner as, the environmental grab samples.

Field duplicates will be submitted “blind” to the laboratory using the “***Newt Creek***” site name pseudonym. The date and time of sampling should be noted on the log sheet.

Laboratory duplicates are samples that are split by the laboratory. Each half of the split sample is then analyzed and reported by the laboratory. A pair of field duplicates is two samples taken at the same time, in the same manner, and into two unique containers.

Field and laboratory duplicates will be collected as specified in ***Table 11***.

Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Matrix spike analysis involves the introduction of a known spike in the original "matrix" (sample solution) and is a measure of the accuracy of the recovery performance of the laboratory. To perform this analysis, the laboratory generally requires an additional volume of sample. Matrix interference can lead to recovery problems and raised detection limits. Re-analysis is the first corrective action once matrix interference problems are identified, but re-analysis is only possible when sufficient sample volume is available.

Matrix spike duplicate (MSD) analyses are performed to check the precision of the matrix spike recovery. Ideally, triple the normal sample volume is provided to the analytical laboratory for the analysis of a matrix spike and a matrix spike duplicate. Relative Percent Differences (RPDs) are calculated from the matrix spike and matrix spike duplicate percent recoveries.

Matrix spike and matrix spike duplicates will be run at one site for each event.

Table 11. QC Schedule

Site	Event[1]			
	WW63	**WW64**	**WW65**	**DW29**
UR2S	MS/MSD	Field Blank	Field Duplicate	MS/MSD
UR3	Field Duplicate	MS/MSD	Field Blank	Lab Duplicate
UR5	Field Blank	Lab Duplicate	MS/MSD	Field Blank

[1] WW = wet weather; DW = dry weather

Sample Handling and Shipment

Following collection of each sample, the sample container must be labeled, the chain-of-custody form must be filled out, and the sample must be delivered to the appropriate laboratory. These actions are described below.

LABELS/STATION CODES

Sampling sites shall be designated by the names and site codes listed in **Table 12**.

Table 12. Monitoring Site Identification Codes

Site Code	Site Name
UR2S	Strong Ranch Slough
UR3	Sump 111
UR5	North Natomas Detention Basin No. 4

In addition, quality control samples submitted "blind" to the laboratory should be designated by the pseudonyms and site codes listed in **Table 13**.

Table 13. Quality Control Sample Identification Codes

Site Code	Site Name	QC Sample
UR6	Clear Creek	(field blank)
UR7	Newt Creek	(field duplicate)

SAMPLE ID CONVENTIONS

Sample bottles submitted to laboratories for analysis shall be labeled with the sampling site name, sampling site code, the date of sample collection, and a sample ID devised as follows:

SAC SW *SITE Type XX*

Where: *SITE* = Site code (see above)

Type = Event type (Wet or Dry)

XX = Event number (i.e., 01, 02, 03, or 04)

For example, the sample ID used for a grab sample collected from Strong Ranch Slough during the first event would be "SAC SW UR2S Wet01".

CHAIN-OF-CUSTODY FORMS

Chain-of-custody (COC) forms will be filled out for all samples submitted to each laboratory. Sample date, sample site, and analysis requested shall be noted on each COC. See **Appendix B** for example COC forms. Analytical methods, quantification limits, and holding times for each analyte monitored are presented in **Table 14**.

Table 14. Analytes, Methods, Reporting Limits, and Holding Times

Constituent	Method	Reporting Limit	Holding Time
Field Measurements			
Date	NA	mm/dd/yyyy	NA
Sample Time	NA	hr:min (24-hour clock)	NA
Weather Conditions	NA	NA	NA
Air Temperature	SM 2550 B	degrees C	NA
Water Temperature	SM 2550 B	degrees C	NA
pH	SM 4500-H+-B	0 – 14	NA
Dissolved Oxygen	SM 4500-O G	Sensitivity to 5 mg/l	NA
Electrical Conductivity (EC)	EPA 120.1	1 µmhos/cm	NA
Turbidity	EPA 180.1	0.1 NTU	48 hrs
Bacteria		*units = MPN/100ml*	
Fecal Coliform	SM9221	<20	6 hours
Escherichia coli (fresh waters)	SM9221	<20	6 hours
General		*units = mg/l, except where noted*	
Total Petroleum Hydrocarbons	EPA 8015M	5	14 days
Total Suspended Solids	EPA 160.2	2	7 days
Total Dissolved Solids	EPA 160.1	2	7 days
Total Organic Carbon	EPA 415.1	1	28 days
Dissolved Organic Carbon	EPA 415.1	1	Filter ASAP
Biochemical Oxygen Demand	EPA 405.1	2	48 hours
Chemical Oxygen Demand	Hach 8000	20 – 900	28 days
Total Kjeldahl Nitrogen	EPA 351.3	0.1	28 days
Alkalinity	SM 2320 B	2	28 days
Nitrate-Nitrite	EPA 353.2	0.1	28 days
Total Phosphorus	STM 4500	0.05	28 days
Total Hardness	EPA 130.2 / SM2340C	2	6 months
Methylmercury	CV-AFS	0.05 ng/l	6 months
Metals		*units = µg/L, except where noted*	
Copper (Dissolved)	EPA 1638/200.8 ICP-MS	0.5	6 months
Copper (Total)	EPA 1638/200.8 ICP-MS	0.5	6 months
Iron (Total)	EPA 1638/200.8 ICP-MS	100	6 months
Lead (Dissolved)	EPA 1638/200.8 ICP-MS	0.5	6 months
Lead (Total)	EPA 1638/200.8 ICP-MS	0.5	6 months
Mercury (Total)	CV-AFS	0.5 ng/l	6 months
Zinc (Dissolved)	EPA 1638/200.8 ICP-MS	1	6 months
Zinc (Total)	EPA 1638/200.8 ICP-MS	1	6 months
Organophosphate Pesticides			
Chlorpyrifos	GCMS-SM by EPA 625m	0.01 µg/l	7/40 days
Diazinon	GCMS-SM by EPA 625m	0.05 µg/l	7/40 days
Malathion	GCMS-SM by EPA 625m	0.05 µg/l	7/40 days
PAHs		*units = µg/L*	
Perylene	GCMS-SM by EPA 625m	0.005	7/40 days
Benz[a]anthracene	GCMS-SM by EPA 625m	0.005	7/40 days

Constituent	Method	Reporting Limit	Holding Time
Chrysene	GCMS-SM by EPA 625m	0.005	7/40 days
Fluorene	GCMS-SM by EPA 625m	0.005	7/40 days
Benzo[b]fluoranthene	GCMS-SM by EPA 625m	0.005	7/40 days
Benzo[e]pyrene	GCMS-SM by EPA 625m	0.005	7/40 days
Benzo[k]fluoranthene	GCMS-SM by EPA 625m	0.005	7/40 days
Benzo[a]pyrene	GCMS-SM by EPA 625m	0.005	7/40 days
Indeno[1,2,3-c,d]pyrene	GCMS-SM by EPA 625m	0.005	7/40 days
Dibenz[a,h]anthracene	GCMS-SM by EPA 625m	0.005	7/40 days
Benzo[g,h,i]perylene	GCMS-SM by EPA 625m	0.005	7/40 days
Pyrene	GCMS-SM by EPA 625m	0.005	7/40 days
Acenaphthylene	GCMS-SM by EPA 625m	0.005	7/40 days
Acenaphthene	GCMS-SM by EPA 625m	0.005	7/40 days
Naphthalene	GCMS-SM by EPA 625m	0.005	7/40 days
2-Methylnaphthalene	GCMS-SM by EPA 625m	0.005	7/40 days
1- Methylnaphthalene	GCMS-SM by EPA 625m	0.005	7/40 days
2,6-Dimethylnaphthalene	GCMS-SM by EPA 625m	0.005	7/40 days
2,3,5-Trimethylnaphthalene	GCMS-SM by EPA 625m	0.005	7/40 days
Fluoranthene	GCMS-SM by EPA 625m	0.005	7/40 days
Phenanthrene	GCMS-SM by EPA 625m	0.005	7/40 days
Anthracene	GCMS-SM by EPA 625m	0.005	7/40 days
1-Methylphenanthrene	GCMS-SM by EPA 625m	0.005	7/40 days
Pyrethroid Pesticides in Water		*units = ng/L*	
Bifenthrin	NCI-GCMS	2	7/40 days[1]
Cyfluthrin	NCI-GCMS	4	7/40 days[1]
Cypermethrin	NCI-GCMS	4	7/40 days[1]
Deltamethrin/Tralomethrin	NCI-GCMS	4	7/40 days[1]
Esfenvalerate/Fenvalerate	NCI-GCMS	2	7/40 days[1]
Fenpropathrin	NCI-GCMS	4	7/40 days[1]
Lambda-cyhalothrin	NCI-GCMS	2	3/40 days[1]
Permethrin	NCI-GCMS	5	3/40 days[1]
Malathion	GCMS-SM by EPA 625m	0.05 µg/l	7/40 days

[1] Michelle L. Hladik, James L. Orlando, and Kathryn M. Kuivila, "Collection of Pyrethroids in Water and Sediment Matrices: Development and Validation of a Standard Operating Procedure" (U.S. Department of the Interior, U.S. Geological Survey, Prepared in cooperation with U.S. Environmental Protection Agency)

TRANSPORT TO LAB

Samples will be hand delivered, sent via FedEx, or couriered to the appropriate laboratory as listed in **Table 3** (composite samples) and **Table 4** (grab samples). Because of the short holding times required by the bacteriological analytical methods (i.e., 6 hours), bacteriological grab samples must be delivered to the Sacramento Regional County Sanitation District (SRCSD) laboratory immediately. BOD should also be delivered to Caltest as soon as possible to meet the 48 hour hold time. Arrangements to transport and receive bacteriological samples at the SRCSD lab should be made by the monitoring manager in advance of collection of these samples to allow the lab to set up the analyses within the holding time. This is especially important when sample collection is expected outside normal business hours.

Bacteriological

Samples for *Escherichia coli* and fecal coliform will be analyzed by the SRCSD lab and should be delivered to the sample submission window at the treatment plant lab with proper chain of custody documentation. The lab can provide sample containers for these analyses, if necessary. Contact information and the laboratory's address are:

SRCSD EL
ATTN: Celeste Patena
8521 Laguna Station Road
Elk Grove, CA 95758

Phone: 916.875.9027 (direct)
916.875.9000 (main)
Fax: 916.875.9069
E-mail: patenac@sacsewer.com

Conventionals, Nutrients, Total Petroleum Hydrocarbons, Organic Carbon, OP Pesticides, Mercury, Methylmercury, Metals, and Pyrethroid Pesticides

Samples for BOD, alkalinity, TDS, TSS, turbidity, electrical conductivity, total phosphorus, TKN, nitrate-nitrite, COD, TPHs, OP pesticides, mercury, methylmercury, metals, pyrethroids, TOC, and DOC are transported to Caltest (Napa, California). Caltest provides courier service and should be contacted in advance to schedule a pick-up.

Alternatively, the samples can be sent via California Overnight to:

CalTest Analytical Laboratory
ATTN: Greg Martindale and Melinda Kelley
1885 N. Kelly Road
Napa, CA 94558

Phone: 707.258.4000
Fax: 707.226.1001

OP Pesticides and PAHs

PHYSIS will serve as the primary lab for OP Pesticides and PAHs and will provide backup analytical support for pyrethroid pesticides. The field crew, with assistance from the monitoring manager, will prepare samples for delivery and will be responsible for shipment.

Ship samples to:

PHYSIS Environmental Laboratories
ATTN: Misty B. Mercier
1904 East Wright Circle
Anaheim, CA 92806

Phone: 714.602.5320 x202
E-mail: mistymercier@physislabs.com

Appendix A.
Site Checklists and Field Data Forms

Sump 111 (UR3)

Sump 111 drains the smallest area, but it also drains the fastest due to a large percent of impervious surface. The sampler fills fast and we only take grabs when the pumps are on. The following procedures should be followed during each storm event site visit.

SITE SPECIFIC SAFETY NOTES

- **Be mindful of your surroundings, especially when entering the site**
- **Do not cross the safety barrier surrounding the wet well**

ACCESS NOTES

- Single key unlocks entry gate and shed.
- Lock is daisy-chained.
- Control 12 should be notified when visiting during any period other than a storm event

SITE SPECIFIC SAMPLING PROCEDURES

- ☐ Inspect sampling unit and bottle. Check with monitoring manager to see how many samples should have been taken
- ☐ Take grab samples in wet well using rope and bailer.
    - TOC/DOC
    - TPH Diesel and Gasoline
    - Fecal coliform and e. coli
    - Extra Volume for LWA
    - QAQC (blanks should be run through clean bailer before sampling environmental)
- ☐ Take field measurements using an intermediate container
- ☐ Take total mercury and methylmercury grabs
    - Return to the pump station and notify the monitoring manager that you are taking mercury grabs
    - Pause the sampler (press **Change/Halt**)
    - Pump mercury samples using clean hands/dirty hands
        - Remove tube from carboy
        - Press **Purge** (5 seconds)
        - Press and hold **Pump** until bottle is full
        - Replace tube in carboy
    - Notify monitoring manager when finished with grabs. Monitoring manager might request additional manual grab. If so, press **Take Sample**.
    - When finished press **Resume Program**
- ☐ Make sure screen shows Program Running and wait until sample is collected before leaving site

Strong Ranch Slough (UR2S)

Strong Ranch Slough responds fairly quickly to precipitation but it can take about twice as long as the storm event to fully drain.

SITE SPECIFIC SAFETY NOTES

- **Only visit site during daylight hours. Notify monitoring manager if sampling activities are not complete and it is becoming dark**
- **Always be mindful of your surroundings, especially when entering the site**
- **Bring vehicle into gated area and close and lock gate behind you.**
- **Do not enter the channel during a storm event**
- **Most if not all of the sampling should be performed inside gated area. Notify monitoring manager if any activities need to be performed on the other side.**

ACCESS NOTES

- Single key unlocks entry gate and sampling box.

SITE SPECIFIC SAMPLING PROCEDURES

- ☐ Inspect sampling unit and bottle. Check with monitoring manager to see how many samples should have been taken
- ☐ Take grab samples by pausing the sampler and pumping sampler through the peristaltic pump.
    - TOC/DOC
    - TPH Diesel and Gasoline
    - Fecal coliform and e. coli
    - Total mercury and methylmercury
    - Extra volume for LWA
    - Volume for field measurements
    - QAQC
  - Pause the sampler (press **Change/Halt**)
  - Pump mercury samples using clean hands/dirty hands
    - Remove tube from carboy
    - Press **Purge** (5 seconds)
    - Press and hold **Pump** until bottle is full
    - Replace tube in carboy
  - Notify monitoring manager when finished with grabs. Monitoring manager might request additional manual grab. If so, press **Take Sample**.
  - When finished press **Resume Program**
- ☐ Make sure screen shows Program Running and wait until sample is collected before leaving site

North Natomas Detention Basin No. 4 (UR5)

North Natomas Detention drains slowly and is generally the last site to visit.

SITE SPECIFIC SAFETY NOTES

- **Always be mindful of your surroundings, especially when entering the site**
- **Do not enter the channel if conditions appear unsafe**
- **Most if not all of the sampling should be performed inside gated area. Notify monitoring manager if any activities need to be performed on the other side.**

ACCESS NOTES

- Key to unlock gate at the street
- Combination lock to unlock gate and sampling box (1514)

SITE SPECIFIC SAMPLING PROCEDURES

- ☐ Inspect sampling unit and bottle. Check with monitoring manager to see how many samples should have been taken
- ☐ Take grab samples from the channel by using a grab pole:
    - TOC/DOC
    - TPH Diesel and Gasoline
    - Fecal coliform and e. coli
    - Total mercury and methylmercury
    - Extra volume for LWA
    - QAQC
- ☐ Take field measurements from the channel
    - Pump mercury samples using clean hands/dirty hands
- ☐ Make sure screen shows Program Running and wait until sample is collected

Bottle Change Procedure

- ☐ Notify monitoring manager before changing bottle
- ☐ Press **Change/Halt**
- ☐ Remove tubing from carboy and secure in sanitary glove or bag
- ☐ Place lid on carboy
- ☐ Slowly and safely remove carboy and place it in cooler or bucket
- ☐ Replace with clean carboy and reinsert tube
- ☐ Press Resume Program
- ☐ Make sure screen says **Program Running**
- ☐ Notify monitoring manager
- ☐ Ice carboy with sample

Composite Filter (dissolved metals)

Dissolved metals need to be poured off and filtered upon removal of the last carboy at each site. This needs to be done within 15 minutes from when the carboy took the last sample

- ☐ Notify monitoring manager
- ☐ If more than one carboy, monitoring manager will provide composite amounts. For example, 200 mL from carboy 1 and 300 mL from carboy 2
- ☐ Carefully pour amounts into filter receptacle
- ☐ Turn on vacuum pump.
- ☐ When completed label and place container on ice.

Field Sampling Data Log Sheet

Sacramento Stormwater Monitoring Program

Site: **Strong Ranch Slough** **Site Id:** **UR2S**

Sample Crew: _____ Personnel: _____

Arrival time: _____ Departure Time: _____

Habitat Observations: Circle your observations

Dominate Substrate concrete cobble gravel sand mud unknown other

Site Odor none sulfides sewage petroleum mixed other

Other Presences vascular nonvascular oily sheen foam trash other

Water Odor none sulfides sewage petroleum mixed other

Water Clarity clear (can see bottom) cloudy (>4" vis.) murky (<4" vis.)

Water Color clear brown green grey yellow other

Sky Code clear partly cloudy overcast fog haxy

Current Precipitation none foggy drizzle rain snow

Prec (last 24 hours) unknown <1" >1" none

Wadeable Yes No

Photos	
upstream	☐
downstream	☐
other	

Field Measurements

Time	pH*	EC (µS/cm)	DO (mg/L)	Water Temp (°C)	Air Temp (°C)	Turbidity (NTU)
Range:	6.5-8.5	≤240	≥7	NA	NA	NA
Instrument(s)	_____	_____	_____	_____	_____	_____
Calibration Date(s)	_____	_____	_____	_____	_____	_____

* Recalibrate if pH or DO are outside the specficied range. Record post-calibration results as field measurements

Samples Collected

Sample Location: **Collection Time:**

Analytes	Sample Type	Collection Depth (m)	Bottle Number	Bottle Type	Notes
TPH Diesel and Motor Oil	Grab		2	1L AG	
TPH Gasoline	Grab		3	40 mL VOA w/HCl	
TOC	Grab		3	40 mL VOA w/HCl	
DOC	Grab		1	125 AG	
Methylmercury	Grab		1	500 AG w/HCl	
Mercury, total	Grab		1	500 G w/HCl	
Fecal Coliform and E. coli	Grab		1	100 mL Sterile Plastic	
LWA Extra Volume	Grab		2	1L AG	
Composite	Composite		_____	20L G	
Dissolved Metals	Composite		1	500mL Filter	

Additional Notes or Comments

Field Sampling Data Log Sheet

Sacramento Stormwater Monitoring Program

Site: **Sump 111** **Site Id:** **UR3**

Sample Crew: _____ Personnel: _____

Arrival time: _____ Departure Time: _____

Habitat Observations: Circle your observations

Dominate Substrate	concrete cobble gravel sand mud unknown other
Site Odor	none sulfides sewage petroleum mixed other
Other Presences	vascular nonvascular oily sheen foam trash other
Water Odor	none sulfides sewage petroleum mixed other
Water Clarity	clear (can see bottom) cloudy (>4" vis.) murky (<4" vis.)
Water Color	clear brown green grey yellow other
Sky Code	clear partly cloudy overcast fog haxy
Current Precipitation	none foggy drizzle rain snow
Prec (last 24 hours)	unknown <1" >1" none
Wadeable	Yes No

Photos	
upstream	☐
downstream	☐
other	

Field Measurements

Time	pH*	EC (µS/cm)	DO (mg/L)	Water Temp (°C)	Air Temp (°C)	Turbidity (NTU)
Range:	6.5-8.5	≤240	≥7	NA	NA	NA
Instrument(s)	_____	_____	_____	_____	_____	_____
Calibration Date(s)	_____	_____	_____	_____	_____	_____

* Recalibrate if pH or DO are outside the specficied range. Record post-calibration results as field measurements

Samples Collected

Sample Location: **Collection Time:**

Analytes	Sample Type	Collection Depth (m)	Bottle Number	Bottle Type	Notes
TPH Diesel and Motor Oil	Grab		2	1L AG	FD
TPH Gasoline	Grab		3	40 mL VOA w/HCl	FD
TOC	Grab		3	40 mL VOA w/HCl	FD
DOC	Grab		1	125 AG	FD
Methylmercury	Grab		1	500 AG w/HCl	FD
Mercury, total	Grab		1	500 G w/HCl	FD
Fecal Coliform and E. coli	Grab		1	100 mL Sterile Plastic	FD
LWA Extra Volume	Grab		2	1L AG	FD
Composite	Composite		_____	20L G	FD
Dissolved Metals	Composite		1	500mL Filter	FD

Additional Notes or Comments

Appendix B.
Chain of Custody Forms

LARRY WALKER ASSOCIATES 1480 DREW AVE, DAVIS, CA 95618 TEL: 530.753.6400 FAX: 530.753.7030

CHAIN-OF-CUSTODY RECORD

DATE: **Lab ID:**

DESTINATION LAB:

ADDRESS:

PHONE:

FAX:

SAMPLED BY:

LWA TASK MANAGER:

LWA PROJECT MANAGER:

LARRY WALKER ASSOCIATES

	Client Sample ID	Sample Date	Sample Time	Sample Matrix	Container #	Container Type	Container Pres.	REQUESTED ANALYSIS				Grab NOTES
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												

SENDER COMMENTS:

RELIQUINSHED BY

Signature:

Print:

Company:

Date: Time:

LABORATORY COMMENTS:

RECEIVED BY [2]

Signature:

Print:

Company:

Date: Time: