

Quality Assurance Plan Hg Analytical Laboratory, 2012



National Atmospheric
Deposition Program

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General Mission of the MDN:

The National Atmospheric Deposition Program – Mercury Deposition Network (NADP/MDN) is a long-term monitoring program in support of research on the effects of atmospheric Mercury deposition. Our mission is to monitor our chemical climate for total mercury and methyl mercury in rain and snow precipitation through a national network of standardized monitoring stations. This enables the measurement of temporal and geographic trends.

Quality Assurance Plan Approval Form

The Quality Assurance Plan has been reviewed and approved by the following authorized National Atmospheric Deposition Program, Frontier Global Sciences, signatories for quality assurance documents.

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Table of Contents

| | |
|--|-----------|
| Section A: Program Overview | 7 |
| A1 Introduction | 8 |
| A2 Organization and Responsibilities | 8 |
| A3 Training Program | 11 |
| A4 Quality Assurance | 12 |
| A5 HAL Capital Equipment for Analytical Use | 14 |
| A6 Ultra Clean Facilities Monitoring | 14 |
| Section B: Laboratory Operations | 15 |
| B1 Laboratory Procedures | 16 |
| B2 Sample Analysis | 19 |
| B3 Performance and System Audits | 23 |
| B4 Corrective Action | 23 |
| B5 Proficiency Testing Program | 24 |
| B6 Laboratory Intercomparison Studies | 24 |
| Section C: Data Management Operations | 25 |
| C1 Preventive Maintenance/Service | 26 |
| C2 Data Management Operations | 26 |
| C3 Recordkeeping | 27 |
| C4 Network Field Supplies | 28 |

Appendixes

| | |
|--|----|
| Appendix 1: HAL Sample Flow Chart | 32 |
| Appendix 2: Lab Data Management Flow Chart | 33 |
| Appendix 3: MDN Equipment Flow Chart | 34 |

Figures and Tables

| | |
|---|----|
| Figure 1: Mercury Analytical Laboratory Organizational Chart | 8 |
| Table 1: Calibration Frequency of Support Equipment used at HAL | 17 |
| Table 2: MDN Specific SOP List | 29 |
| Table 3: Supplemental SOP List | 30 |
| Table 4: Example of an Analytical Run Sequence | 31 |

Definitions of Abbreviations and Acronyms

| | |
|----------|---|
| APDC | Ammonium PyrrolidineDithioCarbamate |
| AS/ASD | Analytical Spike/ Analytical Spike Duplicate |
| ASTM | American Society for Testing and Materials |
| BS/BSD | Blank Spike/ Blank Spike Duplicate |
| CCB | Continued Calibration Blank |
| CCV | Continued Calibration Verification |
| CFR | Code of Federal Regulations |
| CHP | Chemical Hygiene Plan |
| CRM | Certified Reference Material |
| CVAFS | Cold Vapor Atomic Fluorescence Spectrometry |
| DBMS | Database Management System |
| DMRQA | Discharge Monitoring Report-Quality Assurance |
| DQO | Data Quality Objectives |
| EPA | Environmental Protection Agency |
| EMOF | Electronic Mercury Observer Form |
| FGS | Frontier Global Sciences |
| HAL | Mercury (Hg) Analytical Laboratory |
| IAEA | International Atomic Energy Agency |
| ICB | Initial Calibration Blank |
| ICV | Initial Calibration Verification |
| LCS/LCSD | Laboratory Control Sample/Laboratory Control Sample Duplicate |
| LIMS | Laboratory Information Management System |
| LOD | Limit of Detection |
| LOQ | Limit of Quantitation |
| MD | Matrix Duplicate |
| MDL | Method Detection Limit |
| MDN | Mercury Deposition Network |
| MMHg | Methyl Mercury |
| MOF | Mercury Observer Form |
| MRL | Method Reporting Limit |
| MS/MSD | Matrix Spike/ Matrix Spike Duplicate |
| NADP | National Atmospheric Deposition Program |
| NELAC | National Environmental Laboratory Accreditation Conference |
| NELAP | National Environmental Laboratory Accreditation Program |
| NIST | National Institute of Standards and Technology |
| NTN | National Trends Network |
| NPDES | National Pollutant Discharge Elimination System |
| NRCC | National Research Council Canada |
| PO | Program Office |
| PQL | Practical Quantitation Limit |
| PT | Proficiency Test |
| QA | Quality Assurance |

Definitions of Abbreviations and Acronyms Continued

| | |
|------|---------------------------------|
| QC | Quality Control |
| QAP | Quality Assurance Plan |
| RPD | Relative Percent Difference |
| SOP | Standard Operating Procedure |
| THg | Total Mercury (Hg) |
| TNI | The NELAC Institute |
| USGS | United States Geological Survey |

Section A: Program Overview

A1 Introduction

Since January 1996, Frontier Global Sciences Inc, previously named Frontier GeoSciences Inc., (FGS) has served as the Mercury Analytical Laboratory (HAL) and the Network Operations Center, for the Mercury Deposition Network (MDN). The MDN, coordinated through the National Atmospheric Deposition Program (NADP), was designed with the primary objective of quantifying the wet deposition of mercury in North America to determine long-term geographic and temporal distributions. The Network has grown to incorporate over 110 sites in North America by the end of 2010. For the current site map go to <http://nadp.isws.illinois.edu/maps>. At the HAL, FGS provides site support, sample processing, sample analysis, and data validation services for precipitation samples collected at the NADP/MDN monitoring sites. All these processes must follow documented quality assurance and quality control procedures. The Quality Assurance Plan (QAP) describes these procedures and indicates how they are to be monitored and quantified. The QAP is reviewed annually and updated as necessary.

A2 Organization and Responsibilities

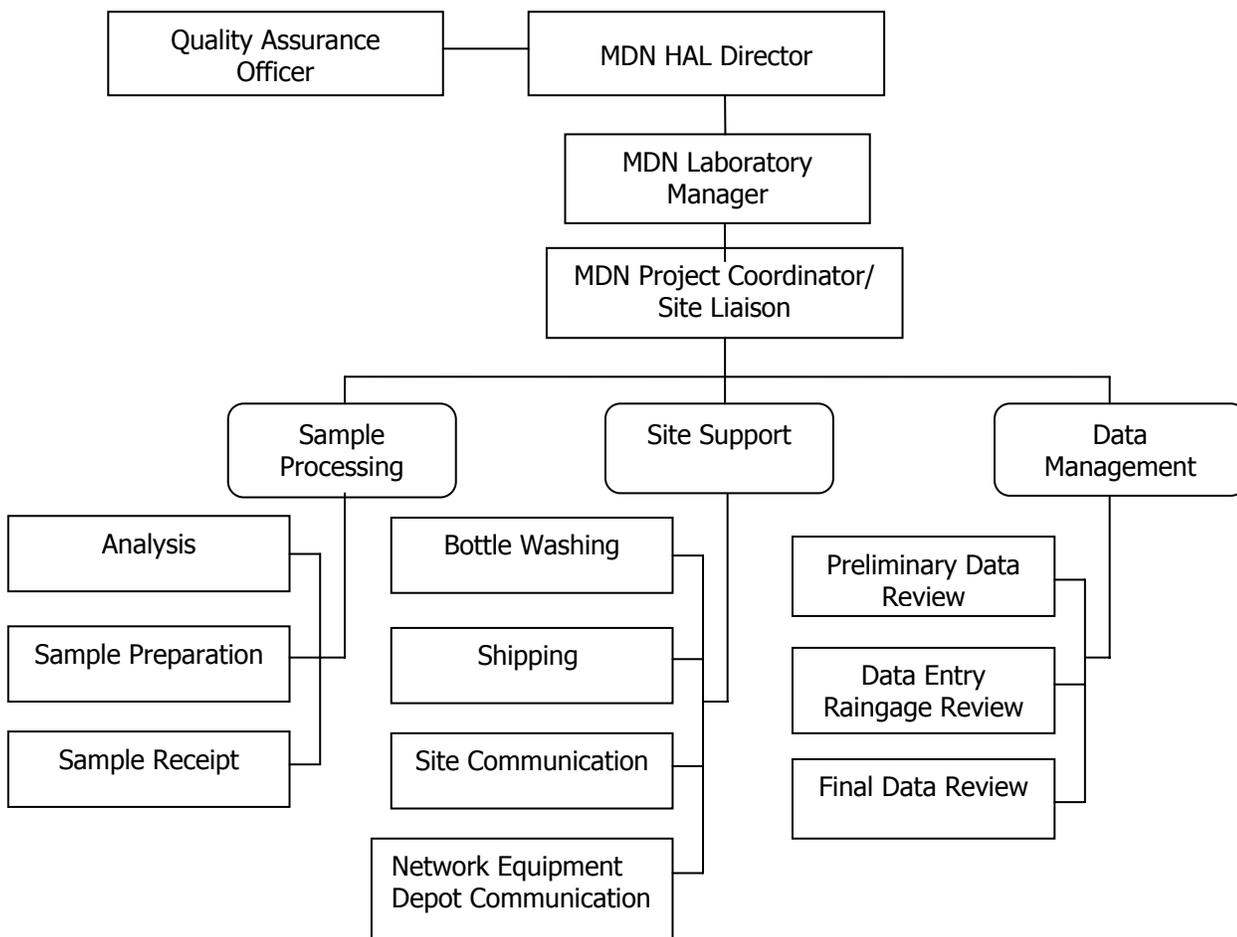


Figure 1: Mercury Analytical Laboratory Organizational Chart

A2.1 HAL Director

The HAL Director oversees HAL's involvement in the MDN. The Director serves as the HAL contact for the multiple agencies currently sponsoring the MDN. The Director provides guidance and direction to all HAL staff and maintains proficiency in all aspects of HAL activities including:

- Site selection and equipment installation,
- Equipment troubleshooting,
- Field and laboratory training,
- Analysis and report writing, and
- Research on new initiatives.

A2.2 MDN Laboratory Manager

The MDN Laboratory Manager reports directly to the HAL Director.

- The Laboratory Manager's goal is to produce data that meets the Data Quality Objectives (DQO) while maintaining required supplies and data turn-around-times, cost effectiveness, sustainable laboratory practices, employee job satisfaction, and supportive customer relations.
- The Laboratory Manager has ultimate responsibility for the quality of all analytical laboratory data, reports, practices, and safety.
- The Laboratory Manager ensures that data meet all quality control requirements, and takes appropriate and documented corrective action if it does not.
- It is the Laboratory Manager's responsibility to ensure that all staff members understand and adhere to this QAP and relevant Standard Operating Procedures (SOP).
- The Laboratory Manager maintains proficiency in, site selection and equipment installation, equipment troubleshooting, field and laboratory training, analysis and report writing.

A2.3 Project Coordinator

The MDN Project Coordinator manages and supports the HAL by scheduling and supervising the lab staff, and providing backup assistance with glass cleaning and preparation, shipping and receiving, sample preparation, digestion and preservation.

- Ensures that the MDN area is maintained and kept clean.
- Demonstrates proactive commitment and adherence to industry and company safety regulations and procedures through scientific literature, user groups and seminars.
- Together with Quality Assurance Officer, ensures training protocols are up-to-date and properly documented.
- Revises the SOPs used by the group according to the schedule.
- It is the MDN Project Coordinator's responsibility to ensure that all group members have up-to-date documentation of Demonstration of Capability.
- Reviews and reports MDN Analytical and Field data to Site Operators and to the NADP Program Office.

A2.4 Site Liaison

The Site Liaison is the primary contact with the monitoring sites and supports tracking shipments, troubleshooting equipment, reading raingage charts, assisting clients with requests, and providing backup assistance with glass cleaning and preparation, shipping and receiving, sample preparation, digestion and preservation.

- Proactively tracks and manages all shipments to MDN sites, ensuring that they arrive promptly and to the correct location.
- Communicates with off-site research project staff, nationally and internationally, on procedural and troubleshooting issues via phone, fax, email, and internet site.
- Assists clients with troubleshooting MDN equipment when issues arise.
- Gives reports and participates in discussions at NADP committee meetings twice a year.
- Logs all MDN communications and documents all conversations with clients.
- Prepares and updates SOPs, operation manuals, memos, QA documents, and communications related to site operations including support materials for operational protocols, and equipment troubleshooting and repair.
- Conducts data analysis and review from sites for completeness and accuracy, and communicates with site operators and data validation staff to ensure high quality data records are obtained.
- Troubleshoots precipitation collection and raingage equipment.
- Reads, interprets and monitors raingage charts and electronic records.
- Plans and performs an Annual (or as needed) Field Training Course for MDN Site Operators.

A2.5 Quality Assurance Officer

The Quality Assurance (QA) Officer's goal is to improve the laboratory's quality assurance/quality control (QA/QC) processes in a manner consistent with the MDN mission statement. This requires support from the Management and laboratory staff. The QA Officer ensures that all laboratory decisions are considered from a QA standpoint. Specifically, the QA Officer has the following responsibilities relating to laboratory QA systems:

- Coordinates and documents training procedures for laboratory staff, including QA orientations and ethics training.
- Advises when problems occur from facilities testing programs (e.g., reagent water, bottles, equipment, and air).
- Investigates rejected datasets.
- Investigates corrective actions and ensures their proper implementation.
- Manages proficiency tests and interlaboratory comparison studies.
- Maintains, reviews, and updates controlled documents including the QAP and SOPs used by HAL.
- Provides staff members with QA information as needed.
- Performs other relevant tasks associated with FGS's QA requirements.
- Generates the annual Quality Assurance Report for MDN.
- Member of the NADP Quality Assurance Advisory Group.
- Performs annual internal audit of the HAL.

The QA Officer works closely with the HAL Laboratory Manager, the Project Coordinator, and the Site Liaison to ensure that all staff members adhere to this QAP and relevant SOPs, and that scientific excellence remains FGS's top priority.

A3 Training Program

All personnel are trained appropriately in their assigned tasks before they contribute to functions that can affect data quality. Staff members are trained in new skills or methods through a mentorship process. It is management's responsibility to ensure personnel are trained. Training records are used to document management's approval of personnel competency.

A3.1 Training of New Staff

New staff members are given the following training:

- Initial Quality Assurance training on the day of employment.
- Ethics training. The employee must read the "Quality Assurance Standards and Policies" section of this Quality Manual. This shall be done on the first day of employment.
- All new full time employees shall read the general Frontier Global Sciences Quality Manual, within the first week of employment.
- Employees associated with the MDN network shall also read this document, the Quality Assurance Plan for the Mercury Analytical Laboratory, within the first month of employment.
- New staff members receive a binder with the SOPs they need to read. The binder contains general SOPs that all employees need to read and also SOPs specific to their working area. The binder shall be returned to the QA office together with a form documenting the training signed by the employee and the supervisor.
- The Chemical Hygiene Plan (CHP). The employee must read and correctly answer the questions in the CHP before doing any laboratory work. Incorrect answers will be discussed with the new employee.
- The employee shall be given an initial safety tour on the day of employment.
- An overview of the Employee Handbook will be given by the Human Resource Manager.
- Signing of confidentiality agreement.

All initial training must be documented and a signed. Signed records are maintained in the employee training file.

New employees or staff members, who are learning a new skill or method, are assigned to their immediate supervisor or a senior coworker. The new method is taught according to the following steps:

- Reading the SOP.
- Observing performance of the method.
- Closer reading of the SOP, associated literature, and other notes.
- Supervised practice of the method on non critical work, until the supervisor is satisfied that the employee is competent. Competency is demonstrated when an acceptable Initial Demonstration of Capability (IDOC) has been submitted and approved by the Quality Assurance Officer. This shall be done both for methyl mercury distillation process, total mercury analysis, and methyl mercury analysis.

A3.2 Ongoing Training

All technical staff shall be given the following annual training:

- Annual Ethics and Data Integrity training. All employees are required to sign the Ethics and Data Integrity Policy.
- All technical staff members shall undergo annual general laboratory safety training.
- All employees shall attest annually, by signing the training form that they have read, understood, and agreed to follow the current version of the QAP and any SOPs that are related to their job duties.
- The analysts shall show ongoing demonstration of capability in applicable areas on an annual basis.

A4 Quality Assurance

A4.1 Quality Assurance Policy Statement

HAL is committed to Quality Assurance, viewing it as both a program and a philosophy. Quality control begins at the bench level, and management continuously works to improve processes with a focus on prevention of analytical problems. HAL's laboratory staff is trained to troubleshoot and initiate corrective actions. Process improvements and problem solving are solicited from the technicians and analysts, and management implements the solutions. This helps keep management informed while at the same time promoting the professional growth of HAL's staff.

HAL is dedicated to providing high-quality data that meets the needs of the MDN. Accurate and precise data depends on these basic principles:

- Sample integrity must be preserved. All documented sample handling procedures for preservation, custody, storage, labeling, and recordkeeping are followed.
- Trace metal-free ("ultra-clean") sample handling must be employed. Samples that are analyzed for low-level mercury or methyl mercury concentrations are handled according to established protocols. This includes the use of Class-100 clean hoods, clean gloves, and pre-tested and approved reagents, water, and equipment. High-level (contaminated) samples are kept segregated from ultra-clean samples during storage and sample preparation.
- Approved analytical methods must be followed. The analyst's fundamental understanding of analytical methods is paramount for effective quality control. Emphasis on scientific understanding and adherence to procedure is part of every analyst's training. QC results from each method are evaluated to identify and correct method weaknesses, and to detect any need for further training.
- Analytical instrumentation must be in proper working order. Optimum instrument performance is ensured by analyzing daily calibration and performance evaluation samples. Preventative maintenance is performed on a regular basis and is documented in the instrument logbooks.
- Raw data must be reduced properly and accurately transcribed into the correct reporting format.
- Data review, from acquisition to the final report, is performed throughout to minimize error.

A4.2 Quality Assurance Objectives

HAL data quality is assessed against FGS's DQO to ensure production of high-quality coherent data. The DQO consist of five elements: precision, accuracy (bias), representativeness, comparability, and completeness. These elements are evaluated annually and the results are presented in Annual QA Reports.

- *Precision* is a measure of our ability to use our methods to analyze a sample repeatedly and get the same results each time. To demonstrate precision of a method, sample duplicates are analyzed and the results compared. The acceptance criterion for Matrix Duplicates is $\leq 25\%$ Relative Percent Difference (RPD).
- *Accuracy* or bias is a measure of how close the result is to the true or expected value of the target analyte in the sample. Accuracy may be determined by the analysis of reference materials, blank spikes, or matrix spikes where the results can be compared with a true or expected value. The acceptance criteria for Reference Materials and Matrix Spikes are 75-125% recovery.
- *Representativeness* describes how well a single sample can characterize the conditions of the entire sample population. Appropriate sampling techniques and artifact-free procedures, combined with sample homogenization, help achieve representative data.
- *Comparability* is a particularly important QA criterion for long-term projects. Individual data sets are evaluated with respect to other data from the same project to ensure the validity of trends in the data.
- *Completeness* is a measure of how many collected data points are usable. HAL strives for at least 95% analytical data completeness for the MDN project.

A4.3 Facilities and Equipment

Frontier's 18,000 ft² analytical laboratory is located in Bothell, Washington. The location is close to a FedEx ship center and has easy access to interstate 405. The space contains large laboratory areas for sample analysis, sample preparation, and bottle washing and is equipped with several Class-100 clean air stations. The facility has specially designed areas for sample storage, shipping and receiving, and hazardous waste disposal. HAL has a dedicated sample shipping and receiving area for the Mercury Deposition Network (MDN) that was designed especially for MDN. Frontier's entire space is a locked facility.

The laboratories are served by a custom-designed HVAC system, providing an atmosphere that is clean and well isolated from outside dust and dirt. Disposal of all other toxic materials is carried out under contract with a certified disposal company. The entire FGS space is inspected periodically for compliance with all city and state code requirements for fire and emissions.

The offices are equipped with document production equipment including laser printers, document and image-processing software, high volume photographic-quality color printer, large-capacity collating copiers, and a binding machine. A LAN connects staff computers and printers for local access, as well as providing external email, fax, and Internet access. Frontier also maintains a web site at www.FrontierGS.com (www.FrontierGeosciences.com is still active), and has a FedEx Powership shipping computer with access to FedEx pick-up as late as 5:00 PM Pacific time. The laboratory has staff available on Saturdays to receive sample shipments.

A4.3.1 Building Security

Access to Frontier offices and laboratories is regulated and limited to authorized personnel. All outside doors are kept locked at all times. Visitors must first identify themselves before being admitted by an FGS employee. Visitors are required to check in and sign the logbook (LOG- HS-001 Visitor Log) on arrival, and to sign out on departure. All visitors must wear a "Visitor" batch while on-site. Regular visitors may be allowed unescorted access to general areas of the building, provided that their names and other details are recorded at the front desk. All other visitors in laboratory areas must be accompanied by a Frontier employee.

A5 HAL Capital Equipment for Analytical Use

| Quantity | Instrumentation |
|-----------------|--|
| 12 | Cold Vapor Atomic Fluorescence Hg Detector |
| 3 | Isothermal GC for Hg Speciation |
| 2 | Class-100 Clean Air Hood |
| 6 | Methyl Hg Distillation Units |
| 1 | Gold Sputter Coater |
| 1 | RO Reagent Water System |

A6 Ultra Clean Facilities Monitoring

A6.1 Air Monitoring

HAL's mercury analyses require ultra low levels of mercury in laboratory air. All laboratories at HAL are monitored for mercury contamination by direct measurements with a real time low level atmospheric Hg detector. The action limit for laboratory air is 25 ng/m³. If a laboratory's air exceeds the action limit, air flow is increased and the location is monitored until levels agree with previously collected background data from this location. Records of each test are maintained by the QA Office and are available upon request.

A6.2 Reagent Water Monitoring

Ensuring that reagent water is free of contamination sources for sampling and analysis of ambient water is critical to HAL's laboratory facilities. The reagent water monitoring program gives additional quantitative evidence that the process is contaminant-free. Records of each test performed under the reagent water monitoring program are maintained in the Memo Note section associated with the Work Order.

The mercury warning limit for the weekly waters is set at <0.25 ng/L. If the concentration is greater than 0.5 ng/L for mercury, a new sample shall be collected and tested. If the source comes out high two consecutive times the Laboratory Manager, the Project Coordinator, the Site Liaison, and the Quality Assurance Officer shall be notified in an email message and the water shall not be used. A maintenance visit may need to be scheduled to resolve the problem.

Section B: Laboratory Operations

B1 Laboratory Procedures

B1.1 Documentation

HAL's goal is to be able to trace all laboratory measurements to their original source. The HAL uses traceable reagents, standards, and reference materials in all procedures. Instrument calibration, reagent and bottle testing, and equipment maintenance are all thoroughly documented. All calibrations are traceable to certified standards or manufacturer lot numbers. For analytical instruments, high purity calibration standards are obtained from chemical suppliers. Certificates attesting to the concentration ranges of the covered analytes are retained by the QA Officer.

B1.2 Reagents and Standards

Standards and reagents are documented in LIMS upon receipt or creation. A LIMS generated label is affixed to each standard and reagent, with the name of the solution, the person who prepared or received it, the date it was prepared or received, and the expiration date. All standards and reagents are logged into LIMS individually (one LIMS ID per sample container). The LIMS documentation must include the following:

- A description of the standard;
- Department,
- Expiration date of the standard (not to exceed the expiration of the parent standard),
- The name of the person that prepared the standard or reagent,
- The date it was prepared (or received),
- Final volume,
- A reference date (date entered into LIMS),
- Concentration units ($\mu\text{g}/\text{mL}$),
- The vendor and the vendor lot (the solvent lot is not applicable),
- The correct parent standard must be documented, as well as the aliquot used; and
- Analytes are entered individually.

Where possible, the HAL uses reference materials that are certified and traceable to national or international standards of measurement. These do not require testing, provided there is a Certificate of Analysis on file with the QA Officer.

The mercury analyst shall notify the QA Officer each time a new standard is prepared, the LIMS ID of the new standard, and requests a work order to document standard testing. The QA Officer creates a work order and enters the work order into the comments section of the standard. Working reagents are prepared by the analyst and logged into LIMS and assigned a unique identifier. All reagents used during analysis and prep should be added to the bench sheets. Additionally, reagents undergo continuous monitoring through analysis of method blanks. A method blank is a sample of reagent water and analytical reagents that undergoes the same analytical process as the corresponding samples. A minimum of three method blank samples are prepared with each analytical batch. For MDN, a typical analytical batch consists of 30 samples.

B1.3 Expiration Date and Opening Dates on Standards and Reagents:

The expiration date is set to no longer than three years if no expiration date is given by the manufacturer. Expiration dates can be extended if the reference standard's or material's integrity is verified. The extended date may not be beyond the expiration date of the referenced standards used to re-verify. All standards and reagents shall be labeled with the date they were opened and the initials of the analyst who opened the container.

B1.4 Calibration of Support Equipment

Support equipment used at HAL is calibrated an external ISO certified calibration company or calibrated internally. The equipment used is;

| Equipment | Frequency | Source | Comments |
|----------------------|--------------------|------------|---|
| Balances | bi-yearly | externally | used to weigh out sample aliquot size |
| Balances | daily before usage | internally | used to weigh out sample aliquot size |
| ASTM Class 1 Weights | yearly | externally | used for internal balance calibration |
| Pipettes | daily | internally | used for BrCl preservation |
| Pipettes | weekly | internally | all, except the pipettes used for BrCl preservation |
| Repipettors | bi-yearly | externally | used for preparing 1% HCl charge solution |
| Repipettors | monthly | internally | used for preparing 1% HCl charge solution |
| Thermometers | yearly | externally | used for temperature monitoring |
| Refrigerators | daily | internally | temperature verified daily |

Table 1: Calibration Frequency of Support Equipment used at HAL.

Equipment that has been subject to overloading, mishandling, given suspect results, or shown to be defective or outside specifications is taken out of service. The equipment shall be labeled clearly as being out of service until it has been shown to function properly and the QA department has related paperwork on file for documentation. If it is shown that previous tests are affected, then procedures for nonconforming work in FGS-039 is followed and results are documented.

When support equipment is checked or calibrated, measurements are recorded in laboratory logbooks or in the calibration file in the QA Office. The calibration tolerances of the analytical support equipment are listed in their respective SOPs (FGS-002 "Balance Verification, Calibration and Maintenance," FGS-003 "Pipette Verification, Calibration & Maintenance," and FGS-004 "Refrigerator & Freezer Calibration and Maintenance").

B1.5 Calibration of Analytical Instruments

Every instrument used to analyze samples at the HAL must pass the calibration criteria in the relevant SOP. Initial calibration criteria for instrument reproducibility and sensitivity must be

met before samples may be analyzed. Continuing calibration verification (CCV) checks establish whether ongoing instrument calibration is acceptable. Before a new mercury instrument is used a PQL/MDL study must be performed on the instrument. Instrument approval must be documented and kept on file with the Quality Assurance Officer. New support equipment, such as pipettes, must be received with a record of calibration, which is turned in to the QA department for archiving.

The calibration protocols and the control criteria for total mercury and methyl mercury analysis are outlined in SOP MDN-05 "MDN Total Mercury Analysis" and MDN-08 "MDN Methyl Mercury Analysis

The lowest calibration standard is the lowest concentration for which quantitative results can be reported without qualification. The lowest calibration standard is at the Limit of Quantitation (LOQ or PQL), or lower, and is greater than the Limit of Detection (MDL or LOD). Results that are less than the lower calibration standard are considered to have increased uncertainty.

The highest calibration standard is the highest concentration for which quantitative results can be reported. The sample shall be diluted and reanalyzed within the calibration curve. If the volume has been exhausted and the analytical result was above the highest calibration point a standard greater than the sample result shall be analyzed to verify the linearity of the calibration curve at the level of the sample. The sample shall be reported with a qualifier.

B1.6 Calibration Verification for Analytical Instruments

An ICV is analyzed following each calibration curve to verify the accuracy of the primary standard solution. The ICV is a solution made from a second source standard, traceable to a national standard when commercially available, and independent of that used in the primary standard solution.

CCVs verify that the analytical system is in control, or to demonstrate analytical drift. The CCV is a standard solution that is made from a traceable stock standard (usually the same source as the primary calibration stock). CCVs are analyzed at a frequency of every ten samples or less and at the end of each analytical sequence. All ICV/CCVs reference a unique identification number and are traceable through LIMS. All MDN raw data references a unique laboratory ID number and includes a unique identifier for each standard used in the analysis. These identification numbers are traceable through LIMS.

B2 Sample Analysis

B2.1 Laboratory Quality Control Samples

A laboratory control sample (LCS) may be a certified reference material or a Blank Spike (BS). A BS is a sample of reagent water or analytical reagents that has predetermined quantities of analyte added. It undergoes the same preparation and analytical processes as the corresponding samples. Blank spikes are used to evaluate the daily performance of a method, but are not subject to matrix effects that may occur in matrix spikes (MS). They are used primarily when no appropriate reference material is available for a particular matrix. The quality control criteria are discussed in the annual QA report, which also contain an example of an Analytical Run Sequence, see Table 4.

B2.2 Laboratory Bottle Blanks

B2.2.1 Description

Following cleaning, MDN sample bottles are charged with 20 mL of 1% hydrochloric acid. One sample bottle is selected randomly from each cleaning event and is analyzed for total mercury. On average, 2-3 laboratory bottle blanks are analyzed each week for total mercury. At least one bottle blank should be collected per month and analyzed for methyl mercury. The quality control criteria are discussed in the annual QA report. For each bottle blank, the vat in which the bottle was cleaned is recorded on the bottle blank form in Appendix A, FGS MDN-009. The acid vats in the bottle washing rooms are tested on an as needed basis. The cleanliness of the bottles demonstrates the effectiveness of the vats used for bottle cleaning. Each vat should include what acid it contains, the acid's LIMS ID, the concentration of the acid, when the vat was started, and by whom. This information should be included when additional acid is added.

B2.2.2 Purpose

Even in an ultra-clean laboratory, mercury exposure is inherent to the handling of MDN sample bottles. Because such contamination is inevitable, it must be analyzed and quantified so that it can be subtracted objectively from final sample results. The final sample results are corrected by the average bottle blank results from the previous month.

B2.3 Preparation Blanks

B2.3.1 Description

Preparation blanks for total mercury consist of bromine monochloride (1 % (v/v) BrCl), hydroxylamine hydrochloride (0.200mL), and stannous chloride (0.300mL) in 100mL of reagent water. The quality control criteria are discussed in the annual QA report.

Preparation blanks for methyl mercury consist of 45 mL reagent water, hydrochloric acid (0.4%), ammonium pyrrolidine dithiocarbamate (0.200mL of APDC) solution, ethylating agent (38.5 μ L), acetate buffer (0.300mL), and reagent water. The quality control criteria are discussed in the annual QA report.

B2.3.2 Purpose

Mercury contamination is inherent in sample preparation and in analytical reagents, in any laboratory setting. Preparation blanks are a measure of how much of each sample result can be attributed from these necessary reagents. Preparation blanks also help when investigating possible sources of contamination.

B2.4 Initial and Continuing Calibration Verification Standards

B2.4.1 Description

The Initial Calibration Verification (ICV) is a solution made from a second source standard, independent of what is used in the primary standard solution. For the MDN total mercury project, NIST 1641d is the secondary source analyzed after the calibration curve and also after the second set of matrix spikes, and is discussed under the Certified Reference Material (CRM) section.

A minimum of one Continuing Calibration Verification (CCV) standard is analyzed for every 10 samples during the course of the run, and at the end of each analytical run. The CCV is a standard solution that is made from a traceable stock standard (usually the same source as the primary calibration stock). A 10ng/L standard for total mercury and a 2ng/L standard for methyl mercury are analyzed as an ongoing calibration standard. The MDN control limits for ICVs and CCVs for total mercury are set to 80-120% and for methyl mercury ICVs are 80-120 and CCVs are 75-125%.

B2.4.2 Purpose

An ICV is analyzed following each calibration curve to verify the accuracy of the primary standard solution and to validate the calibration curve. CCVs verify that the analytical system is in control, or demonstrate analytical drift. All ICV/CCVs reference a unique identification number and are traceable through LIMS. All raw data references a unique laboratory ID number and includes a unique identifier for each standard used in the analysis.

B2.5 Continuing Calibration Blanks

B2.5.1 Description

Continuing Calibration Blanks (CCBs) are analyzed during the course of sample analysis directly after the ICV and the CCVs, with a minimum frequency of one per 10 samples, and at the end of each analytical run. The run must end with a CCB. Individually, the Initial and Continuing Calibration Blanks (ICB/CCBs) shall be less than 0.25ng/L to be within control limits for total mercury. For MHg the mean of the ICB/ CCB shall be less than 0.025 ng/L.

B2.5.2 Purpose

Instrument blanks are used to demonstrate freedom from system contamination, carryover, and to monitor baseline drift.

B2.6 Matrix Duplicates

B2.6.1 Description

Matrix Duplicates (MD) are created when an existing sample is split into two portions and then are compared analytically. The MDN control limit for the Matrix Duplicates is set at 25% RPD for total mercury. US EPA methods 1630 and 1631 do not require a MD. One MD is performed for every ten analyzed samples and during a standard MDN THg analytical run three MDs are analyzed. The source samples are selected depending on the available volume. For total mercury analysis, 100 mL is ideal, though when samples with sufficient volume are not available, HAL uses 50 mL or 75 mL aliquot volumes for the source sample, the MD and the MS, and for potential reanalysis of these QC samples. The quality control criteria are discussed in the annual QA report.

B2.6.2 Purpose

Replicate samples provide information about analytical precision. MDs are part of the same sample. As such, their Relative Percent Difference (RPD) is expected to be less than 25%. Out of control results are indications of a heterogeneous sample matrix and/or poor analytical precision.

B2.7 Matrix Spikes

B2.7.1 Description

A Matrix Spike (MS) for total mercury is created when a sample with known mercury content is split in two fractions and one fraction is supplemented with an additional 1.00ng of mercury standard.

For both EPA method 1631 and 1630, there must be 1 MS and 1 MSD sample for every 10 samples (a frequency of 10%) and the spiking level shall be at 1–5 times the background concentration or at 1-5 times the MRL (0.5ng/L for THg and 0.06ng/L for MHg), whichever is greater.

For MDN runs, due to limited sample volume, only one matrix spike (MS) is performed for every ten analyzed samples and during a normal analytical run three matrix spikes are analyzed. The source samples are selected depending on the available volume. 100mL is ideal, though when samples with sufficient volume are not available, HAL uses 50 mL or 75 mL aliquot volumes for the source for the source sample, the matrix duplicate and the matrix spike, and for potential reanalysis of these QC samples. No RPD data for MS/MSD is available for total mercury since only a MS is analyzed. A MS/MSD is performed for methyl mercury and the control limit for the RPD is <25%.

B2.7.2 Purpose

The purpose of analyzing a MS and MSD is to demonstrate the performance of the analytical method in a particular sample matrix, and to recognize matrix interference. To prepare a MS/MSD, predetermined quantities of the analyte are added to a sample matrix before (when possible) extraction or digestion of samples, in this case preservation with BrCl for total mercury and preservation with HCl and distillation for methyl mercury analysis. If the sample is spiked with the analyte of interest after extraction or digestion, this is considered an analytical spike and an analytical spike duplicate (AS/ASD). Low recovery of a matrix spike is a sign of matrix interference. After investigation by trap and bubbler test, the samples should be reanalyzed at a dilution. The purpose is to ascertain the largest aliquot size a sample can be analyzed at without matrix interference. The source sample shall then also be reanalyzed at the same aliquot size.

B2.8 Certified Reference Materials

B2.8.1 Description

Certified Reference Materials (CRMs) are matrix specific standards that are accompanied by a certificate of analysis for the analytes of interest. The HAL generally purchases reference materials from the National Institute of Standards and Technology (NIST), the National Research Council of Canada (NRCC), or the International Atomic Energy Agency (IAEA). The HAL maintains the position that matrix equivalent reference materials are the best measure of precision and accuracy (bias), as issues associated with matrix type and homogeneity may be assessed.

Currently, there is no available CRM matching the MDN rainwater matrix. Therefore, HAL uses National Institute of Standards and Technology (NIST) reference material 1641d "Mercury in Water." The percent recovery control limits for total mercury are currently set at 75-125% with a RPD of 25%. There is no CRM available for methyl mercury and therefore a Blank Spike and a Blank Spike Duplicate (BS/BSD) are analyzed for methyl mercury with acceptance criteria of 70-130%, with a RPD of 25%. The US EPA methods 1630 and 1631 do not require a certified reference material.

B2.8.2 Purpose

CRM are used to demonstrate HAL's ability to recover a target analyte from a specific matrix. The first CRM is analyzed right after the calibration curve to verify the validity of the analytical curve.

B2.9 Blank Spikes

B2.9.1 Description

A BS is a sample of reagent water or analytical reagents that has predetermined quantities of analyte added. It undergoes the same preparation and analytical processes as the corresponding samples.

B2.9.2 Purpose

Blank Spikes are used to evaluate the daily performance of a method, but are not subject to matrix effects that may occur in matrix spikes. They are used primarily when no appropriate reference material is available for a particular matrix.

B2.10 Method Detection Limits

Method Detection Limits (MDL) are determined according to 40 CFR Part 136, Section B. Ten replicates ($t-1$, 9 degrees of freedom, where t is the Student's T-value for the number of replicates) of matrix matched samples that are spiked at 1-10 times the expected MDL are analyzed. There is no recovery criterion for an MDL analysis, but the new calculated MDL value must be within 2*times of the previous established MDL. The standard deviation (σ) is taken from the resulting data and the MDL is determined as $t * \sigma$ of the replicates. For ten replicates, the MDL is calculated as follows: $MDL = 2.821 * \sigma$. This value should not be interpreted as the method reporting limit.

The Practical Quantitation Limit (PQL) is the reporting limit for the method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration that must normally meet a recovery of 70-130% (or the same recovery criteria which is applicable for the low non-standard calibration point, depending on the method). The PQL is also referred to as the Method Reporting Limit (MRL).

All MDL and PQL studies are on file with the Quality Assurance officer and are available upon request.

B2.11 Control Charts

For MDN the QC points include: LCS% Recovery, LCS/LCSD RPD, MS% Recovery, MS/MSD RPD, Duplicate RPD, ICV% Recovery, CCV% Recovery and Blanks are presented in graphs and are included in the annual QA report. Control charts allow the QA Officer and staff to spot unfavorable analytical trends as they are developing. Corrective actions for those trends can in

turn be assessed in real time. Additionally, control charts are used periodically in the calculation of efficiency factors for the methyl mercury distillation method.

B3 Performance and System Audits

B3.1 Internal Laboratory Audits

It is the responsibility of the QA Officer to coordinate and conduct annual internal audits of the laboratory according to SOP FGS-041, "Internal Quality Assurance Audits" to verify that the activities continue to comply with the requirements of the quality system and 2003 NELAC Standards/TNI standards. After the audit, the QA Officer lists the findings and observations in a table that is sent to the manager for the group. A meeting will also be held where the findings and the observations are discussed, and the time frame for the completion of the corrective actions is decided. Follow-up audit activities shall verify and record the implementation and effectiveness of the corrective action taken. Findings and Observations are defined as:

- **Findings** - items that deviate from NELAC standards, the FGS QAP, MDN QAP, and standard operating procedures.
- **Observations** - items that suggest omissions or potential improvements in the laboratory's quality systems.

B3.2 External Laboratory Audits

Frontier views third-party audits as a form of consultation and welcomes the opportunity to improve the quality of the laboratory and the quality management system. On average, FGS is audited four times each year. External audits enable FGS to qualify for and maintain accreditation through state governments and NELAP. Additionally, clients may audit us as part of a potential or ongoing contract. The Quality Assurance Officer maintains records of all such audits, the findings, and the corrective actions. Currently the HAL is reviewed by the NADP once every three years.

B4 Corrective Actions

Corrective action is the taken to eliminate the causes of an existing non-conformity, laboratory error, or other problematic situations and prevent its reoccurrence. Corrective action can be initiated by external or internal audits findings, employee observations, data reviews, customer feedback/complaints, or management reviews. All deficiencies are investigated and a corrective action plan is developed and implemented, if necessary. The investigation and action taken is depending of the problem and the degree of risk. Corrective actions may include filing an incident report, revising an SOP, revising the QAP, revising a safety procedure, or writing a new SOP.

B4.1 Incident Reports

Mistakes and accidents occur in the course of analytical laboratory work. These must be reported immediately to the supervisor and documented on an Incident Report Form (SOP FGS-039, "Incident Report Forms"). If there are safety concerns, a report is also filed with the Health & Safety Officer, or other assigned staff member. An Incident Report Form is completed when a problem arises that requires a deviation from the applicable SOP or method. The deviation may be due to a mistake or accident. It also may be due to unforeseen problems with a sample, instrument or dataset. Whatever the circumstance, it must be recorded as soon as possible. It is the responsibility of each Group Supervisor (or delegate) to complete the Incident Report Forms

and submit them to the QA group for review and follow-up. Completed Incident Report Forms are kept on file in the QA office. It is the procedure that the supervisor for the affected laboratory area starts the investigation and is writing up the incident report. The Quality Assurance Officer shall review the actions taken and the root cause analysis before the IR are complete and is submitted to all involved parties.

B5 Proficiency Testing Program

HAL started to participate in proficiency studies for total mercury in September of 2011. There are currently no available proficiency studies for methyl mercury. The PT sample shall be treated in the same manner as a client sample. The successive PT studies are analyzed at least five months apart and no more than 7 months apart unless the PT is being used for corrective action to maintain or reinstate accreditation. In these cases the dates of successive PT samples for the same accreditation has to be at least fifteen days apart. A failing result for a proficiency study must be reported to all the accreditation bodies, as per FGS-039.06 "Incident Report File."

Before the closing date of a study, laboratory personnel shall not:

- Subcontract the PT sample to another laboratory.
- Knowingly receive and analyze a PT sample from another laboratory.
- Communicate with an individual from another laboratory regarding the analysis of the PT sample.
- Attempt to find out the assigned value of a PT from the PT Provider.

The above listed situations are not ethically acceptable.

B6 Laboratory Intercomparison Studies

The HAL is participating in inter-laboratory comparison studies provided by USGS on a monthly basis. Samples are submitted for mercury analysis in both spiked and ultrapure deionized water.

Section C:
Data Management Operations

C1 Preventive Maintenance/Service

C1.1 Computer Systems and Software

HAL employs a number of servers, all which will conform to the latest industry best practices. Some of the servers act as domain controllers to control and maintain security access and access policies. Separate servers are utilized to control remote access to the network, terminal services, file and print services as well as the email server. All servers are equipped with backup drives and appropriate backup software that provides scheduling, automation, and monitoring of back-ups.

The server room is located on the second floor in a locked room with a metal door. It is closed each evening according to the lab lockup procedure to protect against fire. The servers and other network hardware are installed at least three inches above the floor to protect from water damage. Each server is attached to a UPS system with monitoring software and has enough battery power to keep the server running for at least twenty minutes. If the power is out for more than ten minutes, the software will shut down the server automatically while storing all data before battery power runs out. Network devices such as routers, switches, and firewalls are also attached to a UPS device. All other computers also have some form of UPS to minimize data loss, and loss of instrument control due to a short power failure. The servers, network hardware, and all computers' AC power supplies are plugged into power strips with built-in surge/spike protection.

Antivirus software with immediate file protection services is installed on each server. Files on the server disks are scanned daily. Virus definitions are updated automatically each day via an Internet connection to the software vendor. All incoming email is filtered external to the HAL network by an external email protection service. It is scanned for virus, malware, phishing and SPAM content before reaching the HAL network. Potentially harmful attachments are deleted from all e-mails that are sent to HAL. E-mail alerts are sent to IT personnel upon detection of viruses or unauthorized attachments. If HAL gets a large number of infected attachments in a day, the Internet mail service may be suspended until the problems are rectified. Each employee's computer to protect against infected files brought in through the Internet, outside e-mail accounts, portable diskettes, or flash drives.

Access to computers and files is limited to domain users with passwords that grant access to job-specific files and folders using the file securities built into the file system. Data security has been divided into three categories: access, protection against corruption, and redundancy. Access to data is subject to levels of control. The data owner determines data criticality. Non-critical data is available throughout the network. Critical data is available to members of predefined groups only. Sensitive and proprietary data is restricted at the user level. Data is protected from corruption by a strategy of limited access and redundancy. Redundancy takes the form of data backups via computer and secure storage of data in hard copy. Daily backups cover domain controllers, email server, database server, file and web servers, user files. Individual portable workstations are backed up weekly.

C2 Data Management Operations

C2.1 Description

The data management task involves collecting, entering, transferring, verifying, validating, summarizing, and reporting data. Data include descriptive and historical information about each network site, all field and laboratory data, quality assurance documentation, and summaries and reports of site and network operations.

Data records are transferred from the HAL to the NADP Program Office on a monthly basis. Data records may include paper or hardcopy documents, as well as electronic documents.

Preliminary, monthly data reports are sent to the Site Operators and Site Supervisors within 60 days of the end of the month during which sampling occurred. Corrections to the data are made, and documented, within 30 days of the preliminary data report being sent. All changes to the database are documented with a minimum of: who made the change, when the change was made, and why the change was made.

Final data, and supporting documentation, are shipped to the NADP PO at the end of this review process. For total mercury, final data are shipped within 90 days of the end of the month during which sampling occurred. For methyl mercury, final data are shipped within 120 days of the end of the month during which sampling occurred. Methyl mercury reporting requires additional time as composite samples from multiple sampling periods are used.

C2.2 Data Completeness

The goal is to achieve a continuous record of valid samples for the duration of each site's operation. Data completeness can be impacted by problems (e.g., weather, staffing, or equipment) at the field site, problems with shipping, and/or sample handling at the laboratory.

C2.3 Data Entry and Validation

Field and laboratory data are entered into the database using the method of double entry. This ensures correct entry of the data records. Following double entry, data records are screened using automated scripts, and quality codes are assigned. Data records that are assigned a quality code of "C" (invalid) are investigated by the Site Liaison. This helps achieve the goals of data completeness.

When practical, laboratory instruments interface with the LIMS directly. This eliminates the possibility of transcription error, and reduces the effort needed to support the system.

C3 Recordkeeping

C3.1 Laboratory Records

Results of the analytical measurements including original paper records and quality assurance results from instrumentation that are filed by the analysts and the laboratory QA Officer are also archived at HAL. All records (except logbooks) are archived for the life of the project. The logbooks are archived for a period of ten years after the last entry to the logbook according to FGS procedures.

Computerized data records (e.g., database, scanned field records) are maintained at the NADP PO.

Records maintained at both HAL and the Program Office are stored for the life of the project. At the HAL both paper and electronic records are kept under the supervision of the Project Coordinator. At the Program Office, records are maintained under the supervision of the NADP Coordinator.

C3.2 Quality Assurance Reporting

Changes in chemical analysis, new laboratory equipment, laboratory personnel, data verification or validation procedures, and site liaison procedures are documented on an annual basis in the QA Report that is submitted to the NADP PO. The QA Report is written by the QA Officer with assistance from the MDN Laboratory Manager. The QA Report summarizes laboratory performance during the year, including the results of all internal QA/QC activities (e.g., blank tests, spike tests, duplicate and split samples, reagent blanks, bottle blanks, etc.)

C4 Network Field Supplies

The HAL supplies necessary items to all network monitoring sites on a weekly basis. This may include, but is not limited to, the following:

- Clean sample train, i.e. bottle, thistle tubes, and funnels
- Clean unused dry-side bag (for sites with Aerochem (ACM) collectors only).
- Blank field forms
- Clean, laboratory gloves
- Reagent-grade water

Additional information may be found in FGS MDN-10 "Shipping of MDN Glassware."

Frontier Global Sciences – MDN Specific SOPs

| |
|--|
| MDN-01 Field SOP |
| MDN-02 Sample Receipt Procedures |
| MDN-03 Data Entry |
| MDN-04 Total Mercury Preservation |
| MDN-05 Total Mercury Analysis |
| MDN-06 Methyl Mercury Preservation, Splits and Comps |
| MDN-07 Distillation of MDN Precipitation Samples for Methyl Mercury Analysis |
| MDN-08 MDN Methyl Mercury Analysis |
| MDN-09 Cleaning of MDN Sampling Glassware |
| MDN-10 Shipping of MDN Sampling Glassware |
| MDN-11 Interpretation of the Raingage and Event Recorder Chart |
| MDN-12 MDN Data Review and Validation |
| MDN-13 MDN Journal Procedures |
| MDN-14 Pipette Calibration and Maintenance |
| MDN-15 MDN Monthly Review and Sample Coding |

Table 2: MDN Specific SOP List

Frontier Global Sciences – Supplemental SOPs

| |
|---|
| FGS-002 Balance Calibration and Maintenance |
| FGS-004 Refrigerator and Freezer Calibration and Maintenance |
| FGS-007 Cleaning of Sampling Equipment and Bottles for Mercury Analysis |
| FGS-038 Data Review and Validation |
| FGS-039 Incident Report File |
| FGS-041 Internal Quality Assurance Audit |
| FGS-048 Creation and Control of Standard Operating Procedures |
| FGS-061 Gold Trap Construction |
| FGS-062 Preparation of Carbo-Traps for Methyl Mercury Analysis |
| FGS-067 Passive Diffusion Monitoring for Gas Phase Atmospheric Mercury |
| FGS-072 Ordering Laboratory Supplies |
| FGS-074 Stock and Working Standards for Trace Metals Analysis |
| FGS-086 Documentation of Equipment Maintenance |
| FGS-087 Procedures for Deviation from Laboratory Policy |
| FGS-089 Sputter Coating Quartz Sand |
| FGS-087 Procedures for Deviation from Laboratory Policy |
| FGS-089 Sputter Coating Quartz Sand |
| FGS-099 Waste Dumping Procedure for Client Sample Waste |
| FGS-101 Traceability Protocols |

Table 3: Supplemental SOP List

| MDN Precipitation Sample Analysis Lab Sheet | | | | | | Dataset Code | | | | |
|---|----|-----|---------|------------------|------|--------------|----------------|-----------------|-----------------|-----------|
| Analysis Date | | | | | | Dataset ID | | | | |
| Instrument | | | | | | Analyst | | | | |
| Run | Tp | Bub | HalCode | SampleID | BrCl | PA | Aliquot Volume | THg per Aliquot | THG Conc. (NET) | Remarks |
| 1 | 1 | 1 | | 4.00 | 0 | | | | | |
| 2 | 2 | 2 | | 2.00 | 0 | | | | | |
| 3 | 3 | 3 | | 1.00 | 0 | | | | | |
| 4 | 4 | 4 | | 0.5 | 0 | | | | | |
| 5 | 5 | 1 | | 0.05 | 0 | | | | | |
| 6 | 6 | 2 | | BB-1 | 1 | | 100 | | | |
| 7 | 7 | 3 | | BB-2 | 1 | | 100 | | | |
| 8 | 8 | 4 | | BB-3 | 1 | | 100 | | | |
| 9 | 9 | 1 | | NIST1641d | 1 | | 0.2 | | | % Rec |
| 10 | 10 | 2 | | BrCl-1 | 1 | | 100 | | | |
| 11 | 1 | 3 | | BrCl-2 | 1 | | 100 | | | |
| 12 | 2 | 4 | | BrCl-3 | 1 | | 100 | | | |
| 13 | 3 | 1 | | BB-4 | | | | | | |
| 14 | 4 | 2 | | Sample # O1 | 1 | | 100 | | | |
| 15 | 5 | 3 | | Sample # D1 | 1 | | 100 | | | Mean, RPD |
| 16 | 6 | 4 | | Sample # S1 | 1 | | 100 | | | % Rec |
| 17 | 7 | 1 | | Sample # 2 | 1 | | 100 | | | |
| 18 | 8 | 2 | | Sample # 3 | 1 | | 100 | | | |
| 19 | 9 | 3 | | Sample # 4 | 1 | | 100 | | | |
| 20 | 10 | 4 | | Sample # 5 | 1 | | 100 | | | |
| 21 | 1 | 1 | | Sample # 6 | 1 | | 100 | | | |
| 22 | 2 | 2 | | Sample # 7 | 1 | | 100 | | | |
| 23 | 3 | 3 | | Sample # 8 | 1 | | 100 | | | |
| 24 | 4 | 4 | | Sample # 9 | 1 | | 100 | | | |
| 25 | 5 | 1 | | Sample # 10 | 1 | | 100 | | | |
| 26 | 6 | 2 | | CCV1 (1.00 ng/L) | 0 | | 100 | | | % Rec |
| 27 | 7 | 3 | | CCB-1 | 0 | | 100 | | | |
| 28 | 8 | 4 | | Sample # O2 | 1 | | 100 | | | |
| 29 | 9 | 1 | | Sample # 12 | 1 | | 100 | | | |
| 30 | 10 | 2 | | Sample # 13 | 1 | | 100 | | | |
| 31 | 1 | 3 | | Sample # 14 | 1 | | 100 | | | |
| 32 | 2 | 4 | | Sample # 15 | 1 | | 100 | | | |
| 33 | 3 | 1 | | Sample # 16 | 1 | | 100 | | | |
| 34 | 4 | 2 | | Sample # 17 | 1 | | 100 | | | |
| 35 | 5 | 3 | | Sample # 18 | 1 | | 100 | | | |
| 36 | 6 | 4 | | Sample # 19 | 1 | | 100 | | | |
| 37 | 7 | 1 | | Sample # 20 | 1 | | 100 | | | |
| 38 | 8 | 2 | | Sample # D2 | 1 | | 100 | | | Mean, RPD |
| 39 | 9 | 3 | | Sample # S2 | 1 | | 100 | | | % Rec |
| 40 | 10 | 4 | | CCV2 (1.00 ng/L) | 0 | | 100 | | | % Rec |
| 41 | 1 | 1 | | CCB-2 | 0 | | 100 | | | |
| 42 | 2 | 2 | | NIST1641d | 1 | | 0.2 | | | |
| 43 | 3 | 3 | | Sample # O3 | 1 | | 100 | | | |
| 44 | 4 | 4 | | Sample # 22 | 1 | | 100 | | | |
| 45 | 5 | 1 | | Sample # 23 | 1 | | 100 | | | |
| 46 | 6 | 2 | | Sample # 24 | 1 | | 100 | | | |
| 47 | 7 | 3 | | Sample # 25 | 1 | | 100 | | | |
| 48 | 8 | 4 | | Sample # 26 | 1 | | 100 | | | |
| 49 | 9 | 1 | | Sample # 27 | 1 | | 100 | | | |
| 50 | 10 | 2 | | Sample # 28 | 1 | | 100 | | | |
| 51 | 1 | 3 | | Sample # 29 | 1 | | 100 | | | |
| 52 | 2 | 4 | | Sample # 30 | 1 | | 100 | | | |
| 53 | 3 | 1 | | Sample # D3 | 1 | | 100 | | | Mean, RPD |
| 54 | 4 | 2 | | Sample # S3 | 1 | | 100 | | | % Rec |
| 55 | 5 | 3 | | CCV3 (1.00 ng/L) | 0 | | 100 | | | % Rec |
| 56 | 6 | 4 | | CCB-3 | 0 | | 100 | | | |

Table 4: Example of an Analytical Run Sequence

