

Mallinckrodt Inc.

**Cell Process Dismantling
Perimeter Air Monitoring Program**

**HoltraChem Manufacturing Facility
Orrington, Maine**

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Work Plan

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Section 1

Introduction

1.1 Purpose

The purpose of perimeter air monitoring is to measure ambient conditions at or before the property line during the cell dismantling process to determine compliance with the 0.30 $\mu\text{g}/\text{m}^3$ ambient air quality guideline.

1.2 Approach

Perimeter monitoring stations to collect 24-hour average samples will be established at four monitoring locations at the HoltraChem site property line or between the Cell Building and the property line. In addition, a perimeter air monitoring program will be performed that will have the capability to take “real-time” measurements to assess short-term mercury releases and to monitor at locations other than the fixed location established for long-term monitoring. Fixed and portable methods and instruments will have detection limits low enough to assess compliance with the Maine ambient air quality guideline for mercury, 0.30 $\mu\text{g}/\text{m}^3$.

1.3 Methodology

Real-time air monitoring will be performed using a Lumex 915+ mercury vapor analyzer. This device has a reported method detection limit of approximately 0.2 ng/m^3 (0.0002 $\mu\text{g}/\text{m}^3$). The device is portable and will be used to survey and monitor selected locations of interest during the cell process dismantling. These locations will vary depending upon conditions on a particular day including, which way the wind is blowing, the types of tasks being conducted and/or specific requests by the Project Superintendent or MEDEP. Frequency of monitoring is described in Section 2.

Four fixed monitoring stations will be established and equipped with enclosures for sampling pumps, flow meters, sample traps and associated equipment. Mercury samples will be collected on specially prepared iodated carbon sorbent traps supplied by Frontier GeoSciences. These traps combined with very sensitive analytical methods (cold vapor atomic fluorescence) enables routine quantification of ambient air mercury with a 0.5 ng/m^3 detection limit. The four components of the analytical program are:

Low-Level Hg Sample Media Traps manufactured in clean-room environments and tested to document extremely low blank mercury concentrations. The material used to chemically impregnate the special carbons is highly efficient at capturing mercury and has been shown to be 99.999% efficient at capturing mercury. The traps have two sections, one designed as the sample trap and the second used to measure (quality assure) potential mercury breakthrough.

Analytical Method (functional equivalent of US EPA 1631 CVAFS) capable of measuring 0.08 $\text{ng Hg}/\text{L}$ (8 picograms per liter).

Sampling Equipment including mass flow meters and mass flow totalizers capable of quantification of sample volume down to a tenth of a liter of air.

Basic Clean Sample Handling Techniques and clean room laboratory standards.

In comments on the Cell Process Dismantling Work Plan, the MEDEP required that the Perimeter Air Monitoring Program be capable of measuring down to the ambient air quality criteria of $0.30\mu\text{g}/\text{m}^3$ and suggested that the gold bead traps used in the EPA IO-5 method would accomplish that. CDM has reviewed the IO-5 methodology, and although the gold bead traps would provide a lower detection limit than the NIOSH 6009 method originally proposed, the IO-5 method has limitations and is not be appropriate for this program for several reasons.

The US EPA adopted Method IO-5 as a compendium method for measuring global background level concentrations of mercury in ambient air. It is not ideal for long-term monitoring at a site where concentrations could potentially reach higher than global background levels. The method is complicated and difficult and expensive to deploy and maintain in the field.

IO-5 sample traps have many potential interferences. They are sensitive to humidity, acid gases and organics that may be present near a remediation site. The IO-5 trap adsorption sites for mercury can become “fouled” with water vapor, acid gases and organics. When these sorption sites are coated with these substances, the trap will not capture mercury and therefore allow mercury to pass through undetected. Further, the IO-5 traps are re-used after each sampling. They can become damaged from acid gases and slowly degrade their ability to capture mercury.

Since the IO-5 traps are very sensitive to water vapor, the method requires that a special device is applied to keep the sample trap heated to a temperature that ensures water vapor will not condense in the trap. Further, it is critical that the temperature of the trap is carefully kept at this temperature or the sample could be considered invalid. This is difficult and requires special equipment.

The dynamic range of mercury capture on the IO-5 gold traps is limited to background levels of mercury and slightly higher. The IO-5 has a sorption capacity for a large amount of mercury. However, the IO-5 traps are thermally desorbed directly into the CVAFS detector. The CVAFS detector is calibrated to a certain range of concentrations and if the amount of mercury on the IO-5 trap is higher than the standard curve of the CVAFS detector, the value is not analytically valid. If there is a “hit” where a higher concentration is experienced at the sampling site, the analytical system is overwhelmed and the analytical data is lost. There is no capability for a rerun because there is only one opportunity to desorb the sample trap into the collector. Therefore, if a high concentration of mercury was measured with the IO-5 trap, it is likely that the lab would not be able to quantify and report the value.

The flow rate of the IO-5 trap is limited to 0.5 lpm. If this sample flow rate range is exceeded, the trap can experience breakthrough. This restricts the volume of air matrix that can be pulled through the trap and therefore only allows for a very small sample volume to be quantified on the trap. This restricted sample volume and flow rate does not allow flexibility to adjust the sample program.

IO-5 is not capable of rerunning the same sample due to the fact that it is a “one-shot” analysis. Analytical Duplicate analysis is a critical analytical measure for assessing how well the analytical system is performing. In addition, analytical spikes are also a critical QA measure for the analytical system and are impossible when using the IO-5 method.

For the reasons stated above, the proposed iodated carbon sorbent trap method is better for this site and does meet the objective expressed by the MEDEP. Furthermore, it has many practical advantages over the IO-5 method. These are described below.

The sorbent traps are rugged and can withstand humidity, acid gases and organics. The sorbent traps have been compared with methods used to capture mercury in flue gas (US EPA 101A and Ontario Hydro), a very complicated matrix compared to ambient air, and have shown excellent comparison. Therefore, the data has been shown to be reliable using this method.

The sorbent trap method does not require temperature control and therefore can be deployed and sampled at ambient temperature. They are not sensitive to UV or temperature exposure. The sample traps can capture mercury and be heated to 500°F and not lose mercury. Further, the sorbent sample traps actually become more efficient at capturing mercury with increasing temperature and therefore, the traps do not need to be kept on ice during storage or shipment.

The sorbent trap method involves a digest. Since the trap is digested, the lab can dilute this digest and analyze at a dilution within the analytical calibration curve. If the first aliquot of the digest analyzed is too high (outside the calibration curve), an additional sample can be run at a lower aliquot volume. The digest also provides for laboratory duplicate analyses.

In summary, the iodated carbon sorbent trap method will meet the needs of the project, specifically: detection levels low enough to compare the results to the Maine ambient air quality guideline; and sufficient quality assurance/quality control (QA/QA) provisions to assess and document the accuracy of the monitoring program.

1.4 Action Levels

The ambient air quality guideline for mercury established by the State of Maine Bureau of Health is the Reference Concentration (RfC) published by the USEPA. The

EPA published this number as a conservatively calculated guidance value that represents a concentration that people (including sensitive individuals) can be exposed to every day over a lifetime and have no adverse effects occur from inhaling that pollutant. It is expressed as a 24-hour average, with the assumption that the person would be exposed to this value every day.

The results of the 24-hour average samples will be compared to the ambient air quality guideline. These samples require laboratory analysis so there will be a delay in receipt of results. If a 24-hour sample exceeds the guidance value an assessment will be conducted of work performed, the air controls implemented and the meteorological conditions occurring during that period. The results of this assessment will be provided to the MEDEP and changes to the work practices made, as appropriate.

Real-time readings with the Lumex will be collected as described in Section 2.3 and in accordance with the SOP provided as Appendix A. The readings will be compared to the guidance value but with a recognition that, because cell process dismantling will not proceed on a 24-hour basis and wind directions and meteorological conditions will vary during the execution of the work, momentary exceedances of the air quality guideline can occur and not result in a 24-hour average approaching the guidance value.

If readings with the Lumex exceeding the ambient air quality guidance value are obtained, a second measurement will be taken downwind of the first sample location but no farther than the property line. If the second or property line reading exceeds the guidance value, the Project Superintendent will be notified and the work practices assessed. Assessment will include identification of the activities that may be resulting in air emissions exceedances, an evaluation of whether the activities will continue and steps that can be taken to reduce emissions. The frequency of downwind monitoring will be increased to approximately hourly until two consecutive property line readings below the ambient air quality guideline are obtained.

If additional measurements exceed the guidance value at the property line, more monitoring will be performed to estimate the 24-hour average value and to document ambient air quality between the site and the first downwind residences or business'. If measurements indicate that the 24-hour value will be exceeded the Project Superintendent will be notified and work will be suspended until mercury emissions can be controlled and perimeter monitoring indicates a return to compliance with the ambient air quality guidance. Additional data that will be used to assess the 24-hour average concentration include the results from the Lumex measurements combined with wind direction, speed, and temperature.

Because the air monitoring program requires actions to further control mercury emissions if concentrations greater than the guideline are documented at the property line, it is not anticipated that the 24-hour average ambient air quality guideline will

ever be exceed off-site of the former HoltraChem property. However, in the event that a mercury release to air results in sustained ambient air quality guideline exceedances at the property line, the MEDEP will be notified and additional monitoring will extend directly downwind of the cell building until concentrations below the guidance value are obtained or the first residence or business is encountered.

Section 2

Sample Collection and Analysis

2.1 Sampling Equipment

The sampling equipment for portable ambient air quality measurements consists of a Lumex brand model 915+ mercury vapor analyzer.

Sampling equipment for fixed locations consists of the following:

- Sample pump
- Mass Flow Meter and Totalizer
- Iodated carbon sample traps
- Flow control systems
- Sample box containing all equipment

2.2 Sampling Locations

Monitoring locations were selected based on site-specific wind rose data gathered during the 1998-1999 Ambient Total Gaseous Mercury And Meteorological Monitoring Program and based on comments from the MEDEP. Four sampling sites located in principal downwind locations at distances ranging from 450 - 1500 feet from the cell room were selected with assistance from MEDEP. Location designations, and respective distances from the cell room are summarized below and are presented on the attached figure.

Perimeter Monitoring Locations

Monitoring Location	Description	Distance From Cell Room (ft)
A1	Plant entrance near former weigh station	450
A2	Old entrance road at Rte. 15	1500
A3	Between Lined Process Lagoon and River	500
A4	Near Landfill 4	500

2.3 Sampling Frequency

Ambient air will be monitored downwind of the cell building to evaluate the potential for dismantling activities to result in unacceptable exposures to the general public offsite. Previous air monitoring programs have demonstrated that former day-to-day operational and maintenance procedures would not create an exceedance of the

Insert Figure 2-1

0.30 $\mu\text{g}/\text{m}^3$ guidance value at the property line. Therefore, periodic perimeter monitoring will be performed in conjunction with monitoring within the cell room.

A perimeter survey will be performed with the Lumex mercury vapor analyzer daily during cell process dismantling operations. The time of day will be coordinated with cell process dismantling work to assess activities that might generate the most emissions. Additional monitoring will be performed if exceedances of the ambient air quality guidance value are recorded as described in Section 1.4, Action Levels. The perimeter monitoring program may be modified if comparison of the perimeter monitoring and cell room ambient air concentrations indicate additional or less frequent monitoring is warranted or appropriate. As the project progresses, the frequency of perimeter surveys may be modified, with MEDEP approval, based on the results of previous surveys and the specific or remaining dismantling activities planned. For example, if previous monitoring results have show no exceedances and future work has less potential for mercury vapor releases, CDM may request a reduction in perimeter monitoring frequency.

Initial 24-hour monitoring at the fixed locations will be performed weekly unless Lumex surveying indicates that more frequent monitoring should be performed. The monitoring day will be selected at the beginning of the week to assess potential “worst case” conditions considering the work being performed that week and the anticipated meteorological conditions.

2.4 Sampling Procedures

Real time measurements will be collected with the Lumex Mercury Vapor Analyzer. The instrument will be calibrated and operated in accordance with manufacturer’s instructions and the protocol provided in Appendix A. Readings will be recorded in a field logbook used for all perimeter air monitoring purposes. Minimum related data that will be recorded include time, date, location description, temperature and general weather.

Twenty-four hour composite air samples will be collected from the four sampling locations, weekly during the dismantling process. Sampling will be performed using clean techniques following procedures provided by Frontier GeoSciences. A protocol for 24-hour sampling at fixed locations is provided in Appendix B. MEDEP will be notified when sampling is initiated so they can observe sampling methods and practices.

2.5 Sample Analysis

Real time mercury in ambient air measurements will be provided by the direct readout of the Lumex mercury vapor analyzer.

Sorbent samples traps will be analyzed by Frontier GeoSciences for total mercury using Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS) at a wavelength of 253.7 nm (equivalent of US EPA 1631). Laboratory SOPs are provided in Appendix C.

Concentration of mercury in ambient air will be calculated from the total mercury collected at each location divided by the measured volume of air pulled through the sample trap.

2.6 Quality Assurance/Quality Control

Field Measurements

The Lumex mercury vapor analyzer will be operated, calibrated and maintained in accordance with manufacturer's instructions and the SOP provided in Appendix A.

Laboratory Blanks

The analytical laboratory, Frontier GeoSciences, will analyze approximately 5% of each batch of sorbent traps to determine the batch blank concentration of mercury.

Field Blanks

Field blanks will be collected at a minimum rate of one per 20 analytical samples (5%). Initially, field blanks will be collected weekly for the first month. Field blanks will be handled identically to field sample (ends broken, attached to the sampling device, checked for leaks, etc.) except that a sample of ambient air will not be drawn through the trap. The field blank sample will capped and returned with the other samples to the laboratory for analysis.

Field Duplicates

Field duplicates require additional sampling related equipment set up adjacent to the primary sampling location. Based on consultations with MEDEP Air Bureau personnel, duplicate sampling equipment will be installed at the sampling location at the plant entrance. This location was selected as the closest to the cell building, PERC and the residences at Ferry Road. One duplicate sample will be collected each week for one month. Provided the results of the field duplicate analyses are consistent with the parent sample concentrations the frequency of duplicate analyses will be reduced to monthly.

Analytical Data Package Reporting

The following are the initial analytical data report deliverables. After initial data quality review, the contents of the report may be modified to reduce the amount of raw data transmitted provided that raw data is maintained at the laboratory.

1. Table Of Contents
2. Case Narrative
3. Data Set Approval Checklist
4. Tables Of Analytical Results

Table 1: Total Atm. Mercury (Incident Particulate Bound and Gas Phase Hg)

Table 2: Frontier Ambient Air Hg Field Blanks

Table 3: Frontier Ambient Air Hg Lab Blanks

Table 4: Frontier Geosciences Lab Control Spike Recovery (30 ng)

Table 5: Estimated Field/Analytical Minimum Detection Limit

Table 6: Analysis QA/QC Performance Summary – SRM Results

Table 7: Analytical Spike Recovery

Table 8: Lab Replicate Results

Table 9: Frontier Solid Sorbent Method Lab Control Spike Recovery

Table 10: Frontier Ambient Air Hg Method Field Duplicate Recovery

Table 11: Initial Calibration and Continued Calibration Blanks (ICB)

Table 12: Initial Calibration and Continued Calibration Verifications (ICV)

5. Laboratory QA/QC Control Charts
6. Graph – ng Hg/Sample Trap
7. Lab Data Sheets With Cover Page
8. Chart Recorder Raw Data (Copies)
9. Example Calculations (Example Of Actual Sample Calculation)
10. Chain Of Custody Record (Original)
11. RMA Lot AAC FedEx Shipping Label – Proof Of Receipt (Copy)
12. Laboratory Sample Digestion Logbook (Copy From Bound Book)
13. Laboratory Standard Preparation Log Book (Copy From Bound Book)
14. Copy Of Sample Receipt Electronic Data Deliverable
15. Copy Of Report Electronic Data Deliverable

2.7 Reporting and Notification

2.7.1 Periodic Reporting

The results of the daily perimeter surveys will be summarized and faxed to MEDEP on a weekly basis.

The analytical results from the 24-hour sample analyses will be tabulated and provided to MEDEP on a monthly basis.

2.7.2 Notification

If concentrations greater than the ambient air quality guideline are documented which require the cessation of work or the collection of off site air quality measurements the MEDEP will be notified by phone call.

If monitoring is performed on private property, the persons at that property will be notified of the reasons for monitoring, provided with the results of the Lumex readings, a description of the ambient air quality guidance value and a name and number of a contact at MEDEP.

Section 1 Introduction

This protocol is a guideline for operating the Lumex RA-915 for mercury vapor analysis. It is based on a protocol obtained from the Maine Department of Environmental Protection that was intended to be a Standard Operating Procedure for their measurement of mercury vapor. The procedures are identical. This protocol document has only been modified to remove MEDEP-specific information and to address the needs of the HoltraChem Cell Process Dismantling Air Monitoring Program.

The Lumex RA-915 is applicable for ambient air testing of mercury vapor in the range of 20 ng/M³ to 50,000 ng/M³. (50,000ng/M³ = .05mg/M³, the PEL for mercury) For areas of higher concentration, a Jerome meter should be used. Do not directly expose the RA-915 to elemental mercury as this may permanently contaminate the instrument.

The Maine ambient air guideline for mercury is 300 ng/M³.

Section 2 Purpose

The purpose of this document is to describe the procedure for collecting and analyzing air samples for mercury vapor analysis.

Section 3 Responsibilities

Personnel conducting perimeter air monitoring and other site related air monitoring will be trained and must follow this procedure when using the Lumex RA-915 for mercury vapor analysis.

Section 4 Procedures

4.1 Starting the Instrument

The instrument can be powered by either 120-v AC line current [with adapter cord], a battery pack in the instrument, or vehicle cigarette lighter adapter. The battery pack is intended for a maximum of 4 hours continuous use, and should be recharged using the included cord plugged into 120 volt AC line current. The instrument may be used with batteries if the battery indicator is flashing red. A steady red indicates the battery needs to be charged and AC power must be used to run the instrument. A supplemental battery pack is stored in the side pocket and can be plugged into the AC adapter cord port. The supplemental battery will provide an additional 2 hours use.

Pre-operational procedures:

1. Before operating the RA-915, conduct a visual inspection of the analyzer's component parts. The instrument may be used while in the carrying case.
2. Place the RA-915 in a horizontal position with the Palm monitor (controls and display screen) on top. The power switch will be the front end. (See photo 1)

3. Set the test cell control handle (on the side of instrument) to the **OFF** position. This can be accessed inside the side pocket of the carrying case.
4. Check to make sure Palm monitor is securely connected to the base unit.
5. The handle for optical bridge switch at the back and opposite the power switch should be pre-set to position III.
6. Turn on the power switch on front of the instrument. The Palm monitor will then show the Lumex version screen (See photo 2).
7. Press the "Ent" button on the Palm monitor. The MAIN MENU display will appear. There will be an * next to the words MAIN MENU.
8. Press [3-5 sec] and release the Lamp Ignition button on front of the machine. When the lamp lights the * next to the words MAIN MENU will disappear. Repeat this step as necessary to light the lamp.
9. Allow the instrument to warm up for 5 minutes prior to testing.

4.2 Menu Screens

The MAIN MENU will have the following options:

- Parameter - Used to change parameter settings (See below).
- On Stream - Used to analyze background and environmental samples.
- On-time - Not used for air analysis
- Test - Used to verify instrument calibration.
- Settings - Used to save new parameter settings or restore factory settings. This should not normally be used.

To select an option, highlight the option and push the **Ent** button.

To return to the main menu, push the **Esc** button.

Parameter settings for air analysis should generally follow preset values. The following settings have been stored:

<i>Parameter</i>	<i>Value</i>	<i>Units</i>
Average Time	1	seconds
Baseline Cor Time	20	seconds
Frame Time	10	seconds

Integr. Time	120	seconds
Low limit	20	ng/M ³
High limit	300	ng/M ³

4.3 Background Air Analysis

Prior to taking the instrument to a potentially contaminated site, a background air sample should be analyzed to demonstrate that the instrument reading is below the reporting limit for this instrument, 20 ng/M³.

A background sample must be taken at the beginning and end of each analysis day. All results must be below 20 ng/M³. Do not proceed until this condition has been met.

For this analysis the Lumex RA-915 should be operated in the ON STREAM mode as described below:

Operation in ON STREAM (AIR ANALYSIS) mode

1. The optical bridge handle should already be in the OFF position as described in the starting instructions above [Section 4.1].
2. Use the arrow buttons, on the Palm monitor indication unit to select the ON STREAM mode and press the Ent button. This will switch the compressor on, and the zero signal will be measured. The following will occur on the display
 - The current S value, which corresponds to the mercury concentration in the pumped air in ng/M³, is displayed in the upper right of the palm monitor.
 - The Si level is also displayed below the S value. This result [Si] corresponds to the value S averaged over a given time range.
 - The bottom right displays a countdown [in seconds] of the time over which S values were averaged. The current setting is for values to be averaged over 10 seconds.
 - An **Alarm!!** Message is displayed across the top of the screen if the mercury concentration exceeds the ambient air guideline.
3. Press the **Ent** button a second time: three Si readings and S_c [the average of these three Si readings] are displayed. In this mode three 10-second average readings are repeated, averaged, and displayed with the corresponding relative deviation [R] in the measurements.
 - The average, $S_c = (S_1+S_2+S_3)/3$.
 - The relative deviation of three measured concentrations is displayed as R

$$R = 100 * (\max(S1, S2, S3) - \min(S1, S2, S3)) / S_{ave}, \%$$

- If S_c is less than the parameter "Low limit" (20 ng/M³), "< 20" is displayed.
4. Record the three S_i readings, S_c and R for the background sample in a field notebook and any analysis record developed for the current sampling event.
 5. If the background reading does not fall below 20 ng/M³, remove the intake hose and repeat the procedure to determine whether the intake hose is contaminated.
 6. To quit the On Stream mode, press the **ESC** button, which causes the air pump to switch off. The device switches over to the standby mode waiting for the next command. The message MAIN MENU appears on the Palm display.

4.8 Calibration Verification

The instrument calibration must be verified on each analysis day prior to analyzing samples, and again at the end of the day.

The calibration is considered verified if the relative deviation [designated with R on the instrument] is below 20%.

Calibration verification is measured in the TEST mode as described below:

Operation in the TEST Mode (Serviceability Check)

1. Use arrow buttons on the indication unit to select the (TEST) mode and press the **Ent** button. After the instrument measures the zero signal the display will show the message "Enter Test Cell."
2. Set the test cell handle on the side of the instrument to the ON position, and wait for 20 seconds before pressing the **Ent** button. The following will be displayed:
 - The current S value, which represents the measured mercury concentration in the test cell in ng/M³;
 - The S_k value, which represents the mercury concentration which should be measured based on the test cell temperature; (See table on page 21 of the RA-915+ Operation Manual for reference);
 - The average measured mercury concentration [S_i];
 - The relative deviation [R] of the measured value average [S_i] from the theoretical value is automatically calculated by: $R = 100 * |(S_i - S_k) / S_k|$; and
 - A countdown [in seconds] of the time over which S_i values were averaged. The current setting is for values to be averaged over 10 seconds.

- The message “Temperature” is displayed across the top, if the temperature of the test cell is beyond the admissible temperature range for proper operation of the analyzer.
3. Record the Si, Sk, and R values associated with the calibration check in a field notebook and any analysis record developed for the current sampling event.
 4. If the relative deviation [R] of the measured values Si from its table value is below 20%, the RA-915+ analyzer is ready for operating, otherwise see “Maintenance” in the Operation Manual.
 5. To quit the TEST mode, press the ESC button whereupon the analyzer switches over to the standby mode for the removal of the test cell. The display will show the message Remove Test Cell. Remove test cells and press the ESC button again and the analyzer switches over to the standby mode waiting for the next command. The message appearing on the display reads MAIN MENU.

4.5 Analysis

1. Allow the Lumex RA-915 to equilibrate to site temperature.

Sample locations should be selected in accordance with the pools of the parameter air-monitoring plan and considering the meteorological conditions (e.g. wind directions of the day). It is important to note that environments with high levels of mercury are not suitable for the Lumex RA-915. Several precautions should be taken at possibly contaminated sites:

- Use a Jerome meter to delineate areas possibly contaminated above 0.05 mg/M³.
 - If a Jerome meter is not available, start the investigation outside the possibly contaminated areas and work toward the contaminated areas stopping when the mercury readings exceed the calibration range of the instrument [0.05 mg/M³].
 - Do not place the instrument on any potentially contaminated area, including floors or surfaces where mercury has been spilled.
 - Do not place the inlet sample tube on any potentially contaminated surface.
2. Air temperature should also be measured and recorded concurrently with the mercury sample results. A digital thermometer is included in the travel case with the mercury analyzer for this use.
 1. For this analysis the Lumex RA-915 should be operated in the ON STREAM mode as described in section 4.3, making sure to record the three Si values, Sc, and R in a field notebook and any analysis record developed for the current sampling event.

5. Check a [low] background sample and calibration verification at the end of the sampling day.
6. To turn the instrument off press the Esc key to go to the main menu. Then turn the power toggle switch off. If the instrument was operated on battery power, the battery must be recharged prior to storing the instrument. Storing the instrument with an uncharged battery may cause damage to the battery.

4.6 Instrument Maintenance and Storage

4.6.1 Maintenance procedures for the analyzer include

1. Daily [when in use] visual inspection;
2. Periodic preventive maintenance;

All the maintenance operations should be duly recorded in the analyzer log.

Daily [when in use] inspection is performed in the work place and involves visual inspection of the analyzer and serviceability check. The service ability check consists of a background air check for contamination (section 4.3) and a calibration verification check (section 4.4).

Periodic prevention maintenance is performed in the work place and involves:

1. Quarterly:
 - Checking the fastening of the body covers;
 - Checking the connectors for cleanness;
 - Checking the state of the cables;
 - Checking the dust filter: A small dust filter is located inside the intake hose attachment port. This filter should be checked on a quarterly basis [sooner if used in high dust areas] and replaced if the dust filter has turned color from white to brown and appears to be clogged. To remove the filter for inspection/ replacement, use a pair of tweezers; and
 - The built-in absorption filter (located in the left-hand inlet on the front -wall of the base unit) should be replaced as needed. Typically this will be once or twice per year. If the instrument is used often, or in a mercury environment above 10,000ng/M³ for a period of time the filter should be replaced more often.
2. Annually prevention maintenance is recommended. It is performed by OhioLumex and involves recalibration and checking the RA-915+ for conformity to the technical specifications. For further information refer to the Operation Manual. OhioLumex is in the process of updating the recommended maintenance

procedures for this instrument. When these updates are completed the maintenance section of this SOP will be modified to reflect any changes.

4.6.2 Storage

- The instrument should be stored in a low mercury [$<20 \text{ ng/M}^3$] atmosphere at temperatures between 40°F and 100°F with relative humidity less than 80%. If it is inadvertently stored below 32°F, it should be taken to and kept at a temperature of 60°F or higher for up to 24 hours [temperature dependent] prior to use.
- When the analyzer is used with battery power, the battery must be recharged before returning the instrument to storage. Storage of a discharged battery for 3 days may permanently damage the battery.

4.8 Documentation

All sampling activities must be documented either in a field notebook or on pre-printed sampling worksheets. At a minimum the following items must be documented:

- Project name;
- Date and time of sample;
- Background air results;
- Calibration verification results;
- Sample location;
- Name of person[s] performing air sampling/analysis;
- Temperature;
- Mercury result;
- Any special considerations or sampling conditions;

4.8 Quality Assurance/Quality Control

4.8.1 QA Sample Collection

Collection and analysis of the following QA samples is mandatory:

- **Background sample** - A background air sample should be taken outside of the site and in a location where there is no [low] mercury contamination. Results must be below 20 ng/M^3 . This sample is taken to ensure that the instrument is free of contamination. At a minimum, background samples should be taken at the beginning and end of each sampling day. If the instrument is taken into an environment where mercury vapor concentrations exceed the calibration range of

the instrument [50,000 ng/ M³] a background sample must be re-analyzed before continuing with the sampling event.

- **Calibration verification** - The instrument calibration must be verified at the beginning and end of each sampling day. The calibration is considered verified if the relative deviation [designated with R on the instrument] is below 20%. The instrument must be returned to the factory for calibration yearly, and when calibration falls outside the designated range.
- **Duplicate samples** - Each time a sample is analyzed the instrument automatically takes three 10 second average readings [S_i] and averages the three readings to arrive at a result [S_c]. A relative deviation [displayed as R] is also calculated by the instrument by the following formula:

$$R = 100 * (\max(S_1, S_2, S_3) - \min(S_1, S_2, S_3)) / S_c$$

$$S_c = (\max(S_1, S_2, S_3) + \min(S_1, S_2, S_3)) / 2$$

4.8.2 Deviations from Protocol

All deviations from the procedures outlined in this or in any other protocol must be documented in field notes.

Section 5 References

1. Multifunctional Mercury Analyzer RA-915+ Operation Manual, OhioLumex Co, Inc. Analytical Equipment, Cleveland, Ohio, 2001.
2. Protocol for collecting and analyzing mercury vapor in air with a Lumex RA-915+Mercury Analyzer. Maine Department of Environmental Protection Standard Operating Procedure Hg01, April 2, 2002.

**HoltraChem Manufacturing Site
Cell Process Dismantling
Perimeter Air Monitoring
Daily Lumex Survey Log**

Date: _____ **Time Start:** _____ **Time Stop:** _____

Weather Conditions: Description _____

Temperature _____ **Wind Speed** _____ **Wind Direction** _____

Initial Calibration Check: S _____ **Sk** _____ **Si** _____ **R** _____ **Time** _____

Initial Background Measurement:

Location _____

Si₁ _____ **Si₂** _____ **Si₃** _____ **Sc** _____ **R** _____ **Time** _____

Downwind Survey: * If readings exceed 300 ng/m³ – Notify Project Superintendent

Approximate Distance and Direction from Cell Building _____

Si₁ _____ **Si₂** _____ **Si₃** _____ **Sc** _____ **R** _____ **Time** _____

Si₁ _____ **Si₂** _____ **Si₃** _____ **Sc** _____ **R** _____ **Time** _____

Si₁ _____ **Si₂** _____ **Si₃** _____ **Sc** _____ **R** _____ **Time** _____

Project Superintendent: _____

Signature _____ **Time** _____ **Date** _____

Action Taken: _____

Final Background Measurement:

Location _____

Si₁ _____ **Si₂** _____ **Si₃** _____ **Sc** _____ **R** _____ **Time** _____

Final Calibration Check: S _____ **Sk** _____ **Si** _____ **R** _____ **Time** _____

Sampler (name, signature): _____

Total Atmospheric Hg Sampling via The Frontier Solid Sorbent Method

Section 1 Introduction

The following protocol is designed to instruct sampling personnel on how to perform ambient air mercury sampling on a weekly basis. The focus of this document is to give guidance to ensure trace clean sample handling techniques are followed and a standard protocol is followed to provide consistency. This protocol is intended to provide all of the detail needed to perform this sampling effort.

Section 2 Sampling Protocol

This protocol covers the following steps:

1. Obtain the Mercury Sampling Supply Kit.
2. Record the Total Atmospheric Hg Solid Sorbent Trap Final Sample Volume.
3. Approach the Collector Sampling Arms From Down Wind.
4. Make Observations While the Sample Media Is Still In The Sampling Arm.
5. Perform A Post Sample Leak Check of the Total Hg Sorbent Trap.
6. Release the vacuum after performing the Post Leak Check.
7. Retrieve the Total Hg Solid Sorbent Trap.
8. Store The Samples and Field Data Clean The Sampling Arms.
9. Deploy "Dummy" Sample Media and Set Sample Media Flow Rate.
10. Deploy A New Total Hg Solid Sorbent Sample Trap.
11. Fill Out The Field Data Sheet.
12. Final Preparations Before Leaving Site.

2.1 Obtain the Mercury Sampling Supply Kit

This Kit should have the following items:

- a. **1 set of double zip-lock bagged gloves.** These specialized gloves should always be double bagged, in protective zip-lock bags and most importantly, kept sealed. These are class-100 vinyl clean gloves and are virtually particle free. Dirt and dust particles can be a source of low-level mercury contamination. Ambient air mercury is typically low in mercury and therefore it is

critical to hand the samples with particle free gloves. As a special warning, do not use latex gloves as they attract dirt and dust. Further, do not use powdered latex gloves as the powder has a measurable amount of mercury. Let Frontier know when more class-100 clean gloves are needed.

- b. ***Sealed Zip-Lock Bag With Previous Weeks Total Hg Solid Sorbent Trap's End Plugs.*** These are the white, Teflon end plugs you removed from the previous weeks Hg sample trap before deploying for sampling. The Teflon end plugs will be going back into the ends of this sample trap, in order to seal, protect and store the trap, prior to shipping back to Frontier. It is therefore critical to keep these end plugs, sealed in the bag during the sample period, so they remain clean.
- c. ***Total Hg Solid Sorbent Trap - For Flow Rate Settings.*** This is the Total Hg Solid Sorbent Trap, when hooked up to the sample line and deployed, will help set the flow rate dial on the sample box to the proper flow rate for Total Atmospheric Hg capture. This is so the actual Total Hg Sample Trap, when deployed and activated later by a timer, will start at the desired flow rate. It is not necessary, however it is good practice to keep the flow rate setting Total Hg Sample Trap in a zip-lock bag for protection. Keep this bag and Solid Sorbent Trap clearly labeled to ensure it is not mistaken as an actual sample.
- d. ***Sealed Zip-Lock Bag - Paper Towels.*** Paper towels are basically particulate free, mercury free and are suitable to clean off the PVC sampling arms and locations where the sample media resides to ensure the new sample media is being deployed in a clean environment.
- e. ***Spray Bottle of Formula 409 cleaner.*** Formula 409 is mercury free (Frontier tested it) and is an effective surfactant/degreaser. It is used on the PVC sampling arms and areas where the sample media resides to remove wind blown dust and particles.
- f. ***Field Data Sheets.*** A field form to record critical sampling information for each sample: Site ID (location where the sampling occurred), Sample Type, Sample Start Date, Sample End Date, Sample Start Time, Sample End Time, Flow Rate Settings, Zero Offset, and Sample Volume.

2.2 Record the Total Atmospheric Hg Solid Sorbent Trap Volume

The Final Sample Volume for the Total Hg Solid Sorbent Trap is adjacent to the LCD display identified as "TAHg" which stands for Total Atmospheric Mercury. Record the final sample volume on the field form.

2.3 Approach the Collector Sampling Arms From Down Wind

With the Sampling Supply Kit and Field Data Sheet, proceed to the sample platform. Carefully approach the sampling arm that is holding the Solid Sorbent Trap (approach from down wind if possible). Try to avoid standing directly upwind of the open sample media. The sampler can be a potential source for mercury as hair and dirt/dust can blow off clothing and into sample media

2.4 Make Observations While the Sample Media is Still in the Sampling Arm

Inspect equipment and sample media, make observations, and record on field data sheet:

- Does everything appear to be as deployed?
- Is the sample media still secured and in its proper place?
- Does the sample arms appear to have an unusual amount of particulate?
- Was the site secured (no sign of anyone getting into the secured platform)?
- Were there any unusual conditions during the test run (wildfires in the area, wind/dust storm, heavy rain)?

2.5 Perform A Post Sample Leak Check of the Total Hg Solid Sorbent Trap

The purpose of this effort is to ensure that there was no leak in the sample line during the sample event. A successful Post Sample Leak Check is a good quality assurance measure and gives confidence that the sample taken is of high quality. A Post Sample Leak Check that fails indicates that there was a leak somewhere in the sample line and the sample volume measured is not the true sample volume as some of the air that passed through the system did not go through the sample trap.

- a. Obtain the Sealed Zip-Lock bag with the Teflon end plugs from the Solid Sorbent Trap.
- b. Open the Zip-Lock bag and place the bag upright in the plastic container (that holds all of the supplies).
- c. Don a pair of clean gloves.
- d. Without touching anything with your glove, reach into the open Zip-Lock that contains the Teflon end plugs and obtain one.
- e. Place the Teflon End Plug into the inlet of the Total Hg Solid Sorbent trap that is currently deployed.
- f. Proceed back to the sample box and double check the final sample volume recorded on your field data sheet for accuracy. Verify recorded value on your field data sheet.
- g. Record the Zero Offset from the Mass Flow Meter. The Zero-Offset is the reading on the Mass Flow Meter when there is no flow through the system. The Mass Flow Meter should be on for at least 15 minutes and the flow control valve should be off (turned all the way to the right). Read the zero-offset value and record on the field data sheet. This value should be close to zero

and could be positive or negative. This value will be used to correct for electronic drift in the sample flow rate.

- h. Record the Final Zero-Offset value.
- i. Turn on the sample pump.
- j. Open the flow control valve. Open the valve slowly and open to $\frac{3}{4}$ of the full open flow.
- k. With the Teflon end plug in place, you are now evacuating the air from the sample media all the way back through the sample line to the mass flow meter. The flow rate should go to zero if this is a successful leak check.
- l. A failed leak check is any mass flow reading that exceeds 0.07 standard liters per minute. If this occurs, you will need to begin to leak check the system starting at the sample box and progressing through the sample line to the sample media.

2.6 Release the vacuum after performing your Post Leak Check

After performing the post leak check, there is a vacuum behind your sample media. **Do not release the vacuum at the sample trap!** The sudden decompression behind the sample trap could push the sample media out of the trap or at least disturb the sample beds. This could lead to the loss of a sample.

Release the vacuum, after the post leak check, by unscrewing the Teflon swage fitting on the face plate of the sample box, labeled as the inlet for the VHg (0-5 slpm) side of the sample box. Unscrew the swage nut holding the sample line that leads to the Total Hg Solid Sorbent Trap. Slowly pull up the $\frac{1}{4}$ inch sample line out of the swage fitting, just for a moment. Immediately replace the sample line and secure the Teflon nut. Do not over tighten the Teflon nut. Over tightening the nut can actually cause a leak. Hand tight pressure is sufficient to make a seal.

2.7 Retrieve the Total Hg Solid Sorbent Trap

- a. Proceed to the sample arm holding the Total Hg Solid Sorbent trap. The Total Hg Solid Sorbent Trap is “housed” at the end of the sampling arm, inside a plastic junction box. The side of the junction box has a panel that can be opened. This panel will give access to the sorbent trap and where the sorbent trap is connected to the sample line that runs back to the sampling box. Open the “door” on the junction box by removing the top screw that secures the top of the access panel to the box.
- b. Allow the door of the sample box to rotate down and hang off the screw at the bottom of the box that is holding the panel in place
- c. Don a new pair of class-100 clean gloves.

- d. Retrieve the sealed Zip-Lock bag that you saved when you deployed the solid sorbent sample trap. The zip-lock bag should have one more Teflon end plug in it (this from when you removed both end plugs when you deployed the trap).
- e. Label the sample bag with the Sample ID using a “Sharpee” or some other indelible marker with the following convention:

TAHg - Site ID - Sample Date

TAHg = Signifies Total Atmospheric Hg

Site ID = the name of the sampling location (i.e., HMC for HoltraChem)

Sample Date = the date that the actual sample was taken

Example: TAHg-HMC -02-15-03

- f. With a gloved hand, gently disconnect the sample trap from the sample line.
- g. Insert the last Teflon end plug into the open end.
- h. The trap is now sealed. Place the trap in the zip-lock bag and seal the bag.
- i. Record the Final Sample volume on the field data sheet.
- j. Record the Final Zero Offset for the Total Hg trap.

2.8 Store the Samples and Field Data Sheets

Put the field data sheet in with the sample media and seal in a zip-lock bag. Place in the refrigerator. Keeping the filters in a cool, dark atmosphere ensures that Hg does not thermally desorb off the ambient air particulate. The Total Hg Sorbent Traps are very stable with regards to mercury and therefore do not require refrigeration, however, it is best to keep all of the sample media together during this storage phase.

Store the sample media in the refrigerator until the end of each month. After the end of the month, send the sample media on ice, to Frontier in a cooler. Directions for shipping the sample media are presented as step 3.0.

2.9 Clean the Sampling Arms

Clean the sample arms and in particular, clean the areas where the sample media are normally deployed. Using Formula 409, spray down the plastic sample arms with this particle and grease removing surfactant. Use paper towels to wipe down and remove the Formula 409 (along with the particles etc).

2.10 Deploy “Dummy” Sample Media and Set Sample Media Flow Rates

- a. Obtain the “dummy” sample media.
- b. Wearing gloves (for practice/habit purposes only) obtain the Solid Sorbent Trap. Remove the Teflon end plugs and connect the outlet of the trap to the Teflon sample line. Run the Inlet of the sample trap down into the bottom hole intended to expose the inlet of the Total Hg Sample Trap.
- c. Once the dummy sample media is secured, proceed to the sample box.
- d. Turn the flow rate control knob on the Mass Flow Meter all the way off (to the right) until it stops.
- e. Plug the power cord in for the pump that powers the Total Hg Sorbent Trap. This is the pump that is connected to the sample box via the ¼” sample line.
- f. Slowly adjust the flow rate to - 4.0 slpm by rotating the flow control valve to the left. Allow the system to continue to flow and stabilize to as close to 4.0 slpm as possible.
- g. When the flow rate signal has stabilized for the Solid Sorbent Trap, unplug the power cord.
- h. You have now set the flow rate for the sample media, so do not change the setting of the flow control knob.
- i. Plug pump power cord into the timer.
- j. Set the timer for the desired time for sampling to start and end.
- k. **IMPORTANT:** The power for the sample box itself should be plugged directly into a power socket. The sample box will need to always have power supplied to it. Therefore, do not plug the sample box power into the timing system used to turn on the pumps.

2.11 Deploy A New Total Hg Solid Sorbent Sample Trap

- a. Wearing clean gloves, remove the Solid Teflon End Plugs on either end of the sample trap.
- b. Place the Solid Teflon End Plugs into the Ziplock bag that the trap came in and seal the bag.
- c. There is a sample flow direction arrow on each trap. This is critically important. The arrow on the sample trap indicates how you should attach the sample trap to the sample line.
- d. Obtain the sample line inside the plastic junction box. Connect the sample line to the back of the sample trap. Again, the arrow on the trap should be pointing towards the sample line.
- e. With the trap connected to the sample line, insert the open end (inlet end of the sample trap) down into the opening of the junction box. The inlet end of the IC trap should only be 1-2

inches down from the bottom of the junction box. Adjust the sample line so it holds the sample trap at the proper location below the junction box.

- f. Rotate the plastic panel on the junction box back to cover the junction box opening. Secure the panel with the screw. Make sure that this panel is properly sealed to ensure that no rain or dust get blown into the junction box. This is to keep the IC trap as clean as possible.

2.12 Fill Out The Field Data Sheet

Obtain a new Field Data Sheet. Record the following in the appropriate locations of the field data sheet:

- a. Record the Start Zero Offset For the Total Hg Solid Sorbent Trap. The Mass Flow Meter will display an “at rest” zero flow value.
- b. Record the Date that the sample was set up in the field.
- c. Record the Date that the sample will actually be activated to start sampling.
- d. Record the Site ID.
- e. Record the Sample ID:

(e.g. TAHg - HMC - Sample End Date)

Store the Field Data Sheet in a zip-lock bag inside the supplies container.

2.13 Final Preparations Before Leaving Site

1. Double check to ensure that pumps are plugged into the timer system.
2. Double check to ensure that the timer is set for the proper time and date required for sampling.
3. Push the red Totalizer Button to the right of the Total Volume display. This zeros the volume that is stored in memory.
4. Double check to ensure that sample box is plugged directly into a power socket and not into the timer. You want to be sure the power is always on for the sample box, otherwise, the mass flow reading could be very noisy from suddenly being turned off and on.

Section 3 Sample Shipment

1. The filter packs and Sorbent Traps should all be packed well with some sort of packing material like bubble wrap to ensure the traps are not crushed by the blue ice (coolant packs) that will be used to keep the filter packs cool.
2. Line the bottom and sides of cooler with ice packs.

3. Ensure that each filter pack and each solid sorbent trap have field data sheets.
4. Place the extremely well packed bubble wrapped filter packs and traps in the cooler. Ensure that all of the spaces in the cooler are filled with packing material to ensure that things do not shift. If there is room in the cooler, the ice packs will move around and could damage the sample traps.
5. Fill out and place a Chain of Custody Record (COCR) in with each cooler.
6. Ship the cooler to the following address:

Attention: Bob Brunette
Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, Washington 98109
Phone: 206 622 6960

7. Ship the cooler with a sufficient priority so it arrives the next day. This to ensure the cooler ice packs keep the filter packs cool all the way to Frontier. FedEx Standard Overnight service is recommended.

Section 4 Sample Media Supply and Sampling Supplies

Frontier will supply the following on a monthly basis:

- Sample media;
- Vinyl clean gloves;
- Field Forms; and
- Chain of Custody Records.
- Formula 409 and paper towels purchase at local store.

Section 5 Field Sampling Questions and Trouble Shooting

If you have problems with your equipment or have questions, please call the CDM Project Manager, Ernest Ashley at 1-800-343-7004, or the Frontier Project Manager, Bob Brunette toll free at: 1-877- 622-6960.

Section 6 References

Gas and Particulate Phase Hg Ambient Air Sampling Via Frontier Solid Sorbent and Total Particulate Hg Method Frontier Geosciences, December 2002.

Atmospheric Mercury Sampling Effort

Field Sample Data Sheet

Date Sample Media Was Deployed: _____

Date Sample Media Began Sampling: _____

Date Sample Media Stopped Sampling: _____

Date Sample Media Was Retrieved From Site: _____

Total Atmospheric Mercury (Solid Sorbent Trap)

Zero Offset = Mass Flow Meter With No Flow

Pre-Sampling Zero Offset: _____

Post- Sampling Zero Offset: _____

Sample ID: TAHg - Site ID - Sample End Date = _____

Final Sample Volume (Solid Sorbent Trap): _____ (Liters)

**HoltraChem Manufacturing Site
Cell Process Dismantling
Total Atmospheric Mercury
Field Sampling Record**

Sample ID (HMC – TAHg – Station Number – Sample End Date): _____

Date/Time Sample Media Was Deployed: _____

Date/Time Sample Media Began Sampling: _____

Date/Time Sample Media Stopped Sampling: _____

Date/Time Sample Media Was Retrieved: _____

Weather Conditions During Sampling: _____

Temperature _____ **Wind Speed** _____ **Wind Direction** _____

Required Sample Data: (Zero Offset = Mass Flow Meter with No Flow)

Pre-Sampling Zero Offset _____

Post-Sampling Zero Offset _____

Final Sample Volume _____

Observations: _____

Sampler: _____

**Total Mercury Digest for Gas/Air Samples
Collected on Frontier Sorbent Total Mercury (FSTM) Traps
FGS-009.2**

Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, WA 98109

Originated by: Nicolas S Bloom and Eric M. Prestbo
Revised by: Paul Laskowski
January 3, 2000

Effective Date: June 27, 2000

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On June 27, 2000, this procedure was reviewed and validated by Michelle L. Gauthier, Laboratory Manager and Beverly H. van Buuren, Quality Assurance Program Director.
Signatures are on file.

1.0 SCOPE AND APPLICATION

1.1. This method is a peer-reviewed, published procedure for the determination of total mercury in air and gas samples collected on dry sorbant traps. All samples must be subjected to an appropriate leaching step, as described herein, prior to analysis by CVAFS.

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- 1.2. The typical estimated method detection limit as derived from the standard deviation of the blank traps is 0.2 ng Hg/sample trap for a 1m³ sample.

2.0 SUMMARY OF METHOD

- 2.1. FSTM traps with air samples collected on them are subjected to a hot (50-60 °C) leaching with a HNO₃/H₂SO₄ mixture of concentrated acids for 1.5 hrs. The leachate is then diluted up with BrCl on the day of analysis by CVAFS method and analyzed according to FGS-069.

3.0 INTERFERENCES

- 3.1. The carbon granules are not dissolved by this procedure, but experience shows that this strong acid leach is sufficient to extract all collected Hg that has adsorbed on the surface. It is critical, however, that the final solution contains a sufficient volume of strong acids to avoid re-adsorption of Hg to the carbon granules.
- 3.2. Due to the amount of FSTM compounds that leach into the digests, a maximum aliquot size of 1.0 mL for each digested trap is used. These compounds have the ability to overwhelm the acid traps on the CVAFS analyzer making for high blanks, and to destroy the gold sample collection traps.

4.0 SAFETY

- 4.1. Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan. This includes, but is not limited to, laboratory coat, safety goggles, and latex gloves under clean gloves.
- 4.2. The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. All laboratory personnel should refer to the MSDS for each chemical they are

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working with.

- 4.3. All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.
- 4.4. Waste Management and Pollution Prevention: Any wastes generated by this procedure should be disposed of according to SOPs FGS-099 and FGS-100, which provide instruction on dealing with laboratory and client waste. Pollution prevention information can be found in the current Frontier Geosciences Hazardous Materials Management Plan (HMMP), which details and tracks various waste streams and disposal procedures.

5.0 PROCEDURE

- 5.1. Each FSTM trap has two sections; the first one exposed to the flow of the gaseous sample is referred to as the FSTM-A trap. The one behind the FSTM-A trap in the flow stream is referred to as the FSTM-B trap. Find the direction flow, usually indicated by an arrow somewhere on the trap, to determine which section is which.
- 5.2. In a clean hood, prepare a digestion vial with the appropriate sample ID and remove the lid. Neutralize as much of the static charge as you can that may reside on the rim and inside the vial with an appropriate anti-static device.
- 5.3. Pull all fittings and shrink fit tubing from the trap and, using a glass tube cutter, open the trap carefully just in front of the plug that holds in the FSTM-A granules. Neutralize as much of the static charge as you can that may reside on and within the FSTM trap.
- 5.4. Clean off the reaming rod with a squirt of ethanol on a kim-wipe. Use it to push the contents of the IC trap from the back of the FSTM-B section until the first foam plug falls into the digestion vial, along with all the FSTM granules up to the middle foam plug. Tap trap to rim of vial to release any loose granules. Hold trap opening over vial while pushing the FSTM-B trap back to its starting

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position. This should release any granules that may be stuck to the middle foam plug.

- 5.5. If the FSTM-B trap for this sample is to be digested, clean off the reaming rod again and use it to push the rest of the contents into a separate digestion vial.
- 5.6. Cap off undigested FSTM-B traps into their tube using the red plastic end plugs that are distributed with the FSTM traps (return to labeled container if the label is not directly affixed to the trap itself).
- 5.7. Add the nitric/sulfuric mixture to the digestion vial immediately after collecting the trap sections into the vial, and cap tightly. This will prevent loss of the granule due to a buildup of static charge, which makes granules “jump” out of the vial.
- 5.8. After all the sample traps are collected into the digest vials, the digest vials are then heated for 2.0 hours on a hot plate, and then allowed to cool to room temp.
- 5.9. The samples are then diluted up to their digestion vial’s capacity with BrCl. The carbon granules are not dissolved by this procedure, but experience shows that this strong acid leach is sufficient to extract all adsorbed Hg.

6.0 QUALITY ASSURANCE

- 6.1. Maximum Sample Batch Size: 50 samples for standard level QC; 40 samples for high level QC.
- 6.2. Preparation Blanks: 30 percent of the FSTM-B traps are analyzed out of a batch of samples as both a check for breakthrough from the FSTM-A traps, and as the preparation blanks for correction by the mercury inherent in the reagents and on the FSTM traps. Three times the standard deviation is used to determine estimated MDL for each batch.
- 6.3. Analytical Duplicate: Two per batch, 25 RPD limit.

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6.4. Analytical Spike: Two per batch, 75-125% recovery limit. As there is no way to do digestion duplicates, a spike of 1.0 ng of mercury standard goes into the bubbler with the sample aliquot.

7.0 CORRECTIVE ACTIONS

7.1. Since the entire sample is used in the digestion process, it is imperative to do the digestion correctly the first time. This primarily relates to limiting sources of contamination. Including, but not limited to, making sure none of the “A” trap FSTM particles are included in the digestion of the “B” trap, flushing repipettors a minimum of three times before adding reagents to samples, cleaning digestion tools (i.e. reaming rod) between each sample, changing clean gloves when appropriate, and in general following all ultra-clean procedures.

**Total Mercury Analysis by Cold Vapor - Atomic Fluorescence
Spectrometry (CV-AFS)
FGS-069.2**

Frontier Geosciences Inc.
414 Pontius Avenue North
Seattle, WA 98109

Originated by: Sarah DuBord, Lucas Hawkins, Dustin Leen, and Amber Steward
Originated: May 10, 2000

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Last Revision: June 8, 2001

Effective Date: June 11, 2001

On June 8, 2001, this procedure was reviewed and validated by Michelle L. Gauthier,
Laboratory Manager and Beverly H. van Buuren, Quality Assurance Program Director.
Signatures are on file

1.0 SCOPE AND APPLICATION

1.1. This SOP is designed to ensure that reproducible, traceable procedures are followed in the standardization of the total mercury analyzers and in the analysis

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Revised: 06/8/01

of samples for total mercury, as well as to establish the bounds wherein data will be considered acceptable.

- 1.2. This method provides for the determination of total mercury in a wide range of matrices including aqueous, biologic, and geologic media. In general, using clean handling and reagents, the typical detection limit for the method is less than 0.2 ng/L for aqueous samples and 0.5 ng/L for digested solid samples or 0.5 ng/g as Hg.
- 1.3. This SOP consists of three aspects: (1) preparation of total mercury standard solutions, (2) calibration sequence of the total mercury analyzers, and (3) analysis of samples for total mercury as well as Hg (II) determination for tissues.

2.0 SUMMARY OF METHOD

2.1. Preparation of Total Mercury Standards

- 2.1.1. Mercury (Hg) standard solutions are prepared using ultra-clean class volumetric glassware and gravimetrically calibrated pipettors. All waters and reagents are pre-tested and must have very low Hg concentrations. All standard solutions, preparations, and calibrations must be logged in the Mercury Standard Logbook upon receipt or creation and given a unique identification number.
- 2.1.2. Any standard, along with its original documents, should be labeled with the receipt date and the receiver's initials. All documentation should be given to the QA Office. The QA Office is responsible for maintaining standard records as well as updating the folders around the laboratory where copies are kept.

2.2. Total Mercury Analyzer Calibration Sequence

- 2.2.1. The calibration sequence for the determination of total mercury consists of a 5-point curve (0.05 ng, 0.10 ng, 0.50 ng, 2.00 ng, and 4.00 ng), an initial calibration verification (ICV) standard, and an initial calibration blank (ICB).
- 2.2.2. The calibration standard is made from a dilution of NIST-3133; in most cases, the highest calibration standard determines the range of sample concentrations that are considered valid.

2.2.3. The ICV standard is a second-source standard that is made from diluted NIST 1641d; it verifies the accuracy of the standard used for the calibration curve.

2.2.4. The ICB is used to show that the system is low in total mercury as well as to allow for blank correction of standard curve.

2.3. Total Mercury Analysis

2.3.1. All total mercury analyses receive a unique dataset identifier. This is composed of the instrument type and number, the date, and the calibration number for that day. The format is as follows: THG8-010224-1 where “THG” refers to a total mercury analyzer, “8” refers to total mercury analyzer number 8, “010224” refers to the date (February 24, 2001, in YYMMDD format), and “1” refers to the first calibration of that day.

2.3.2. Total mercury analyses are split into two categories: waters and solids. For analysis of aqueous samples, an aliquot of oxidized sample is neutralized with hydroxylamine-hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) and added to a bubbler. For solids, an aliquot of digested sample is directly pipetted into the bubbler.

2.3.3. For the analysis of waters or solids, stannous chloride (SnCl_2) is added to reduce the solution, and the bubblers are sealed with Keck Clips. Blanked gold traps are placed at the end of the soda-lime traps. The bubbler is purged with nitrogen (N_2) for 20 minutes. All gas that flows into the bubbler should only leave the system through the soda-lime trap and then gold trap.

2.3.4. The gaseous mercury amalgamates to the gold traps, which are removed and sequentially placed, one at a time, in the analytical train. The gold trap is heated, thus releasing the mercury into the argon gas stream, which flows into the analyzer. As sample peaks are produced by the strip chart recorder, each peak is labeled with that sample’s unique ID.

3.0 INTERFERENCES

3.1. Due to the high levels of acid and halogens (i.e., bromine) in digested solids, it is recommended that aliquots of no more than 5.0 mL (1.0 mL if hydrofluoric acid is present at significant concentrations) of the digestates be analyzed, unless otherwise instructed by a Project Manager (PM) or Group Leader.

3.2. When running digested solid samples, bubbler water should be changed and

purged after a total of 10 mL of digestate has been added to the bubbler. This is done to avoid a build up of acidity and halogens in the bubbler water that can result in low sample recoveries as well as a drop in analyzer sensitivity. These interferences are most evident while analyzing digested QC samples.

- 3.3. Water has the potential to create recovery interference. To minimize, if not prevent interference from water, ensure that your soda-lime pre-traps remain dry. All handling of gold traps should be done using dry class-100 clean gloves to prevent water droplets from entering analytical train.
- 3.4. The presence of high concentrations of silver and/or gold can cause the SnCl_2 to precipitate out and adhere to the bubbler walls. High concentrations of these metals can sometimes be found in the matrix spike samples from digestion sets that are being shared with the Trace Metals Group. When analyzing digestates where the matrix spike samples have been spiked with silver or gold, the matrix spike samples should not be analyzed for mercury. Instead, an analytical spike/analytical spike duplicate (AS/ASD) should be analyzed.

4.0 SAFETY

- 4.1. Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan. This includes, but is not limited to, laboratory coat, safety goggles, and latex gloves under clean gloves.
- 4.2. The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the MSDS for each chemical they are working with.
- 4.3. All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.
- 4.4. Waste Management and Pollution Prevention: Any wastes generated by this procedure should be disposed of according to SOPs FGS-099 and FGS-100,

which provide instruction on dealing with laboratory and client waste. Pollution prevention information can be found in the current Frontier Geosciences Hazardous Materials Management Plan (HMMP), which details and tracks various waste streams and disposal procedures.

4.4.1. Quality Control procedures for aqueous samples

4.4.1.1.A high-QA analytical batch is defined as 20 or fewer field samples, not including PBWs, ICB, CCV, CCB and MD/MS/MSD. A standard-QA batch is 25 or fewer field samples.

4.4.1.2.A minimum three PBWs are to be performed per analytical day.

4.4.1.3. A ML spike must be performed for each analytical day. For waters, the ML is 0.05 ng added to a clean bubbler. Similar to the analysis of the lowest standard. For all other preparations, the ML is digested with the sample set.

4.4.1.4.One CRM (200 μ L of 1/200 diluted NIST 1641d) must be analyzed for each analytical day. In the case for waters, this requirement is fulfilled using the NIST 1641d for the ICV of the calibration.

4.4.1.5.One CCV/CCB must be performed every 10 analytical runs for High-QA samples (can be stretched to 11-12 samples for Standard-QA).

4.4.1.6.One Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be performed every 20 samples (25 if standard QA). MS/MSDs are spiked at 1-5 times the ambient concentration, with 0.1 ng being the minimum spiking level. Sample aliquots for MS/MSDs should be the same as the ambient sample aliquot. Spikes are added to the split aliquots for volumes of 10 mL or greater. For less than 10 mL aliquots, spikes are added directly to the bubbler. **NEVER ADD SPIKE DIRECTLY TO ORIGINAL SAMPLE UNLESS OTHERWISE STATED.**

4.4.1.7. A Matrix Duplicate (MD) is required every 20 samples (25 if standard QA). A Matrix Triplicate (MT) sample may be request by the PM. MD/MT should be performed using the same sample aliquots as the ambient sample

4.4.1.8.A Project Manager may ask for a blank spike to be performed. Specific clients have mandatory spiking levels regarding blank spikes. Should a blank spike need to be analyzed, it needs to be 100 mL of reagent water with usually 1-2% BrCl and spiked at requested levels. The created blank spike would be treated just like a normal aqueous sample, and would be noted in the mercury standards logbook.

4.4.1.9.The analytical day must end with a CCV/CCB.

4.4.1.10. All standards used for analysis must be noted on the dataset spreadsheet.

4.5. Analysis of Frontier Sorbent Total Mercury (FSTM) Traps and Particulate Filters

4.5.1. FSTM traps and particulate filters are digested and analyzed as if they were solids (see section 7.8.5), with a few exceptions. The FSTM matrix can cause recovery problems, as well as questionable blanks. Therefore there are a few modifications to the analysis and QC requirements. Due to the complexity of this analysis, inexperienced analyst should not analyze FSTM digests.

4.5.1.1. FSTM traps or particulate filters should be digested according to SOP FGS-011.

4.5.1.2. Aliquot sizes used for analysis should be 1 mL or less. 5 mL may be used at PM request, but not recommended. Should the bubbler contain more than 2 mL of digestate, the water must be changed and repurged before continuing analysis. It is recommended that the smallest possible aliquot sizes be used for this matrix, ensuring that you maintain quality data. All blanks, blank spikes, and low level/non-detect samples must be analyzed at the same aliquot size.

4.5.2. At the end of this analysis, bubblers must be cleaned using potassium hydroxide (KOH).

4.6. Quality Control Requirements for IC Traps and Particulate Filters

4.6.1. A minimum of three preparation blanks per batch: PBFSTM for FSTM traps, PBF for filters. PBFSTMs must use carbon tubes from the same lot number as the samples.

4.6.2. A CCV/CCB must be performed every 10 analytical runs.

4.6.3. A blank MS/MSD pair digested at 100 ng/trap, using carbon tubes from the same lot number as the samples, must be analyzed for each batch.

5.0 QUALITY ASSURANCE

5.1. Analysts are to verify QC sample results in “real-time” as they come off the instrument. This allows for correction of any analytical problems immediately.

5.2. The acceptable recoveries must be met in order to consider a data set valid. Of particular importance to the client is Frontier’s position that a **single non-compliant result on a QC sample does not automatically invalidate a data set**. All data points noted on the analysis day’s spreadsheet as invalid for known reasons may be discarded if rerun during the same analysis day. In the event that the system becomes out of control during the analysis day, all results bracketed between valid QC data points shall still be considered valid.

Quality Control Limits for Determination of Total Hg *

QC Item	Acceptance Criteria
ICV (CRM for aqueous samples)	80-120% recovery (Goal: 90-110%)
ICB and CCBs	Individual limit of ≤ 0.25 ng/L (Instrument blanks are not blank corrected)
CRM (for solids samples) or Blank Spike	75-125% recovery
Calibration curve correlation coefficient (minimum 5 points)	$r \geq 0.995$, linear regression forced through zero
CCVs	80-120% recovery
PBW _s	Each blank ≤ 0.25 ng/L with SD ≤ 0.15 ng/L; 3 per analytical day (3 per calibration curve)
PBS _s	Mean ≤ 0.5 ng (or $< 0.1 \times$ lowest sample) 3 per analytical batch of ≤ 20 samples (≤ 25 for standard QA)
PBT _s	Mean ≤ 0.5 ng (or $\leq 0.1 \times$ lowest sample) 3 per analytical batch of ≤ 20 samples (≤ 25 for standard QA)
MS/MSD	75-125% recovery with RPD ≤ 25 1 per analytical batch ≤ 20 samples (≤ 25 for standard QA)
MD/MT	≤ 25 RPD/RSD
Blank Spike (if requested)	75-125%
Minimum level spike (ML)	1 per matrix per analytical day

***Client QC requirements may be more stringent. Please refer to project sheets prior to analysis.**

6.0 CORRECTIVE ACTION

- 6.1. The Quality Control data gathered throughout the analytical day provides an indication of overall data quality. Therefore, corrective action is required if quality assurance measures are outside of acceptable limits. First, a careful re-examination of the calculations is performed to assure that there are no numerical errors. The Project Manager is informed of any data issue, and they decide what, if any, corrective action, including reruns, is warranted. The Quality Assurance Officer oversees this process and has the final say in what corrective action is to be performed.
- 6.2. If insufficient sample volume remains to repeat analysis for samples analyzed after the last acceptable CCV, use best professional judgment to estimate values (usually through CCV correction). Bracket those samples from previous acceptable QC data points, and provide a narrative explanation on the dataset coversheet.
- 6.3. The above corrective actions apply only to events which have unknown causes. If the analyst is aware of the cause, no corrective action is necessary other than reanalyzing the sample.

7.0 EQUATIONS

7.1. Total Mercury in Water

- 7.1.1. Average all bubbler blanks (B) using the peak height/peak area values from the strip chart/integrator.
- 7.1.2. The slope of the calibration curve (A) is calculated using the chart units per ng of mercury. A standard statistical package is used to determine the slope, using the five initial calibration points. The calibration points are first corrected by subtraction of the mean bubbler blank. The statistical program forces the regression line through zero (0,0). Average the results for the preparation blanks (PB), from the chart values of at least three preparation blanks.
- 7.1.3. To calculate total mercury in waters (ng/L), use the following equations:

$$7.1.3.1. \text{THg/Aliquot (ng)} = [(\text{Peak Height or Peak Area}) - B] / A$$

$$7.1.3.2. \text{THg Gross (ng/L)} = [(\text{THg}/\text{Aliquot})/\text{V}_a/\text{D}] * (1000 \text{ mL/L})$$

$$7.1.3.3. \text{THg Net (ng/L)} = [(\text{THg Gross})/\text{F}] - (\text{PB} * \text{X})$$

Where:

- **B** is the average bubbler blank peak height or peak area (in units)
- **A** is the slope of the calibration curve (in ng/units)
- **V_a** is the volume of sample analyzed (the aliquot size) in mL
- **D** takes into account any dilution of the sample and is expressed as a fraction (0.2 = 1/5 dilution)
- **F** equals: $1 - [\text{BrCl}\% / (1 + \text{BrCl}\%)]$; F is expressed as a fraction which accounts for the dilution of a sample from the addition of BrCl. Taking a 100 mL aliquot of a sample preserved at 5% BrCl would result in F = 0.9524. This corresponds to the percentage of 100 mL volume which actual sample
- **PB** is the average of the preparation blanks in ng/L
- **X** is an integer related to the preservation level of the samples (i.e., X=2 for a sample which is preserved at 2% BrCl), thus accounting for the extra contribution of mercury in the BrCl

7.2. Total Mercury in Solids

7.2.1. To calculate total mercury in a solid (ng/g), use the following equations:

$$7.2.1.1. \text{THg}/\text{Aliquot (ng)} = [(\text{Peak Height Or Peak Area}) - \text{B}] / \text{A}$$

$$7.2.1.2. \text{THg Gross (ng/L)} = [(\text{THg}/\text{Aliquot})/\text{V}_a/\text{D}] * (1000 \text{ mL/L})$$

$$7.2.1.3. \text{THg}/\text{Digest (ng)} = [(\text{THg Gross} - \text{PB}) * \text{V}_d / (1000 \text{ mL/L})]$$

$$7.2.1.4. \text{THg Solid (ng/g)} = (\text{THg}/\text{Digest}) / \text{m}$$

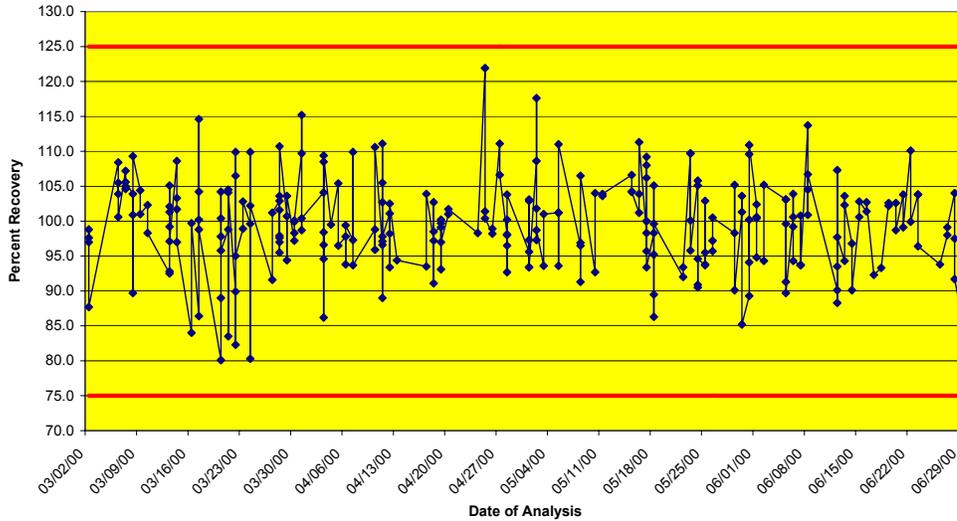
Where:

- **B** is the average bubbler blank peak height or peak area (in units)
- **A** is the slope of the calibration curve (in ng/units)

- V_a is the volume of sample analyzed (the aliquot size) in mL
- V_d is the final digested volume of the digest in mL
- **D** takes into account any dilution of the sample and is expressed as a fraction ($0.2 = 1/5$ dilution)
- **m** is the mass of the sample that can be expressed as either a dry or wet weight. (in grams)
- **PB** is the average of the preparation blanks in ng/L

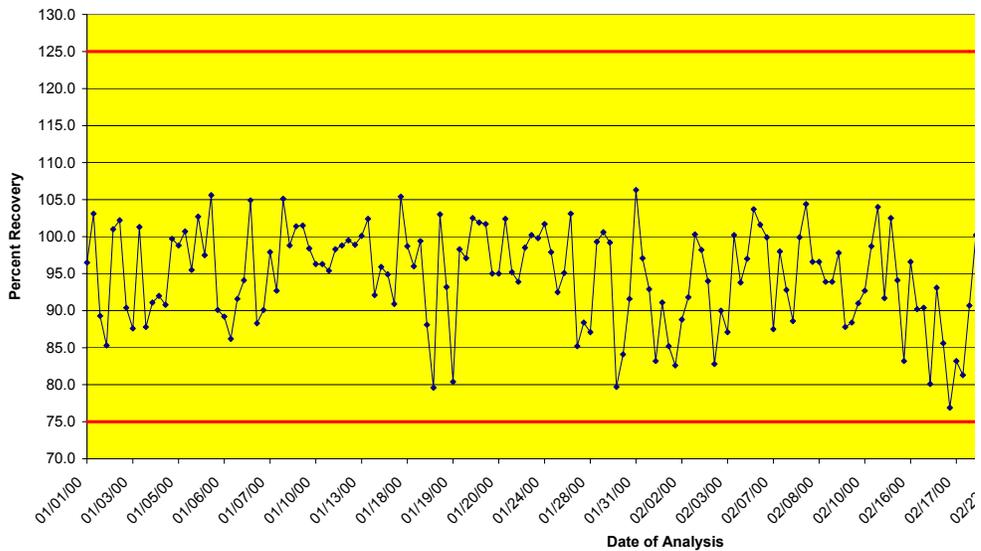
THg NIST 1641d Percent Recovery

mean=99.7
n=273



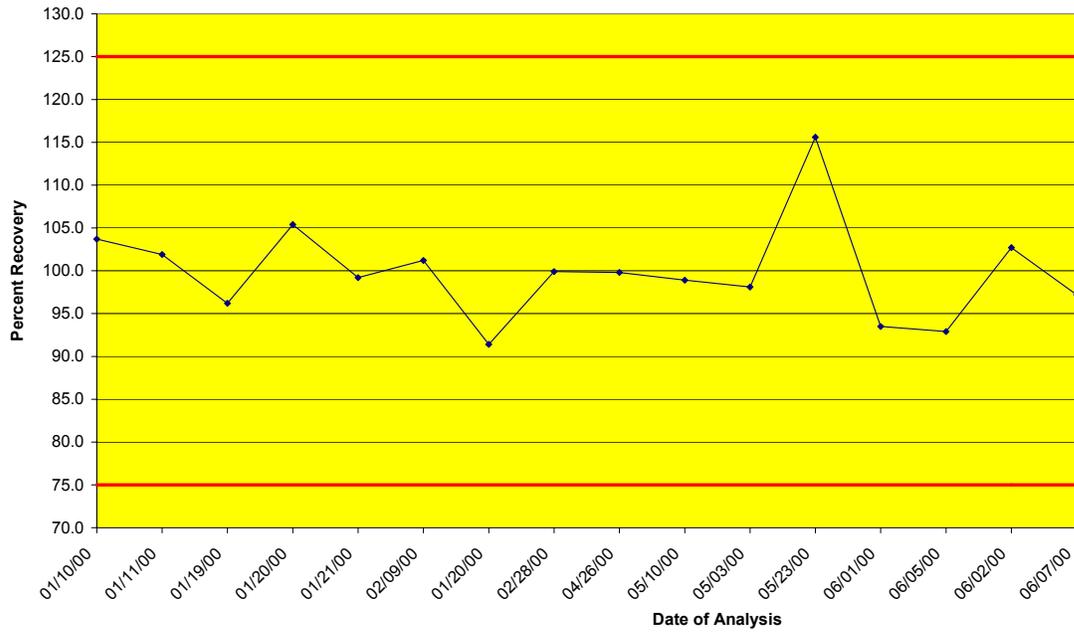
Graph THg Dorm-2 (fish) Percent Recovery

mean=94.1
n=178



All Frontier SOPs are Proprietary Information and protected by WA state law. Proprietary Information shall be kept in the strictest confidence & shall not be used or appropriated to benefit any party without prior written consent to Frontier.

THg NIST-2709 (soil) Percent Recovery
mean=100.1
n=20



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