ANALYSIS OF TOTAL MERCURY IN WATER AND AQUEOUS WASTES BY COLD VAPOR ATOMIC ABSORPTION (CVAA) SPECTROSCOPY

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1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the analysis of water samples for total mercury content utilizing cold vapor-atomic absorption (CVAA) spectroscopy. The procedure is based on EPA Method 245.1 and SW-846 Method 7470A. It is applicable to the determination of mercury in surface, saline, effluent, and waste waters. It is also used for the analysis of TCLP and SPLP extracts. This SOP is applicable to the analysis of samples with Test Identifiers (Test ID) W-HG-H, W-HG-H-F, W-HG-H-R, TCLP-HG-H and SPLP-HG-H. The method detection limit (MDL) is 0.10 µg/L and the practical quantitation limit is 0.50 µg/L.

2. SUMMARY OF THE METHOD

Samples are digested using a combination of acids and strong oxidizers which converts all mercury present in the sample to Hg^{+2}. The samples are then treated with sodium chloride-hydroxylammonium chloride solution to remove excess oxidizing reagents. Each sample digestate is introduced into a gas-liquid separator via an autosampler and peristaltic pump delivery system. The mercuric ions are reduced to atomic mercury vapor by stannous chloride in the gas-liquid separator and purged into the spectrometer's absorption cell by a stream of nitrogen gas or air. The mercury present is measured as a change in absorption in a photomultiplier tube. Mercury in water is measured and reported as µg/L mercury.

3. APPARATUS AND EQUIPMENT

3.1 Varian SpectraAA-220 Atomic Absorption (AA) Spectrophotometer with a Mercury hollow cathode lamp; Serial No. EL-98093105; Software: SpectrAA Pro, Version 5.0.

- 3.1.1 VGA-76/77 reagent pumping unit.
- 3.1.2 Black-Purple sample pump tube for the VGA-76/77 pump (1 needed).
- 3.1.3 Black-Black reagent pump tube for the VGA-76/77 pump (1 needed).
- 3.1.4 Varian gas-liquid separator.
- 3.1.5 Varian cold vapor absorption cell.
- 3.1.6 SPS-5 Sample Preparation System.

3.2 Nippon RA-3320 Reduced Vaporization Mercury Analyzer; Serial No. 06400552. Software: RA3Win, version 1.2.2 (2000).

- 3.2.1 Nippon SC-3 autosampler: Serial No.06410266. Autosampler with a 10 standard sample and 50 test sample rack.
- 3.2.2 Nippon RD-3 reagent dispenser - Serial No. 06420390.
- 3.2.3. Nippon sample test tubes.

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3.3 Pipettes:

3.3.1 100 – 1000 µL Eppendorf pipette

3.3.2 10 – 100 µL Eppendorf pipette

3.3.3 Fisherbrand repipetter; 50 mL capacity

3.4. Ohaus top loading balance, 4000 g capacity

4. REAGENTS AND CHEMICALS

Reagents used for analysis must be logged in to the LIMS standard prep tracker to generate a serial number. The label printed from the LIMS standard prep tracker must be placed on the bottle of reagent in the laboratory. The reagents used in analysis are documented on the 'High Level Mercury Calibration Standard Preparation Reagent Log' located on the Bureau's computer network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Mercury\Prep\Solution Logs for High and Low Level Total Hg\Analysis Reagents\Water\High Level Mercury Calibration. Update the log for each analysis and place a copy in the lab report. See DEP SOP MT-069 for reagent documentation requirements and expiration dates.

4.1 Deionized (DI) water

4.2 Trace Metal Grade Sulfuric Acid (H_2SO_4) - The purchased acid is stored in the fume hood cabinet and the expiration date is provided by the manufacturer.

4.3 Trace Metal Grade Nitric Acid (HNO_3) - The purchased acid is stored in the fume hood cabinet and the expiration date is provided by the manufacturer.

4.4 50 % (v/v) Sulfuric Acid - Add 250 mL of concentrated H_2SO_4 to 500 mL volumetric flask half filled with DI water. Dilute to volume and mix well. Store this reagent in a 1 L Teflon bottle. The expiration date given for this prepared reagent is the same as the manufacturer's expiration date for the concentrated acid.

4.5 12 % Sodium chloride-hydroxylammonium chloride solution ($NH_2OH{\cdot}HCl$) - Add 60 g of hydroxylamine hydrochloride and 60 g sodium chloride to a 500 mL Teflon bottle. Dilute to volume with DI water and mix well. The expiration date for this prepared reagent is 1 year from the preparation date.

4.6 10 % Stannous Chloride Solution ($SnCl_2{\cdot}2H_2O$) - Working in the fume hood, slowly add with gentle mixing 7 mL of H_2SO_4 to a 500 mL Teflon bottle half full with DI water. Weigh 50 g of $SnCl_2$ di-hydrate ($SnCl_2{\cdot}2H_2O$) and add to the acidic solution. Dilute to volume and mix well. The expiration date for this prepared reagent is 2 days after the preparation date.

4.7 5 % Potassium Permanganate ($KMnO_4$) Solution - Add 25 g of $KMnO_4$ crystals to a 500 mL Teflon bottle half full with DI water. Dilute to volume with DI water

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and mix well. The expiration date for this prepared reagent is one day after preparation.

4.8 5 % Potassium Persulfate ($K_2S_2O_8$) Solution - Add 12.5 g of $K_2S_2O_8$ crystals to 250 mL Teflon bottle half full with DI water and dilute to volume with DI water. Mix well. The expiration date for this prepared reagent is one day after preparation.

5. CALIBRATION STANDARDS

Preparation of all Hg standards must be documented in the LIMS standard prep tracker. A label must be printed from the standard prep tracker that shows the identity of the standard, preparation date, expiration date, and serial number. The label must be placed on the bottle of standard in the laboratory. See DEP SOP MT-069 for standard documentation requirements and expiration dates. See DEP SOP HG-012 for expiration dates and additional information about preparing mercury standards.

Support equipment used during calibration standard preparation includes the Ohaus top loading balance as well as various Eppendorf pipettes. Prior to use, verify the balance calibration has been checked and is within acceptable tolerance and verify the pipette calibration has been checked within the last month. Calibration documentation can be found on the network, \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Mercury\Prep\Pipette Calibration\High Level Hg pipette calibration and in the 'Balance Calibration Logbook for the Ohaus Scout Pro'.

5.1 Commercial Stock Standard 1000 µg/mL - Commercially available inorganic mercury stock from SPEX, Accustandard, Baker, Fisher, VSR, etc.

5.2 WTHG-1 (100 mg/L) Instrument Calibration Stock Solution - Pipette 10.0 mL of commercial 1000 µg/mL stock standard into a 100 mL volumetric flask containing about 50 mL of DI water. Add 5 mL of HNO_3. Dilute to volume with DI water and mix well.

5.3 WTHG-2 (500 µg/L) Instrument Calibration Intermediate Solution - Pipette 5.0 mL of WTHG-1 into a 1 L volumetric flask containing about 500 mL of DI water. Add 50 mL of HNO_3. Dilute to volume with DI water and mix well.

5.4 Working calibration standards are prepared according to the following procedure:

5.4.1 Prepare a set of calibration standards using clean, dry and pre-labeled vessels. Erlenmeyer flasks or Teflon bottles may be used, but verify the accuracy of the volume of DI water with a balance and use a calibrated pipette for addition of the WTHG-2 standard.

5.4.2 Using Table 1 as a guide, pipette the appropriate aliquots of WTHG-2 into each container. The concentrations are 0.50, 1.0, 2.0, 5.0 and 10.0 µg/L. W-STD3 is both a calibration standard and the continuing calibration verification (CCV) check standard.

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TABLE 1.

Level	Concentration (µg/L)	Volume of WTHG-2 (µL)	Volume of DI water (mL)
W-STD1	0.50	100	100.0
W-STD2	1.00	200	100.0
W-STD3 (CCV)	2.00	400	99.6
W-STD4	5.00	1000	99.0
W-STD5	10.00	2000	98.0

5.4.3 Add 5 mL of H_2SO_4 to all standard vessels. Add 2.5 mL HNO_3 to all standard vessels. Gently swirl digestion vessels to mix. The solution may become hot. Allow the solution to cool if necessary.

5.4.4 Add 15.0 mL 5 % $KMnO_4$ to all standard vessels. Add 8.0 mL 5 % $K_2S_2O_8$ to all standard vessels. Tighten cap and invert standard vessels to mix. Loosen caps and allow to cool.

5.4.5 The expiration date for the working standards (W-STD1 – W-STD5) is 7 days from the preparation date.

5.4.6 Prepare the calibration blank. The calibration blank must contain all reagents in the same concentration and in the same volume as used in preparing the calibration standards. The calibration blank is also used as the continuing calibration blank (CCB).

6. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Water samples are collected in 1 L polyethylene bottles with screw caps and preserved by acidifying them with nitric acid to a pH below 2. The preservation is done immediately after the samples are collected, prior to shipment to the laboratory. The samples are stored at room temperature.

7. SAMPLE PREPARATION PROCEDURE

7.1 Refer to DEP SOP HG-018 for sample preparation details.

7.2 Prepare the samples for analysis by adding 2.5 mL of the 12 % sodium chloride-hydroxylammonium chloride solution to each sample. This reagent reduces the excess oxidant in the digested sample. Tighten the digestion vessel caps and gently swirl and invert the vessels several times to mix the reagents. Loosen the cap to release pressure. Make sure that you mix all visible particulates into the liquid. The purple color of the digestates should disappear leaving behind a clear colorless liquid.

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7.3 If the purple color persists, add additional 12 % sodium chloride-hydroxylammonium chloride solution to the sample in 1 mL increments, and mix until the solution turns colorless. Record the amount of additional hydroxylamine added to the sample in the comment section of the LIMS Prep Worksheet Manager worksheet. This information will be used later to compensate for changes in volume during calculations.

8. INSTRUMENT SETUP AND OPERATION

Either the Varian SpectraAA-220 atomic absorption spectrometer or the Nippon RA-3320 atomic absorption mercury analyzer may be used for the analysis of digested samples. Both are atomic absorption spectrometers and employ similar techniques for quantifying the mercury content of samples. Section 8.1 details the use of the Varian 220AA and section 8.2 the use of the Nippon RA-3320. Both are atomic absorption instruments with identical detection limits and quality control limits.

8.1 Varian 220AA - Switch on the instrument, including the spectrometer, computer, printer, and autosampler. Turn on the heat lamp above the absorption cell and allow the cell to warm up for 15 minutes.

8.1.1 At the SpectrAA main menu, select ‘Worksheet’ and select the ‘New From’ option to open a new file. Enter the date of analysis (today's date) and indicate in the batch name that it is an Hg water analysis followed by the date (W-HG-YYMMDDA). This information is important because it is used as a label when saving the data to the hard drive. Then enter your name for analyst followed by your comments, if necessary.

8.1.2 Record the date, time, and lamp element in the lamp time logbook or equivalent. During the instrument setup, allow the SpectrAA to warm up for at least 1 hour.

8.1.3 In order to set instrument parameters, click on the menu item Develop and select Edit Methods. Check that the instrument parameters listed in Table 2 have the correct values.

TABLE 2.

Instrument Parameters for Varian SpectraAA-220

Parameter	Value
Element	Hg
Matrix	Water
Units	µg/L
Sampling Mode	Autonormal
Vapor Mode	Cold Vapor
Measurement Mode	Integration

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Parameter	Value
Calibration Mode	Concentration
Minimum Reading	0.0000
Smoothing	5 point
Standard Replicates	3
Sample Replicates	3
Measurement Time (sec.)	5
Read Delay (sec.)	55
Standard Precision	1.0
Sample Precision	1.0
Lamp Position	1
Lamp Current (mA)	4.0
Wavelength (nm)	253.7
Slit Width (nm)	0.5
Background Correction	BC Off
Standard 1 (µg/L)	0.500
Standard 2 (µg/L)	1.000
Standard 3 (µg/L)	3.000
Standard 4 (µg/L)	5.000
Standard 5 (µg/L)	7.500
Calibration Slope Test (%)	20.0 - 150.0
Reslope Slope Test (%)	70.0 - 125.0
Inst. Zero Rate	5
Cal. Zero Rate	0
Recalibration Rate	100
Reslope Rate	100
Reslope Standard No.	1
Expansion Factor	1.0
Conc. Decimal Places	3
Calb. Algorithm	New Rational
Rinse Rate	1
Rinse Time (sec.)	60
Probe Height (nm)	0
Dip Time (sec.)	0.5
Calzero Standard Rack	Tube #1
Standard 1: Standard Rack	Tube #2
Standard 2: Standard Rack	Tube #3

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Parameter	Value
Standard 3: Standard Rack	Tube #4
Standard 4: Standard Rack	Tube #5
Standard 5: Standard Rack	Tube #6
CCV: Standard Rack	Tube #4
CCB: Standard Rack	Tube #1
ICV: Standard Rack	Tube #5
ICB: Standard Rack	Tube #1
Concentration Limit ICB (µg/L)	0.1200
Error Action ICB	Retry and Pause on
Error Flag ICB	Z
Concentration Limit CCB (µg/L)	0.1200
Error Action CCB	Retry and Pause on
Error Flag CCB	Q
Rate CCB	5
Concentration Limit CCV (µg/L)	3.000
Low Limit CCV (%)	90
High Limit CCV (%)	110
Error Action CCV	Retry and Pause on
Error Flag CCV	Q
Rate CCB	10
Cor. Coeff. Limit	0.9950

8.1.4 Select ‘Labels’ from the worksheet menu. Type in the sample IDs as they are to be organized on the autosampler rack. DO NOT include the calibration standards; start from the first SAMPLE.

8.1.5 Arrange the samples on the autosampler rack. A typical sequence of 10 water samples is shown below.

W-STD4*
ICB*
W-STD3*
CCB*
W-BLK (Method Blank)
W-PQL
W-NIST3133
Laboratory Fortified Blank
CCB*
Sample 1
Sample 1 Spike 1

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Sample 1 Spike 2
Sample 2
W-STD3*
CCB*
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
CCB*
Sample 8
Sample 9
Sample 10
W-STD3*
CCB*

* The instrument software automatically inserts an initial calibration verification (ICV/W-STD4) and initial calibration blank (ICB) at the beginning of the run, a CCV every 10 samples, and a CCB every 5 samples. A CCV and CCB must be analyzed at the end of every run.

Since 10 % of samples must be spiked, confirm that a second sample was spiked if there are 11 to 20 samples in the batch.

8.1.6 Check to see that the sample cell is free of any deposits on the cell windows. Rinse inside of cell with 50 % (v/v) HNO_3. In case of excessive deposits, clean cell with concentrated H_2SO_4 or HCl. Rinse the sample cell thoroughly 6-10 times with DI water. Rinse with methanol or acetone and dry with argon gas. MAKE SURE THE CELL IS DRY BEFORE INSTALLING IT IN THE INSTRUMENT. Methanol and acetone absorb in the UV region. Replace the dried cell into the AA unit, reconnecting all sample entry and exit tubes (See manual for details).

8.1.7 Remove the gas-liquid separator from its acid storage solution and rinse 10 times with DI water. Attach the gas-liquid separator to its holder spot on the VGA-77 pumping unit in accordance with the instructions in the SpectrAA 220 Varian instruction manual. The gas-liquid separator is a fairly fragile piece of glassware and care should be exercised in handling it. Attach all the tubes to the gas-liquid separator according to the instruction manual, except the tube to the sample cell (tube that goes from the top of gas-liquid separator). This tube will be attached later. Make sure that the waste line from the gas-liquid separator drains into an empty waste bottle. If the waste tubing line is submerged in waste, it will impede gas flow and give erroneous signals.

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8.1.8 Attach NEW sample and reagent delivery lines to the VGA-77, discarding previously used lines. DO NOT reuse sample and reagent delivery lines. Using the instruction manual as a guide, apply the friction levers to the delivery lines and unscrew the tension screws. Black, black tubing goes on the inside of the rollers and connects to the $SnCl_2$ line. Purple, black tubing goes on the outside of the rollers and connects to the autosampler.

8.1.9 Turn on the nitrogen gas flow and verify that the pressure is reading 50 psi. DO NOT attempt to run the VGA-77 pump without nitrogen flow. Allow system to run for 10-15 minutes to stabilize the nitrogen pressure. After 10-15 minutes, check the pressure again and adjust to 50 psi if necessary. Check occasionally during the run, but do not adjust during the run. Flow adjustments during the run will affect the instrument calibration.

8.1.10 Begin tightening the sample friction screw until there is smooth flow through the sample line (use DI water as your test solution). Then, tighten the screw approximately 1/2 turn more. The flow is now at maximum flow rate. ADDITIONAL tightening will DECREASE the flow rate. Repeat this process for the reagent line.

8.1.11 The peristaltic pump should be allowed to run for 20 – 30 minutes before beginning an analysis. This allows for the establishment of a dynamic equilibrium of moisture content in the absorption cell. Changes in the moisture content in the absorption cell are the primary cause of baseline drift in the instrument. The instrument's hollow cathode lamp is allowed to warm up for one hour before analyzing samples.

8.1.12 Place the reagent line (black, black tubing) into the 10 % $SnCl_2 \cdot H_2O$ solution bottle and place the sample needle into rinse station. Allow the system to run for 10 – 15 minutes before starting.

8.1.13 Transfer samples, calibration standards, and QC samples into clean, disposable 30 mL culture tubes.

8.1.14 Place calibration standards in sample rack # 2 in positions 1 – 4. The rezero blank ALWAYS goes in position number 6.

8.1.15 Go to instrument from the worksheet menu. The screen now displays the optimize icon of energy outputs from the system. Tilt the sample cell out of the path of the light beam. Make sure light path is clear of obstructions. The Hg lamp adjustment knobs are at the right of the machine (base of the lamp). Press the optimize icon to display the bar graph signal. Turn these knobs to maximize the bar graph signal (biggest bar length possible). Press the rescale several times during this optimization procedure to update the photomultiplier voltage. When satisfied with the adjustments, RECORD the photomultiplier voltage in the 'without cell' column in the

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lamp logbook. This number is the direct lamp output value without the sample cell. Recording it regularly will allow the analysts to track the lamp's performance.

8.1.16 Flip the clean sample cell into the path of the light beam. By using the same optimization screen used in step 8.1.15, optimize the Hg output by adjusting the sample cell position (biggest bar length). Use the horizontal and vertical adjustment knobs as well as the *XY* plane lever, all of which are located near the sample cell. DO NOT adjust the lamp at this point. Record the voltage in the 'with cell' column. Compare with numbers in the log book.

8.1.17 To begin the analysis, press the start icon (below the optimize icon) and the instrument will run automatically. The results will be reported on the screen in µg/L with its sample ID. For samples that are out of the calibration range and require dilutions or for samples that have been incorrectly read, place the appropriate diluted samples after the last standard, at the end of the run. Bracket any diluted samples or sample re-reads with a CCV and CCB. When the run has been completed, the instrument will stop automatically.

8.2 Nippon RA-3320 - Start the instrument by turning on the switches at the rear of the RA-3 analyzer and at the front of the SC-3 autosampler. A standby screen will appear on the instrument display for 20 minutes while the system is warming up and stabilizing.

Note: The instrument can be left on overnight. However, if it will not be used on consecutive days it should be shutdown following the procedure in section 8.2.11.

8.2.1 While the instrument is warming up prepare a 50 % H_2SO_4 solution and a 10 % $SnCl_2 \cdot H_2O$ solution. Reagent preparation instructions can be found in section 4.

8.2.2 Fill the bottles on the RD-3. The large bottle should be filled with DI water. The middle bottle should be filled with 50 mL of 50 % H_2SO_4 solution and the front bottle should be filled with 50 mL of 10 % $SnCl_2 \cdot H_2O$ solution. Connect the reagent tube from each pump to its respective bottle.

8.2.3 At the end of the stabilization period the instrument display will show two options, 'SC/RD' and 'Maintenance'. Select the SC/RD by touching it on the screen. On the next screen select 'Measurement Preparation' and hit 'ENT'. Place a tube in the waste position of the autosampler and a rinse test tube in the cleaning holder. Push the start button. When reagent filling is complete press esc to return to the main screen.

8.2.4 Double click on the 'RA3Win' icon on the desktop to launch the software.

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8.2.5 The online profile window displays a peak profile of absorbance during measurement. At the same time, it also indicates an instantaneous absorbance value, a peak value, and an integrated value. The calibration window shows the created calibration curve. The verification result for a calibration curve means the mercury concentration or weight is calculated from absorbance on which a calibration curve is based, and its calculation result is indicated with a linear calibration curve.

8.2.6 In the Table window click on the 'STD' tab. Type in the standard value and check the 'Mes' cell for each line that is being used in the table. The first two standards run should be DI water blanks. Press start.

8.2.7 After pressing start, the calibration sequence initiates. Five calibration standards of varying concentration are run plus a blank. The calibration curve is calculated by the instrument software using the equation $y = mx + 0$.

8.2.8 In the Table window click on the 'SMP' tab. Type in the sample IDs. Check the 'Mes' cell for each line that is being used in the table. Every 10 samples, a CCV and every 5 samples a CCB must be analyzed. In the 'SMP' table window, the CCV and CCB can be typed in the sequence every 10 and 5 samples respectively.

8.2.9 Additional samples can be added to the run while samples are running by typing the sample information into the 'SMP' table and being sure to check the 'Mes' cell.

8.2.10 Measurement conditions can be found by selecting the 'Measurement Condition' option in the Run Menu. Table 3 contains these parameters.

TABLE 3

Instrument Parameters for Nippon RA-3320

Parameter	Value
Common Tab	
Measurement Time (seconds)	120
Time axis (seconds)	180
Analog out range	0.05
Upper limit (Absorbance)	1.50000
Purge time (seconds)	180
Measurement	Continue
Control Tab	
Std (µg/L)	5

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Parameter	Value
Max Dev (%)	10
Abnormal Conditions	Stop
Calibration Curve	y = mx + 0
Peak / Integ	Integ
Unit	µg/L
Decimal places	3
Drift Correction	No
Description of Minus	Minus as it is

8.2.11 When the run is complete select the 'SC/RD' screen on the instrument display. Select the 'Measurement Complete' option and follow the onscreen directions for rinsing the reagent tubes. When the 'SC/RD' screen returns the instrument can be shut down. Flip the switch on the back, right side of the instrument to off and flip the switch on the front side of the autosampler to off.

8.2.12 Nippon test tubes must be cleaned after each run. This is accomplished by rinsing the tubes with water followed by soaking them for a minimum of two hours in aqua regia.

9. DATA ARCHIVAL

9.1 In the SpectrAA 220, raw data is automatically saved by the program at the completion of the run. The data can be exported as a standard comma-delimited *.prn file. The file name can contain up to 128 characters. All data files must use a 12 character naming convention with the following format: Year (4 ch.) Analysis/Instrument (2 ch.) Month (2 ch.) Day (2 ch.) Matrix (1 ch.) Run number (1 ch.). The naming convention for the archived files is best illustrated as follows: A file with name "2000aa0224w1.prn" stores data collected from the first (water) run on February 24, 2000 using the Varian AA on a water matrix. If a second tray of water was also analyzed on the same day, it would have the following name: 2000aa0224w2. The twelve character naming convention identifies the date of analysis, analysis technique, matrix type, and run number. The matrix types use the following identifiers: **w** for water, **s** for sediments or wastes, and **t** for tissue. The *.prn data file is stored on the instrument's computer at location C:\Varian\sp100\Data and needs to be copied the directory \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Mercury\CVAA_220 on the network. Shortcuts to both directories reside on the instrument computer's desktop.

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9.2 The Nippon instrument software does not automatically save the results of an analytical run. After measurements are complete, click File>Save and save the instrument software file (RA3 Data File) on the hard drive of the instrument computer with the format N2009aa0216w1. Then, the worksheet needs to be saved as a comma delimited 'CSV' text file. This is done by selecting 'save as text file' in the edit menu. The text file is saved to \\FLDEP1\DEAR\Labs\Lab3\Chem_Data\Inorganic\Mercury\Nippon_AA. The naming convention is similar to that of the Varian instrument with the exception of putting "N" before the name. A file with the name N2009aa0216w1 would be the first water run on February 16, 2009 using the Nippon RA-3320.

10. QUALITY CONTROL

Table 4 shown below lists the quality control parameters and their acceptable limits for any water or TCLP extract analysis using this SOP. Consult supervisor or see DEP SOP LB-027 for reporting data associated with out-of-control quality control parameters. MDL is the method detection limit, PQL is the practical quantitation level, and LFB is the laboratory fortified blank.

TABLE 4.

WATER

CALIBRATION	R ≥ 0.995		
MDL	0.10 µg/L		
CCB	-MDL < CONCENTRATION < MDL		
	LEVEL	**RECOVERY**	**RPD**
PQL	0.50 µg/L	70 % - 130 %	
W-NIST3133	3.0 µg/L	90 % - 110 %	
DUP. SPIKE	1.0 µg/L	85 % - 115 %	≤ 20 %
ICV	5.0 µg/L	95 % - 105 %	
CCV	3.0 µg/L	90 % - 110 %	
LFB	1.0 µg/L	85 % – 115 %	

Calculations for replicate analyses to evaluate precision, the recovery of laboratory control samples, and the recovery of matrix spikes are detailed in section 5.9 of the Bureau of Laboratories Quality Manual.

11. INTERFERENCES

11.1 Volatile compounds that absorb at the same wavelength (253.7 nm) as mercury constitute a positive interferent for this method.

11.2 Positive interference has been also observed in samples containing high levels of sulfides, copper, and chlorides probably due to the formation of free chlorine.

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11.3 Addition of H_2SO_4 may induce the formation of a heavy precipitate. If this is present, the affected sample cannot be analyzed by this method.

12. CORRECTIVE ACTIONS FOR COMMON PROBLEMS

Corrective actions for common QC failures and out-of-control data are listed in Table 5 below.

TABLE 5.

Corrective Actions

Problem	Corrective Action
Calibration standard's response factor below expected value.	Check the instrument lamp and its alignment. Check absorption cell and its alignment. Check every tubing connection for possible gas leaks.
Calibration curve correlation coefficient out of range.	Remake the standards and recalibrate the instrument.
Failure of CCB.	Check reaction loop in the VGA and gas-liquid separator for presence of precipitate. If precipitate is found clean the phase separator with a solution of 25 % H_2SO_4 and 25 % HNO_3. Change the pump tubing.
Failure of CCV.	Check the detector for signal drift. Recalibrate if necessary.
Failure of second source standard, PQL, LFB, matrix spikes, or matrix spike RPD.	Redigest the samples and repeat the analysis.

13. MAINTENANCE

13.1 Varian 220AA - Light source lamp generally lasts 6-9 months, depending on usage.

13.2 Nippon RA-3320:

13.2.1 Pump Tubing should be replaced once per year

13.2.2 Filter on the autosampler bubbler should be changed every 3 months

13.2.3 Light source lamp needs to be replaced if instrument display shows an alarm message of 'Lamp Life Exceeded' or 'Lamp Broken'. The lamp life error message will appear when the total operating time exceeds 20,000 hours.

13.2.4 The warning message 'Carbon Filter Full' appears when the activated carbon filter in the RA-3 unit has absorbed more than 1.5 g of mercury.

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Section 4.1.3 in the RA-3000 Maintenance Manual explains how to replace this filter.

13.2.5 If contamination or reduced sensitivity become a problem or the error message 'Cell Dark' appears the I joint, L joint, Teflon tubes, dehumidifier tube and joints, cell body, and quartz lenses need to be cleaned. Specific instructions are giving in section 5 of the RA-3000 Maintenance Manual.

14. SAFETY/HAZARDOUS WASTE MANAGEMENT

14.1 See DEP SOP HG-013 for correct waste disposal procedures.

14.2 Always wear safety glasses or protective eyewear and a laboratory coat while working in the laboratory. Power-free latex gloves should be worn while handling chemicals. Concentrated acids should be handled in a well ventilated hood.

15. REFERENCES

15.1 Varian SPS5 autodilutor/autosampler owner's manual

15.2 Varian VGA 76/77 owner's manual

15.3 EPA Method 245.1, Rev. 3.0, Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry

15.4 EPA Method 7470A, Mercury in Liquid Waste (Manual Cold Vapor Technique)

15.5 Varian SpectrAA Pro, Version 5 Software 50 55 110 220 880 QCP

15.6 Varian SpectrAA Pre-installation manual

15.7 Nippon Mercury/RA-3000 system measurement manual

15.8 Nippon Mercury/RA-3 Data Analysis software manual

15.9 Nippon Mercury/RA-3000 system maintenance manual

15.10 DEP SOP HG-012, Mercury Group Standards Preparation Procedures

15.11 DEP SOP HG-013, Mercury Waste Disposal

15.12 DEP SOP HG-018, Digestion of Water Samples for Total Mercury Analysis

15.13 DEP SOP LB-027, Standard Operating Procedure for Reporting Qualified Data

15.14 DEP SOP MT-058, Procedure for Metals Data Review and Authorization

15.15 DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure

15.16 Quality Manual, Bureau of Laboratories, FDEP, located on the Bureau's intranet.

15.17 Bureau of Laboratories Health and Safety Manual, located on the Bureau's intranet.

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Appendix of Significant Changes

07/10/2008 A couple of older sections were consolidated into Section 6. Other minor revisions to the text were made for format and clarity.

09/08/2008 Minor edits were made in Sections 1 and 14 to include the addition of test W-HG-H-R to the SOP.

03/09/2009 The Cetac instrument was surplused. The Nippon RA-3320 sample analysis procedure was added (Section 8.2).

08/04/2014 EPA Method 245.1 was re-validated.

- 12 % Sodium chloride-hydroxylammonium chloride replaces the 12 % hydroxylamine hydrochloride reagent.
- 10 % $SnCl_2 \cdot H_2O$ in 0.5 N H_2SO_4 now used for both instruments instead of 10 % $SnCl_2$ in 5 % H_2SO_4 for Nippon and 12 % $SnCl_2$ in 6% HCl for Varian.
- The concentrations of the $KMnO_4$ and $K_2S_2O_8$ were decreased from 6 % to 5 %.
- HCl and the bromate/bromide reagent were removed from the intermediate standards.

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