ANALYSIS OF MERCURY IN SOLIDS AND SOLUTIONS BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

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1. SCOPE AND APPLICATION

This standard operating procedure (SOP) details the analysis of mercury in sediment, waste, and biological tissue samples by thermal decomposition, amalgamation, and atomic absorption (TDA/AAS). The calibration range is 0.15 ng – 600 ng. The method detection limit (MDL) for the tissue matrix is 0.1 ng. The practical quantitation limit (PQL) for the tissue matrix is 0.3 ng. The MDL for the sediment and waste matrices is 0.05 ng. The PQL for the sediment and waste matrices is 0.15 ng. Laboratory tests covered by this SOP are T-HG-TDA, S-HG-TDA, and WAS-HG-TDA.

2. SUMMARY OF THE METHOD

2.1 This SOP is based on EPA method 7473, Revision 0.

2.2 Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the Milestone DMA-80 instrument. The sample is weighed into a quartz boat and placed on the autosampler. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing air to the catalytic section of the furnace. Oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are

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then carried to an amalgam trap that selectively traps mercury. The analytical system is flushed with flowing air to remove the remaining gases and decomposition products, followed by the rapid heating of the amalgam trap, releasing the mercury vapor. The mercury vapor is carried by flowing air through absorption cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury concentration.

2.3 The Tricell DMA-80 contains three absorption cells with different path lengths for measuring varying concentrations of mercury in the sample. The DMA-80 software automatically chooses which peak to use for sample measurement based on the absorbance. Cell 0 is used for absorbance results of up to 0.5. Cell 1 is used for absorbance of up to 0.85. Cell 2 is used for absorbance of up to 1.0.

2.4 Co-absorbing gases, which are common interferences, such as free chlorine and certain organics, are purged from the analytical system after release by the decomposition furnace and the mercury vapor is selectively trapped on the amalgam trap.

2.5 Memory effects: Mercury vapor may remain in the decomposition tube, amalgam trap, or absorbance cells and be released in a subsequent analysis resulting in a positive bias. For example, this may occur when a low concentration sample is analyzed after a sample of high mercury content. To prevent memory effects, the DMA-80 automatically runs a cleaning cycle after samples that contain more than 30 ng of mercury in the tissue matrix and more than 9 ng in the sediment/waste matrix.

3. APPARATUS AND EQUIPMENT

3.1 Milestone DMA-80 instrument, serial number 14041581.

3.2 Milestone DMA-80 instrument, serial number 15081813.

3.3 Analytical balance.

3.4 Quartz Boats, part number, DMA8347.

3.5 Eppendorf pipettes - 100 µL fixed volume and 100 – 1000 µL adjustable volume.

3.6 Eppendorf pipettes - 1 – 10 mL adjustable volume.

4. REAGENTS AND CHEMICALS

See DEP SOP MT-069 for standard and reagent documentation, labeling requirements, and expiration dates. All bottles of reagents and standards (purchased and prepared) in the laboratory are required to have laboratory information management system (LIMS) labels which includes a serial number.

4.1 Deionized (DI) water - Available from plastic spigots in the laboratory.

4.2 Catalyst – The DMA-80 catalyst is considered a reagent. The catalyst is logged into the laboratory's standard prep tracker and a label with a serial number is printed. Place the label in the instrument maintenance logbook with the entry for

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the catalyst replacement maintenance. The catalyst does not have an expiration date. The DMA-80 software will display a message when it is time to install a new catalyst. This is a general message based on the number of cycles the instrument has run, but the lifetime of the catalyst depends on the type of samples analyzed and will vary for each catalyst.

4.2.1 Conditioning procedure for the catalyst if it is new or has not been used for a long time:

4.2.1.1 Analyze 100 mg of flour using a max start temperature of 200 °C, a 1-minute drying time at a temperature of 200 °C, and a purge time of 60 s.

4.2.1.2 Analyze 0.1 mL of 5 % HNO_3 using a max start temperature of 200 °C, a 2-minute drying time at a temperature of 650 °C, and a purge time of 60 s.

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

4.4 Standards - Preparation of all Hg standards must be documented in the LIMS standard prep tracker. A label should be printed from the standard prep tracker that shows the identity of the standard, preparation date, expiration date, and serial number. See DEP SOP MT-069 for standard documentation requirements and expiration dates.

4.4.1 Primary Commercial Stock Standard 1000 mg/L - Commercially available inorganic mercury stock from SPEX, Accustandard, Baker, Baxter, Fisher, VSR, etc. The expiration date is assigned by the manufacturer and the standard is stored at room temperature. This primary stock standard is used to prepare the calibration standards.

4.4.2 TDA-1, 10 mg/L standard - Pipette 1.0 mL of the 1000 mg/L purchased primary standard into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume with DI water and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.3 TDA-2, 1.0 mg/L standard - Pipette 0.1 mL of the 1000 mg/L purchased primary standard into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume with DI water and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.4 TDA-3, 100 µg/L standard - Pipette 1.0 mL of TDA-1 (10 mg/L) into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume with DI water and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

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4.4.5 TDA-4, 10 µg/L standard - Pipette 0.1 mL of TDA-1 (10 mg/L) into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume with DI water and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.6 TDA-5, 5 µg/L standard - Pipette 2.5 mL of TDA-3 (100 µg/L) into a 50 mL volumetric flask containing 25 mL of DI water. Add 2.5 mL of HCl. Dilute to volume with DI water and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.7 Calibration Standards - The calibration standards are prepared from standards TDA-5, TDA-4, TDA-3, TDA-2, and TDA-1. See section 6 for preparation details.

Note: The absorption cell used for sample measurement is automatically chosen by the DMA-80 software based on the absorbance. Cell 0 is used for absorbance of up to 0.5. Cell 1 is used for absorbance of up to 0.85. Cell 2 is for absorbance of up to 1.0.

Calibration Standards:

STD1 (0.15 ng)

STD2 (0.25 ng)

STD3 (0.5 ng)

STD4 (1 ng)

STD5 (2 ng)

STD6 (3 ng)

STD7 (4 ng)

STD8 (5 ng)

STD9 (10 ng)

STD10 (15 ng)

STD11 (20 ng)

STD12 (30 ng)

STD13 (50 ng)

STD14 (100 ng)

STD15 (200 ng)

STD16 (400 ng)

STD17 (600 ng)

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4.4.8 Second Source Standard (1000 mg/L) - Commercially available inorganic mercury stock from SPEX, Accustandard, Baker, Baxter, Fisher, VSR, etc. The expiration date is assigned by the manufacturer and the standard is stored at room temperature. This purchased standard must be purchased from a different vendor than the primary standard used to prepare the calibration standards.

4.4.8.1 TDA-1C, 10 mg/L standard - Pipette 1.0 mL of the 1000 mg/L purchased second source standard into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.8.2 TDA-2C, 1.0 mg/L standard - Pipette 0.1 mL of the 1000 mg/L purchased second source standard into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.8.3 TDA-3C, 100 µg/L standard - Pipette 1.0 mL of TDA-1C (10 mg/L) into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.8.4 TDA-4C, 10 µg/L standard - Pipette 0.1 mL of TDA-1C (10 mg/L) into a 100 mL volumetric flask containing 50 mL of DI water. Add 5.0 mL of HCl. Dilute to volume and mix well. The expiration date for this prepared standard is 60 days from preparation and it is stored at room temperature.

4.4.8.5 The second source standard is analyzed at three different concentrations for each absorption cell.

4.4.8.5.1 TDA-CA (1.0 ng) - Pipette 100 µL of TDA-4C into a quartz boat.

4.4.8.5.2 TDA-CB1 (15 ng) - Pipette 150 µL of TDA-3C into a quartz boat.

4.4.8.5.3 TDA-CC (100 ng) - Pipette 100 µL of TDA-2C into a quartz boat.

4.5 DORM-4, 0.412 mg Hg/kg - Standard reference material (SRM) purchased from the National Research Council of Canada (NRCC). This standard is used as the

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laboratory control sample (LCS) for each batch of tissue samples analyzed. The expiration date is provided by the manufacturer.

4.6 PACS-3, 2.98 mg Hg/kg - SRM purchased from NRCC. This standard is used as the LCS for each batch of sediment samples analyzed. The expiration date is provided by the manufacturer.

4.7 T-PQL, 0.3 ng Hg – This standard is used as the practical quantitation level check standard for each batch of samples analyzed. Add 30 µL of TDA-4 (10 µg/L) to a quartz boat.

4.8 S-PQL, 0.15 ng Hg – This standard is used as the practical quantitation level check standard for each batch of sediment samples. Add 30 µL of TDA-5 (5 µg/L) to a quartz boat.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Tissue samples are collected and stored in polyethylene or glass vials with airtight closures. They are preserved by storage in a freezer at -20 °C. The frozen containers are shipped in ice-packed coolers via overnight mail to the laboratory. The samples are then stored in a freezer at -20 °C. Samples are removed from the freezer and allowed to thaw to room temperature before analysis. The hold time for tissue samples is 1 year (Table FS 1000-10, DEP-SOP-001/01 FS 1000, General Sampling Procedures).

5.2 Sediment or waste samples are collected and stored in 250 mL wide-mouth glass containers with screw tops. The samples are preserved by refrigerating the containers at a temperature of 4 °C. Prior to sample analysis, the samples are allowed to warm to room temperature before weighing. The hold time for sediment and waste samples is 28 days.

6. CALIBRATION STANDARDS PREPARATION PROCEDURE

Using the table below as a guide, pipette the appropriate amounts of TDA-5 (5 µg/L), TDA-4 (10 µg/L), TDA-3 (100 µg/L), TDA-2 (1.0 mg/L), and TDA-1 (10 mg/L) into quartz boats.

Calibration Standard Concentration	**Amount of Standard to deliver to sample boat**
STD1 0.15 ng	30 µL of TDA-5 (5 µg/L)
STD2 0.25 ng	25 µL of TDA-4 (10 µg/L)
STD3 0.50 ng	50 µL of TDA-4 (10 µg/L)
STD4 1.0 ng	100 µL of TDA-4 (10 µg/L)
STD5 2.0 ng	200 µL of TDA-4 (10 µg/L)
STD6 3.0 ng	30 µL of TDA-3 (100 µg/L)
STD7 4.0 ng	40 µL of TDA-3 (100 µg/L)

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Calibration Standard Concentration	Amount of Standard to deliver to sample boat
STD8 5.0 ng	50 µL of TDA-3 (100 µg/L)
STD9 10 ng	100 µL of TDA-3 (100 µg/L)
STD10 15 ng	150 µL of TDA-3 (100 µg/L)
STD11 20 ng	200 µL of TDA-3 (100 µg/L)
STD12 30 ng	30 µL of TDA-2 (1 mg/L)
STD13 50 ng	50 µL of TDA-2 (1 mg/L)
STD14 100 ng	100 µL of TDA-2 (1 mg/L)
STD15 200 ng	20 µL of TDA-1 (10 mg/L)
STD16 400 ng	40 µL of TDA-1 (10 mg/L)
STD17 600 ng	60 µL of TDA-1 (10 mg/L)

7. SAMPLE ANALYSIS PROCEDURE

7.1 Open the air supply.

7.2 Turn the DMA-80 on with the switch on the front panel of the instrument.

7.3 Turn on laptop computer and open the DMA-80 software. Log in as an administrator with the password 123456, then press enter.

7.4 The instrument will require about 15 to 20 minutes of warm up time.

7.5 Calibration:

The calibration is performed initially and when any significant instrument maintenance is performed. For example, a new calibration should be performed after the decomposition tube or amalgam trap is replaced. A new calibration must also be performed if the daily calibration check does not pass (see section 7.6.5).

7.5.1 To create a new calibration curve, choose from “Method” Standard.m80 and go to “Calibration.” Clear the old calibration (do not delete) using the blank page icon and save the new one in the calibration folder.

7.5.2 Go to the “Measurement Sample”. Clear the old measurements using the blank page icon and create a new file for calibration analysis. Analyze each calibration standard twice. In the “Measurement Sample” window type 2 under “n” to create two standard measurements. Open the small balance icon and choose “calibration”. The software will mark the small balance icon with letter “C.”

7.5.3 To complete the program for calibration switch to the “Measurement Results” window. Enter the concentration for each standard used along with the amount in grams in the “Amount” column.

7.5.4 Save the file.

7.5.5 Push START to start analyzing calibration standards.

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7.5.6 After measurements are finished, the instrument will stop. Save the results.

7.5.7 Go to "Calibration" and choose fit calibration in every cell. Save the results. The calibration curve is non-linear. Select the 'square' fit.

7.5.8 The calibration must be verified with the second source standards prior to any sample analysis.

7.5.9 Use form MT-DMA-RE to calculate the RSD of response factors. See section 10.9.

7.6 Sample Analysis:

7.6.1 Under 'Sample Measurement' create a new file for the analysis.

7.6.2 Select the appropriate calibration under "Measurement Links."

7.6.3 Select the method under 'Measurement/Links'.

7.6.4 For analyzing tissue samples, choose Fish Method.m80 and for analyzing sediment samples, choose Sediment.m80.

7.6.5 Daily Calibration Check for tissue samples - Analyze the following standards at the beginning of every analysis. See Appendix A for recovery limits.

7.6.5.1 Cell 0 daily calibration check - STD4CCVC (1.0 ng) and STD6 (3.0 ng).

7.6.5.2 Cell 1 daily calibration check – STD8 (5.0 ng) and STD10CCVC (15 ng).

7.6.5.3 Cell 2 daily calibration check - STD14CCVC (100 ng) and STD16 (400 ng).

7.6.6 Daily Calibration Check for low level sediment samples – Analyze the following standards at the beginning of every analysis. See Appendix A for recovery limits. Only sediment samples with mercury concentrations measured by Cell 0 or Cell 1 may be reported from the low level sediment analysis.

7.6.6.1 Cell 0 daily calibration check – STD4CCVC (1.0 ng) and STD6 (3.0 ng).

7.6.6.2 Cell 1 daily calibration check – STD8 (5 ng) and STD10CCVC (15 ng).

7.6.7 Daily Calibration Check for high level sediment samples – Analyze the following standards at the beginning of every analysis. See Appendix A for recovery limits.

7.6.7.1 Cell 0 daily calibration check – STD4CCVC (1.0 ng) and STD6 (3.0 ng).

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7.6.7.2 Cell 1 daily calibration check –STD8 (5 ng) and STD10CCVC (15 ng).

7.6.7.3 Cell 2 daily calibration check - STD14CCVC (100 ng) and STD16 (400 ng).

7.6.8 Second Source Daily Calibration Check – Analyze the following second source standards at the beginning of every analysis. The results must be within 10% of their true value.

7.6.8.1 Cell 0 second source check – TDA-CA (1.0 ng).

7.6.8.2 Cell 1 second source check – TDA-CB1 (15 ng).

7.6.8.3 Cell 2 second source check – TDA-CC (100 ng). The cell 2 second source check is not required for low-level sediment analyses.

7.6.9 For tissue samples, use a clean wooden applicator stick to transfer the entire tissue sample (or a ~ 10 g sub-sample if the sample is inordinately large) to a disposable weigh boat. Use a clean scalpel to carefully chop the tissue into very small pieces to homogenize the sample. Carefully transfer 0.05 to 0.2 g of chopped tissue to the quartz boat. Record the exact weight transferred.

7.6.10 For sediment samples, thoroughly mix the sample by removing the lid of the sample container and stirring the sample with a clean spatula. If the sample cannot be thoroughly mixed within its container without spilling, empty the entire sample into a clean stainless-steel tray. Do not decant any liquid or remove any objects from the sample. Contact the supervisor if any non-representative material is found in the sample. A mortar and pestle can be used if necessary. Any large objects should be cut up or crushed, but not removed from the sample. Return the homogenized sample to the sample jar. Weigh into a quartz boat 0.05 – 0.4 g of sample. Record the exact weight.

7.6.11 The sequence of samples and quality control samples to be analyzed, including the daily calibration check, are typed into the sample file. See Appendix A for an example sequence.

8. MAINTENANCE

8.1 During routine maintenance of the DMA-80, both the instrument and laptop computer should be turned off and disconnected from the power supply. Turn off the air supply. Allow the instrument to cool to room temperature before beginning maintenance.

8.2 Refer to the DMA-80 Operator Manual for replacement of the catalyst and the amalgam trap.

8.3 Document all instrument maintenance in the instrument maintenance logbook.

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9. DATA ARCHIVAL

The Milestone instrument software does not automatically save the results from the analytical run. To distinguish files between the two DMA-80 instruments, a suffix is used. The 'DMA' suffix is for S/N 14041581. The'DMA2' suffix is for S/N 15081813. See below for details.

9.1 DMA-80 (S/N 14041581): After measurements are complete, click File > Save and save the instrument software file on the hard drive of the instrument computer with the format 20190805t1-DMA.d80. The file name reflects the year, month, and day the samples were analyzed on. The letter following the date in the file name reflects the matrix of samples that were analyzed ('t' for tissue and 's' for sediment or waste). The number after the letter in the file name indicates the sequence of analyses performed on that day. If more than one analysis is performed on one day, then the second file name should have a '2' following the letter, and so on. Then, the file needs to be saved as a text file with 'DMA' appended to the file name, for example, 20190805t1-DMA.txt. The text file is saved to \\FLDEP1\dear\labs\lab3\Chem_Data\Inorganic\Mercury\DMA-80.

9.2 DMA-80 (S/N 15081813): After measurements are complete, click File > Save and save the instrument software file on the hard drive of the instrument computer with the format 20190805t1-DMA2.d80. The file name reflects the year, month, and day the samples were analyzed on. The letter following the date in the file name reflects the matrix of samples that were analyzed ('t' for tissue and 's' for sediment or waste). The number after the letter in the file name indicates the sequence of analyses performed on that day. If more than one analysis is performed on one day, then the second file name should have a '2' following the letter, and so on. Then, the file needs to be saved as a text file with 'DMA2' appended to the file name, for example, 20190805t1-DMA2.txt. The text file is saved to \\FLDEP1\dear\labs\lab3\Chem_Data\Inorganic\Mercury\DMA-80.

9.3 The absorbance peaks report is saved to the network for every analysis. From the Signal tab, click the print icon. Then click the icon that looks like multiple pieces of paper to print more than one sample per page. Click the print icon, change the printer to 'XPS Document Write' and click OK. Save the file with the format '20190805t1-DMA Peaks'. Saving the file will take several minutes.

10. QUALITY CONTROL

See DEP SOP MT-058 for calculation of relative percent difference (RPD) and percent recovery. Contingencies for out-of-control data are listed in DEP SOP LB-027.

The calculation equation used for matrix spike percent recovery is:

[[(Matrix Spike (ng)) – (QC Sample (ng) * Weight of Matrix Spike (g) / Weight of QC Sample (g))] / Spike Concentration (ng)] * 100

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10.1 One method blank per batch of 20 samples. Prepare a solution of 5 % HCl in DI water. Weigh 0.1 mL of the 5 % HCl into a quartz boat. The result of the method blank must be below the MDL.

10.2 One laboratory fortified blank (LFB) per batch of 20 samples. Standard reference material is used as the LFB. Weigh approximately 0.025 g of DORM-4 for tissue batches. Weigh approximately 0.010 g of PACS-3 for sediment batches (for low-level sediment analyses, 0.0050 g of the PACS-3 SRM is weighed in order to bring the concentration into cell 0 or 1). The acceptable recovery limits for the LFB is 80 – 120 %.

10.3 Matrix spikes - Duplicate matrix spikes are prepared by weighing two aliquots of the same sample and spiking with 50 µL of TDA-2. The acceptable recovery limits for the matrix spikes is 80 – 120 %. The RPD should be below 20 %.

10.3.1 Low Level Sediment Matrix Spikes – Duplicate matrix spikes are prepared by weighing two aliquots of the same sample and spiking with 50 µL of TDA-3. The acceptable recovery limits for the matrix spikes is 80 – 120 %. The RPD should be below 20 %.

10.4 Continuous Calibration Verification (CCV) - Every 10 samples, standards STD4, STD10, and STD14 are analyzed to verify the calibration. The STD4CCV is used for cell 0. The STD10CCV is used for cell 1. The STD14CCV is used for cell 2. If any of the CCV standards are outside of the acceptable recovery limits, data cannot be reported from the absorption cell affected without appropriate qualification. See Appendix A for recovery limits.

10.5 Continuous Calibration Blank (CCB) - An instrument blank (5 % HCl) is analyzed every 10 samples to verify no contamination is present and that no drift has occurred. Acceptable CCB results are those below MDL.

10.6 Second Source Standard - The second source standard (see section 4.4.8) is used to verify the calibration. This standard is analyzed after every calibration. See Appendix A for recovery limits.

10.7 The correlation coefficient of the calibration curve for every Cell must be ≥ 0.995.

10.8 Practical Quantitation Level Check Standard (S-PQL or T-PQL). Each batch of samples requires a PQL level check standard. See sections 4.7 and 4.8 for preparation. The acceptable recovery limits for the PQL is 70 – 130 %.

10.9 The % Relative Error in the calibration is measured at the lowest calibration standard concentration and at the mid-point calibration standard concentration for each absorption cell.

For cell 0, the % Relative Error is calculated for calibration standards STD1 (0.15 ng) and STD5 (2.0 ng).

For cell 1, the % Relative Error is calculated for calibration standards STD8 (5 ng) and STD9 (10 ng).

For cell 2, the % Relative Error is calculated for calibration standards STD12 (30 ng) and STD16 (400 ng).

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Use form MT-DMA-RE to document the measurement of % Relative Error for the calibration.

The DMA-80 calibration report displays ΔHg[ng], the deviation for the calibration standard with units ng. This error is used to calculate the concentration of the calibration standard and the equation below is used to calculate the % Relative Error as % recovery. The acceptance limits for STD1 are 70 – 130 % and the acceptance limits for STD5, STD8, STD9, STD12, and STD16 are 80 – 120 %.

% Recovery = [(Calibration Standard concentration [ng] + Error [ng]) / (Calibration Standard concentration [ng])] * 100

Save each MT-DMA-RE form in network folder \\FLDEP1\DEAR\labs\lab3\Chem_Data\Inorganic\Mercury\Calibration Printouts for DMA-80. The Excel spreadsheet is saved as a pdf by the data reviewer.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT

11.1 Always wear a lab coat and safety glasses or protective eyewear while working in the lab. Nitrile gloves and a lab coat should be worn while working in the laboratory. Concentrated acids should be handled in a fume hood.

11.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury standards.

11.3 Samples with a high organic content (e.g. oil saturated soil) should be analyzed with caution. The sample size should be scaled down as too large of a sample size may result in ignition of the sample within the decomposition tube.

12. REFERENCES

12.1 Milestone operator's manual MA122.

12.2 EPA Method 7473, Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation and Atomic Absorption Spectrophotometry.

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

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

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

12.6 Quality Manual for State of Florida Department of Environmental Protection Bureau of Laboratories.

12.7 DEP Bureau of Laboratories Health and Safety Manual.

12.8 DEP-SOP-001/01, FS 1000, General Sampling Procedures.

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APPENDIX A

Example Sample Sequence

TDA-CA	
STD6	
STD8	
TDA-CB1	**Initial Calibration Verification**
TDA-CC*	Completed at the start of each run.
STD16*	Requires 90-110% recovery.
STD14CCVC *	CCB must be below the MDL.
STD10CCVC	
STD4CCVC	
CCB	
Method Blank	
Sediment/Tissue PQL	
SRM: DORM-4 (tissue) or PACS-3 (sediment)	
Sample 1	
Sample 1 Matrix spike	
Sample 1 Matrix spike duplicate	
Sample 2	
Sample 3	
Sample 4	
Sample 5	
STD14CCV *	**Continuous Calibration Verification / Blank**
STD10CCV	All CCVs & CCB must be analyzed every 10 samples.
STD4CCV	CCVs require 80-120% recovery; CCBs must be below the MDL.
CCB	
Sample 6	
Sample 7	
etc.	

*Not required for low-level sediment analyses

Note: The Method Blank, PQL, SRM, and both matrix spikes are counted when considering CCV bracketing.

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Appendix of Significant Changes

03/03/2016	Separated the procedure for the analysis of sediment samples into a high concentration procedure and low concentration procedure.
09/15/2017	Re-organized and reduced the amount of calibration check standards to improve efficiency.
09/12/2019	Added the Relative Error (%RE) requirement to section 10.
11/26/2019	Edited section 10 to use the RSD of response factors to calculate the Relative Error of the calibration.
12/13/2019	Edited section 10 to use the percent recovery of the lowest and mid-point calibration standards as a measure of % Relative Error.
11/4/2020	The previous calibration range of 0.05 ng – 600 ng was changed to 0.15 ng – 600 ng. MDLs and PQLs were not changed.
11/22/2021	Edited section 10 to state that standards 8 and 12 have acceptance limits of 80 – 120 %.

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