ANALYSIS OF MERCURY IN SEDIMENT, WASTE, AND TISSUES 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 spectrophotometry (TDA/AAS). For the tissue matrix, the calibration range is 0.3 ng – 400 ng, the method detection limit (MDL) is 0.1 ng, and the practical quantitation limit (PQL) is 0.3 ng. For the sediment and waste matrices, the calibration range is 0.15 ng – 200 ng, the MDL is 0.05 ng, and the PQL 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 Mercury is liberated from solid and aqueous samples in the NIPPON MA-3000 instrument by controlled heating in an oxygenated decomposition furnace. The sample is weighed into a ceramic boat and placed on one of the autosampler's stainless steel racks, with 10 ceramic boats fit on each rack, for a total of 100 positions. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace where oxidation is completed, and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to a gold amalgamator that selectively

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traps mercury. The system is flushed with flowing oxygen to remove the remaining gases and decomposition products, followed by the rapid heating of the gold amalgamator to release the mercury vapor. The mercury vapor is then carried by flowing oxygen 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 dual-cell NIPPON MA-3000 contains two absorption cells with different path lengths for measuring varying concentrations of mercury in the sample. The NIPPON software automatically chooses which peak to use for sample measurement based on the absorbance. Cell 1 (LOW) is used for concentrations up to 10 ng. Cell 2 (HIGH) is used for concentrations up to 400 ng for tissues and up to 200 ng for sediments.

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 gold amalgamator.

2.5 Memory effects: Mercury vapor may remain in the combustion tube, gold amalgamator, 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 NIPPON MA-3000 automatically performs a blank check after samples containing more than a set amount of mercury and will repeatedly run a purge cycle until the auto-blank value is below the set point.

3. APPARATUS AND EQUIPMENT

3.1 NIPPON MA-3000-1, Serial # 2174-0758.

3.2 NIPPON MA-3000-2, Serial # 2174-0759.

3.3 Ceramic boats, part number 440531.

3.4 Eppendorf pipette: 100 – 1000 µL adjustable volume.

3.5 Eppendorf pipette: 1 – 10 mL adjustable volume.

3.6 Eppendorf pipette: 100 µL fixed volume.

3.7 Analytical balance.

3.8 Disposable weigh boats.

3.9 Wooden applicator sticks.

3.10 Scalpels.

3.11 Stainless steel spatulas.

3.12 Stainless steel trays.

3.13 Mortar and pestle.

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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 include a serial number.

4.1 Catalyst – The catalyst is a proprietary patented (JP 5001419) consumable reagent designed and produced by Nippon Instruments Corporation (NIC) that is pre-filled in the instrument's sample heating/combustion tube. It does not have an expiration date. After 2000 measurements, the NIPPON MA-3000 software will display a message to install a new sample heating tube, pre-filled with catalyst. This is a general recommendation as performance may be degraded, but the lifetime of the catalyst depends on the type of samples analyzed and will vary for each catalyst. See the NIPPON MA-3000 Instruction Manual for the sample heating tube replacement procedure.

When a new sample heating tube with catalyst is installed, log the catalyst into the LIMS Standard Preparation Tracker to generate a unique ID. Enter the identity, manufacturer, and lot number. Print the label which contains the unique ID for the catalyst and place it in the maintenance logbook alongside the installation date. Be sure to reset the measurement counter in the instrument software.

The conditioning procedure for the catalyst, if it is new or has not been used for a long time, is as follows:

4.1.1 Analyze 100 mg of flour using a max start temperature of 200 °C, a one-minute drying time at a temperature of 200 °C, and a purge time of 60 seconds.

4.1.2 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 seconds.

4.2 Carrier gas delivered by cylinder – Oxygen, purity ≥ 90%, pressure 0.2 - 0.5 MPa, regulated to 0.05 - 0.07 MPa.

4.3 Deionized (DI) water – Provided on tap at the laboratory sink and stored in clean wash bottles.

4.4 L-Cysteine in 0.2 % HNO_3 – Weigh 100 mg of L-Cysteine and dissolve in 1 L volumetric flask with DI water. Add 2 mL of HNO_3. Top off with DI water to 1 L. Mix well.

4.5 Standards – Preparation of all Hg standards must be documented in the LIMS Standard Preparation Tracker, where a label shall be printed and attached to the bottle or flask that identifies the standard with the name, preparation date, expiration date, and serial number. See DEP SOP MT-069 for standard documentation requirements and expiration dates.

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4.5.1 Primary Stock Standard, 1000 mg/L - Commercially available inorganic mercury stock standard 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.

4.5.2 TDA-1, 10 mg/L - Pipette 1.0 mL of the 1000 mg/L purchased primary standard into a 100 mL volumetric flask containing 50 mL of L-Cysteine solution in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.3 TDA-2, 1.0 mg/L - Pipette 0.1 mL of the 1000 mg/L purchased primary standard into a 100 mL volumetric flask containing 50 mL of L-Cysteine solution in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.4 TDA-3, 100 µg/L - Pipette 1.0 mL of TDA-1 (10 mg/L) into a 100 mL volumetric flask containing 50 mL of L-Cysteine solution in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.5 TDA-4, 10 µg/L - Pipette 0.1 mL of TDA-1 (10 mg/L) into a 100 mL volumetric flask containing L-Cysteine solution in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.6 TDA-5, 5.0 µg/L - Pipette 2.5 mL of TDA-3 (100 µg/L) into a 50 mL volumetric flask containing 25 mL of L-Cysteine solution in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.7 Calibration Standards - The calibration standards are prepared from standards TDA-1 – TDA-5. Using the table below as a guide, pipette the appropriate amounts of TDA-5 (5.0 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 ceramic boats.

Note: Cell 1 (LOW) is used up to 10 ng, and Cell 2 (HIGH) is used up to 200 ng for sediments/wastes and up to 400 ng for tissues.

Cell 1 (LOW) Calibration Standard Concentrations for Sediments/Wastes	Amount of Standard to Deliver to Sample Boat
STD1 (0.15 ng)	30 µL of TDA-5 (5.0 µg/L)

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STD4 (0.5 ng)	50 µL of TDA-4 (10 µg/L)
STD6 (3.0 ng)	30 µL of TDA-3 (100 µg/L)
STD7 (5.0 ng)	50 µL of TDA-3 (100 µg/L)
STD8 (7.5 ng)	75 µL of TDA-3 (100 µg/L)
STD9 (10 ng)	100 µL of TDA-3 (100 µg/L)

Cell 2 (HIGH) Calibration Standard Concentrations for Sediments/Wastes	**Amount of Standard to Deliver to Sample Boat**
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)
STD13 (50 ng)	50 µL of TDA-2 (1.0 mg/L)
STD14 (100 ng)	100 µL of TDA-2 (1.0 mg/L)
STD15 (200 ng)	20 µL of TDA-1 (10 mg/L)

Cell 1 (LOW) Calibration Standard Concentrations for Tissues	**Amount of Standard to Deliver to Sample Boat**
STD2 (0.3 ng)	30 µL of TDA-4 (10 µg/L)
STD4 (0.5 ng)	50 µL of TDA-4 (10 µg/L)
STD6 (3.0 ng)	30 µL of TDA-3 (100 µg/L)
STD7 (5.0 ng)	50 µL of TDA-3 (100 µg/L)
STD8 (7.5 ng)	75 µL of TDA-3 (100 µg/L)
STD9 (10 ng)	100 µL of TDA-3 (100 µg/L)

Cell 2 (HIGH) Calibration Standard Concentrations for Tissues	**Amount of Standard to Deliver to Sample Boat**
STD9 (10 ng)	100 µL of TDA-3 (100 µg/L)
STD11 (20 ng)	200 µL of TDA-3 (100 µg/L)
STD13 (50 ng)	50 µL of TDA-2 (1.0 mg/L)
STD14 (100 ng)	100 µL of TDA-2 (1.0 mg/L)
STD15 (200 ng)	20 µL of TDA-1 (10 mg/L)
STD16 (400 ng)	40 µL of TDA-1 (10 mg/L)

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4.5.8 Second Source Stock Standard, 1000 mg/L - Commercially available inorganic mercury stock standard 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 stock standard used to prepare the calibration standards.

4.5.9 TDA-1C, 10 mg/L - Pipette 1.0 mL of the 1000 mg/L purchased second source standard into a 100 mL volumetric flask containing 50 mL of L-Cysteine in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.10 TDA-3C, 100 µg/L - Pipette 1.0 mL of TDA-1C (10 mg/L) into a 100 mL volumetric flask containing 50 mL of L-Cysteine in 0.2 % HNO_3. Dilute to volume with L-Cysteine solution and mix well. The expiration date for this prepared standard is 180 days from the preparation date, and the standard is stored at room temperature.

4.5.11 TDA-CA, Second Source Check Standard, 3.0 ng - The second source check standard is analyzed for Cell 1 (LOW). Pipette 30 µL of TDA-3C into a ceramic boat.

4.5.11.1 TDA-CA (3.0 ng) [30 µL of TDA-3C]

4.5.12 TDA-CB, Second Source Check Standard, 20 ng - The second source check standard is analyzed for Cell 2 (HIGH). Pipette 200 µL of TDA-3C into a ceramic boat.

4.5.12.1 TDA-CB (20 ng) [200 µL of TDA-3C]

4.5.13 DORM-5, 0.310 mg Hg/kg - Standard Reference Material (SRM) purchased from the National Research Council of Canada (NRCC). This standard is used to prepare the Laboratory Fortified Blank (LFB) for each batch of tissue samples analyzed. See Section 7.3. The expiration date is provided by the manufacturer.

4.5.14 SRM 2706, 0.13 mg Hg/kg - SRM purchased from National Institute of Standards and Technology (NIST). This standard is used to prepare the LFB for each batch of sediment/waste samples analyzed. See Section 7.3. The expiration date is provided by the manufacturer.

4.5.15 T-PQL, 0.3 ng Hg - This standard is used as the Practical Quantitation Limit (PQL) check standard for each batch of tissue samples analyzed. Add 30 µL of TDA-4 (10 µg/L) to a ceramic boat.

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4.5.16 S-PQL, 0.15 ng Hg - This standard is used as the PQL check standard for each batch of sediment/waste samples analyzed. Add 30 µL of TDA-5 (5.0 µg/L) to a ceramic 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 freezing 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 maximum holding time for tissue samples is one 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 refrigeration at a temperature of 4 °C. Prior to analysis, the samples are allowed to warm to room temperature before weighing. The maximum holding time for sediment/waste samples is 28 days.

6. SAMPLE ANALYSIS PROCEDURE

6.1 Turn on the computer and open the NIPPON MA-3000 software.

6.2 Turn on the main power switch on the left side of the NIPPON MA-3000.

6.3 Open the main cock of the oxygen gas cylinder (0.2 to 0.5 MPa) and adjust the pressure regulator on the rear panel of the NIPPON MA-3000 until the delivery pressure is between 0.05 MPa and 0.07 MPa. Check the tubes for leaks.

6.4 A dialog box will pop up, asking to check the flow path. Click ‘Yes’. This diagnostic will check the flow rate of oxygen, any leaks, and the operation of V1, V2, and V3 valves. Check the NIPPON MA-3000 Instruction Manual for troubleshooting errors. Once completed, the heaters will automatically start and the conditioning process begins.

6.5 Conditioning:

The temperature of each heater is increased with oxygen so that the system is purged of moisture and other impurities that may be adhered to the combustion tube to prevent obstructions and/or breakages. Each heater is heated up to the temperature set for measurement. The set temperature of heater H1 is 150 °C and that of heater H3 is 500 °C. This warmup time will take about 15 to 20 minutes.

6.6 Discharge any liquid that has accumulated in the drain tank into an appropriate container for disposal by turning the roller of the roller clamp downward.

6.7 Calibration:

A new calibration is necessary when any significant instrument maintenance is performed and when new calibration standards are prepared, at least once every

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six months. For example, a new calibration should be performed after the sample heating/combustion tube (catalyst) or gold amalgamator is replaced.

6.7.1 Navigate to the STD table. Clear the old calibration (do not delete) using the blank page icon and save the new one in the calibration folder. Click the 'STD' box to open the 'STD INPUT' window. Enter the concentrations and volumes of each standard.

6.7.2 Pipette the amount of each standard necessary into unique ceramic boats according to the table in Section 4.5.7 and place in the autosampler stainless steel rack.

6.7.3 Make sure the 'Measurement' box has a check mark next to each standard to be analyzed. Analyze each calibration standard twice. Select 'Run', then 'Measurement start' from the menu or click the 'Start' button to begin analysis.

6.7.4 In the pop-up window, navigate to the Documents folder where the data will be stored as an MA3 file type. Name the file in the format '*YYYY-MM-DD* CALT-N1' for tissues or '*YYYY-MM-DD* CALS-N1' for sediments/wastes. Click 'Save'. The measurements will begin and a pop-up window will appear upon completion. Click 'OK'.

6.7.5 Navigate to 'Calibration' and choose 'fit calibration in every cell'. The calibration curve is linear. The correlation coefficient of the calibration curve for each Cell must be ≥ 0.995. The % Relative Error in the calibration is measured at every calibration point. For STD1 (0.15 ng) and STD2 (0.3 ng), the lowest calibration points for sediments/wastes and tissues respectively, the % Relative Error must be lower than 30 %. All other standards must be lower than 20%. The software also calculates the deviation (DEV) in % for every point in the calibration.

6.7.6 Save the results. Navigate to 'File' > 'Save As Text' and save the file with the same name as a CSV file type in the Documents folder. Also save the CSV file to the network at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Mercury\NIPPON MA-3000-1 in the appropriate folder for the year and quarter.

6.7.7 Fill out the Mercury Calibration Standard Preparation Log MT-HGCAL-STD-1.2 Excel form and save the file in the format '*YYYY-MM-DD* CALT-N1-MT-HGCAL-STD-1.2' for tissues to the network at: \\floridadep\data\Labs\Lab5\Chemistry\InorganicPrep\Mercury\T-HG-TDA in the appropriate folder for the year and quarter. Save the file in the format '*YYYY-MM-DD* CALS-N1-MT-HGCAL-STD-1.2' for sediments/wastes to the network at: \\floridadep\data\Labs\Lab5\Chemistry\InorganicPrep\Mercury\S-HG-TDA in the appropriate folder for the year.

6.8 Sample Analysis:

6.8.1 Under 'Sample', create a new file for the analysis.

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6.8.2 Select the appropriate calibration in the STD table.

6.8.3 Select the method ORGANISM (SOLID) for tissue samples or SOIL&SLUDGE for sediment/waste samples.

6.8.4 The sequence of samples and quality controls to be analyzed are typed into the sample file. See Appendix A for an example sample sequence.

6.8.5 Daily Calibration Check - Analyze the following calibration standards at the beginning of every analysis, whether for tissues or sediments/wastes. The results must be within 10 % of their expected value.

6.8.5.1 Cell 1 (LOW) Daily Calibration Check:

STD4 (0.5 ng) [50 µL of TDA-4 (10 µg/L)]

STD8 (7.5 ng) [75 µL of TDA-3 (100 µg/L)]

6.8.5.2 Cell 2 (HIGH) Daily Calibration Check:

STD9 (10 ng) [100 µL of TDA-3 (100 µg/L)]

STD15 (200 ng) [20 µL of TDA-1 (10 mg/L)]

6.8.6 Second Source Daily Calibration Check - Analyze the following second source check standards at the beginning of every analysis, whether for tissues or sediments/wastes. The results must be within 10 % of their expected value.

6.8.6.1 Cell 1 (LOW) Second Source Daily Calibration Check:

TDA-CA (3.0 ng) [30 µL of TDA-3C]

6.8.6.2 Cell 2 (HIGH) Second Source Daily Calibration Check:

TDA-CB (20 ng) [200 µL of TDA-3C]

6.8.7 For tissue samples, use a clean wooden applicator stick to transfer the entire tissue sample (or a subsample of approximately 10 g 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 g to 0.2 g of chopped tissue to a ceramic boat. Record the exact weight into the sample file and place the ceramic boat into the autosampler stainless steel rack.

6.8.8 For sediment/waste samples, stir the sample within its container with a clean spatula to homogenize the sample. 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 your supervisor if any non-representative material is found in the sample. Any large objects should be cut or crushed – but not removed – from the sample. A mortar and pestle may be used if necessary. Return the homogenized sample to the sample jar. Weigh 0.05 g to 0.4 g of sample into a ceramic boat. Record the exact

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weight into the sample file and place the ceramic boat into the autosampler stainless steel rack.

6.8.9 Make sure the 'Measurement' box has a check mark next to each quality control and sample to be analyzed in the sequence. Select 'Run', then 'Measurement start' from the menu or click the 'Start' button to begin analysis.

6.8.10 In the pop-up window, navigate to the Documents folder where the data will be stored as an MA3 file type. Name the file in the format '*YYYY-MM-DD* T1-N1' for tissues or '*YYYY-MM-DD* S1-N1' for sediments/wastes and click 'Save'. The measurements will begin and a pop-up window will appear upon completion. Click 'OK'.

6.8.11 Save the results. Navigate to 'File' > 'Save As Text' and save the file with the same name as a CSV file type in the Documents folder. Also save the CSV file to the network at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Mercury\NIPPON MA-3000-1 in the appropriate folder for the year and quarter.

6.8.12 Fill out the Mercury Analysis Standard Preparation Log MT-HGANA-STD-1.0 Excel form and save the file in the format '*YYYY-MM-DD* T1-N1 MT-HGANA-STD-1.0' for tissues to the network at: \\floridadep\data\Labs\Lab5\Chemistry\InorganicPrep\Mercury\T-HG-TDA in the appropriate folder for the year and quarter. Save the file in the format '*YYYY-MM-DD* S1-N1 MT-HGANA-STD-1.0' for sediments/wastes to the network at: \\floridadep\data\Labs\Lab5\Chemistry\InorganicPrep\Mercury\S-HG-TDA in the appropriate folder for the year.

6.8.13 For sediments/wastes, calculate the dry weight (g) with Excel form MT-SEDWT-1.0 and save a copy in the format 'MT-SEDWT-1.0 *YYYY-MM-DD* S1-N1' to the network at: \\floridadep\data\Labs\Lab5\Chemistry\InorganicPrep\Mercury\S-HG-TDA in the appropriate folder for the year.

7. QUALITY CONTROL

See DEP SOP MT-058 for calculations 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:

$$\frac{Matrix\ Spike\ (ng) - [QC\ Sample\ (ng) * \frac{Weight\ of\ Matrix\ Spike\ (g)}{Weight\ of\ QC\ Sample\ (g)}]}{Spike\ Concentration\ (ng)} * 100$$

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7.1 Method Blank, MBLK. One method blank is required per batch of 20 samples. Analyze an empty ceramic boat. The result of the method blank must be below the method detection limit (MDL) of 0.1 ng for tissues and 0.05 ng for sediments/wastes.

7.2 Practical Quantitation Limit (PQL), T-PQL (0.3 ng Hg) and S-PQL (0.15 ng Hg). One PQL standard is required per batch of 20 samples. For tissues, T-PQL is prepared by pipetting 30 µL of TDA-4 (10 µg/L) to a ceramic boat. For sediments/wastes, S-PQL is prepared by pipetting 30 µL of TDA-5 (5.0 µg/L) to a ceramic boat. The acceptable recovery limit for the PQL is 70 – 130 %.

7.3 Laboratory Fortified Blank (LFB), DORM-5 (0.310 mg Hg/kg) and SRM 2706 (0.13 mg Hg/kg). One LFB is required per batch of 20 samples. A Standard Reference Material (SRM) is used to prepare the LFB. See Sections 4.5.13 and 4.5.14. Weigh approximately 0.0050 g of DORM-5 into a ceramic boat for tissue batches. Weigh approximately 0.015 g of SRM 2706 for sediment/waste batches. The acceptable recovery limit for the LFB is 80 – 120 %.

7.4 Matrix Spike and Matrix Spike Duplicate. One matrix spike and matrix spike duplicate are required per batch of 20 samples. To prepare the duplicate matrix spikes, weigh two aliquots of the same sample and spike each aliquot with the respective solution below for the appropriate matrix. The acceptable recovery limit for the matrix spikes is 80 – 120 %. The RPD must be below 20 %.

7.4.1 Tissue Matrix Spike Solution, 50 ng [50 µL of TDA-2]

7.4.2 Sediment/Waste Matrix Spike Solution, 3.0 ng [30 µL of TDA-3]

7.5 Continuing Calibration Verification (CCV), STD7CCV (5.0 ng), and STD14CCV (100 ng). The CCVs shall bracket every 10 samples in the sequence to continually verify the calibration. For both tissues and sediments/wastes, STD7CCV is used for Cell 1 (LOW) and STD14CCV is used for Cell 2 (HIGH). The acceptable recovery limit is 80 – 120 %.

7.5.1 STD7CCV (5.0 ng) [50 µL of TDA-3 (100 µg/L)]

7.5.2 STD14CCV (100 ng) [100 µL of TDA-2 (1.0 mg/L)]

7.6 Continuous Calibration Blank (CCB). The CCB shall bracket every 10 samples along with the CCVs to continually verify that no contamination is present and that no drift has occurred. Pipette 0.3 mL of L-Cysteine solution in 0.2 % HNO_3 to a ceramic boat. Acceptable CCB results are below the MDL of 0.1 ng for tissues and 0.05 ng for sediments/wastes.

7.7 Second Source Check Standard, TDA-CA (3.0 ng), and TDA-CB (20 ng). The second source check standards (see Sections 4.5.11, 4.5.12, and 6.8.6) are used to verify the calibration from a second source. These standards are analyzed at the beginning of every analytical run. TDA-CA (3.0 ng) is analyzed for Cell 1 (LOW). Pipette 30 µL of TDA-3C into a ceramic boat. TDA-CB (20 ng) is analyzed for Cell 2 (HIGH). Pipette 200 µL of TDA-3C into a ceramic boat. The acceptable recovery limit for each standard is 90 – 110 %.

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8. DATA ARCHIVAL

8.1 NIPPON MA-3000: After measurements are complete, the MA3 instrument file and a CSV copy of the data shall be saved on the hard drive of the instrument computer in the Documents folder in the format 'YYYY-MM-DD T1-N1', where 'YYYY-MM-DD' reflects the date of the analysis. The first letter and number following the date reflects the matrix of the analyzed samples and the sequence number performed on that day ('T1' in this case for the first sequence of tissue samples; 'T2' for the second sequence, and so on; and 'S' to denote sediment/waste). The second letter and number after the date represents the instrument number ('N1' for NIPPON MA-3000-1; and 'N2' for NIPPON MA-3000-2). An additional copy of the CSV file shall be saved to the computer network at: \\floridadep\data\Labs\Lab3\Chem_Data\Inorganic\Mercury in the appropriate folder for the instrument, year, and quarter.

9. MAINTENANCE

9.1 During routine maintenance of the NIPPON MA-3000, both the instrument and computer shall be powered down and disconnected from the power supply. Close the main cock of the oxygen gas cylinder. Allow the instrument to cool to room temperature prior to performing maintenance.

9.2 Refer to the NIPPON MA-3000 Instruction Manual for the replacement procedures of the sample heating/combustion tube (catalyst), the lamp, and the gold amalgamator. The combustion tube (catalyst) should be replaced approximately every 2000 measurements. The lamp should be replaced approximately after 5000 hours. Be sure to reset the appropriate 'GLP' counters from the Maintenance menu in the instrument software after the respective replacement parts are installed: 'LAMP ACTIVE TIME' for the lamp, and 'MEAS CNT' for the combustion tube (catalyst).

9.3 Document all instrument maintenance performed in the instrument maintenance logbook with your initials and date.

10. SAFETY/HAZARDOUS WASTE MANAGEMENT

10.1 Always wear a lab coat, nitrile gloves, and safety glasses or protective eyewear while working in the lab. Concentrated acids shall be handled in a fume hood.

10.2 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.

10.3 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 the ignition of the sample within the combustion tube.

10.4 Mercury wastes that are generated within the laboratory are environmental pollutants. Their disposal is regulated by the rules that govern industrial

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dischargers. For the City of Tallahassee, the concentration limit for the disposal of mercury into the city's sewer system is 38 µg/L. ANY waste above 38 µg/L in mercury must be handled as hazardous waste. Refer to DEP SOP HG-013 for proper mercury waste disposal.

11. REFERENCES

11.1 NIPPON MA-3000 Instruction Manual.

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

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

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

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

11.6 DEP Laboratory Quality Assurance Manual.

11.7 DEP Laboratory Health and Safety Manual.

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

11.9 DEP SOP HG-013, Mercury Waste Disposal.

11.10 City of Tallahassee, Discharge Restrictions, Sewers and Sewage Disposal (http://talgov.com/Uploads/Public/Documents/you/learn/library/documents/sewer_use_manual.pdf).

APPENDIX A

Example Sample Sequence

STD4
TDA-CA
STD8
STD9
TDA-CB
STD15
Rinse
Rinse
STD14CCVC
Rinse
STD7CCVC
Rinse
CCB
MBLK
T-PQL / S-PQL
LFB: DORM-5 / SRM 2706
Sample 1
Sample 1 Matrix Spike

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Sample 1 Matrix Spike Duplicate
Sample 2
Sample 3
Sample 4
Sample 5
STD14CCV
Rinse
STD7CCV
Rinse
CCB

Note: MBLK, PQL, LFB, and both Matrix Spikes are counted as 'samples' for the purpose of the 10-sample count CCV bracketing rules.

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 %.
02/16/2023	Many sections were re-written due to receiving two new instruments, NIPPON MA-3000-1 and NIPPON MA-3000-2 that replaced the previous DMA1 and DMA2 from Milestone.
02/12/2026	Added disposable weigh boats, wooden applicator sticks, scalpels, stainless steel spatulas and trays, and mortar and pestle to Section 3. Added oxygen carrier gas to Section 4. Updated catalyst information and restructured Section 4. Removed Section 6 Calibration Standards Preparation Procedure and incorporated the concentration table into Section 4. Moved Sample Analysis Procedure from Section 7 to Section 6. Moved Quality Control from Section 10 to Section 7. Moved Data Archival from Section 9 to Section 8. Moved Maintenance from Section 8 to Section 9. Moved Safety/Hazardous Waste Management from Section 11 to Section 10. Moved References from Section 12 to Section 11. Updated the Cell 2 (HIGH) Daily Calibration Check information in Section 6 to reflect that STD15 is now used for both tissues and sediments/wastes instead of

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STD14 for sediments/wastes and STD15 for tissues. Major additions and elaborations to Section 6. Restructured Section 6. Restructured and elaborated on QC details in Section 7. Updated the formula in Section 7. Moved calibration criteria from Section 7 to Section 6. Eliminated all redundant information in Section 8. Added criteria for replacement of combustion tubes and lamps in Section 9. Referred to DEP SOP HG-013 Mercury Waste Disposal in Section 10 and added as a reference to Section 11. Added reference to City of Tallahassee Discharge Restrictions to Section 11. Updated Example Sample Sequence in Appendix A. Updated the proper name of the NIPPON MA-3000 Instruction Manual throughout the document. Grammatical and formatting changes throughout the entire document. Updated all referenced network file paths.

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