ANALYSIS OF MERCURY IN SEDIMENT, WASTE AND TISSUES BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

TABLE OF CONTENTS

1. SCOPE AND APPLICATION 1
2. SUMMARY OF THE METHOD 1
3. APPARATUS AND EQUIPMENT 2
4. REAGENTS AND CHEMICALS 2
5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING 6
6. CALIBRATION STANDARDS PREPARATION PROCEDURE 6
7. SAMPLE ANALYSIS PROCEDURE 7
8. MAINTENANCE 9
9. DATA ARCHIVAL 9
10. QUALITY CONTROL 10
11. SAFETY/HAZARDOUS WASTE MANAGEMENT 11
12. REFERENCES 11

APPENDICES
A. EXAMPLE SAMPLE SEQUENCE 12

APPENDIX OF SIGNIFICANT CHANGES 13

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 for the tissue matrix is 0.3 ng – 400 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 calibration range for sediment and waste is 0.15 ng - 200 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 NIPPON MA-3000 instrument. The sample is weighed into a ceramic boat and placed on the autosampler rack (10 ceramic boats in every stainless steel rack). 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

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

trapped. The remaining decomposition products are 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 two 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 absorbance results of up to 10 ng. Cell 2 (HIGH) is used for concentration up to 400 ng for tissues and 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 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 NIPPON MA-3000 automatically runs a cleaning cycle after samples.

3. APPARATUS AND EQUIPMENT

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

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

3.3 Analytical balance.

3.4 Ceramic boats part number 440531

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 – NIPPON MA-3000 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 the catalyst replacement maintenance. The catalyst does not have an expiration

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

date. The NIPPON MA-3000 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 seconds.

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 seconds.

4.3 L-Cysteine in 0.2 % HNO_3 -Weigh 100 mg of L-Cysteine and dissolve in 1 L volumetric flask. Add 2 ml of HNO_3. Mix well.

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 standard

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 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 preparation and standard 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 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 preparation and standard 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 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 preparation and standard is stored at room temperature.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

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 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 preparation and standard 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 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 preparation and standard 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: Cell 1 is used up to 10 ng and cell 2 is up to 200 ng (sediments) and 400 ng (Tissues)

Calibration Standards for Sediments and Wastes in Cell 1:

STD 1	(0.15 ng)
STD 4	(0.5 ng)
STD 6	(3.0 ng)
STD 7	(5.0 ng)
STD 8	(7.5 ng)
STD 9	(10 ng)

Calibration Standards for Sediments and Wastes in Cell 2:

STD 9	(10 ng)
STD 10	(15 ng)
STD 11	(20 ng)
STD 13	(50 ng)
STD 14	(100 ng)
STD 15	(200 ng)

Calibration Standards for Tissues in Cell 1:

STD 2	(0.3 ng)
STD 4	(0.5 ng)
STD 6	(3.0 ng)
STD7	(5.0 ng)
STD 8	(7.5 ng)
STD 9	(10 ng)

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Calibration Standards for Tissues in Cell 2:

STD 9	(10 ng)
STD 11	(20 ng)
STD 13	(50ng)
STD 14	(100ng)
STD 15	(200 ng)
STD 16	(400 ng)

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 L-Cysteine in 0.2 % HNO_3. Dilute to volume and mix well. The expiration date for this prepared standard is 180 days from preparation and it is stored at room temperature.

4.4.8.2 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 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 preparation and it is stored at room temperature.

4.4.8.3 The second source standard is analyzed at two different concentrations for each absorption cell.

4.4.8.3.1 TDA-CA (3.0 ng) - Pipette 30 uL of TDA-3C into a ceramic boat

4.4.8.3.2 TDA-CB (20 ng) - Pipette 200 µL of TDA-C into a ceramic boat.

4.5 DORM-5 - 0.310 mg Hg/kg - Standard reference material (SRM) purchased from the National Research Council of Canada (NRCC). This standard is used as the laboratory control sample (LCS) for each batch of tissue samples analyzed. The expiration date is provided by the manufacturer.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

4.6 SRM 2706 - 0.13 mg Hg/kg - SRM purchased from NIST. 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 ceramic 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 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 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 ceramic boats.

Calibration Standard Concentration for Sediments and Wastes in Cell 1	Amount of Standard to Deliver to Sample Boat
STD 1 0.15 ng	30 µL of TDA-5 (5 µg/L)
STD 4 0.5 ng	50 µL of TDA-4 (10 ug/L)
STD 6 3.0 ng	30 µL of TDA-3 (100 µg/L)
STD 7 5.0 ng	50 µL of TDA-3 (100 µg/L)
STD 8 7.5 ng	75 µL of TDA-3 (100 µg/L)
STD 9 10 ng	100 µL of TDA-3 (100 µg/L)

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Calibration Standard Concentration for Sediments and Wastes in Cell 2	Amount of Standard to Deliver to Sample Boat
STD 9 10 ng	100 µL of TDA-3 (100 µg/L)
STD 10 15 ng	150 µL of TDA-3 (100 µg/L)
STD 11 20 ng	200 µL of TDA-3 (100 µg/L)
STD 13 50 ng	50 µL of TDA-2 (1 mg/L)
STD 14 100 ng	100 µL of TDA-2 (1 mg/L)
STD 15 200 ng	20 µL of TDA-1 (10 mg/L)

Calibration Standard Concentration for Tissues in Cell 1	Amount of Standard to Deliver to Sample Boat
STD 2 0.3 ng	30 µL of TDA-4 (10 ug/L)
STD 4 0.5 ng	50 µL of TDA-4 (10 ug/L)
STD 6 3.0 ng	30 µL of TDA-3 (100 ug/L)
STD 7 5.0 ng	50 µL of TDA-3 (100 ug/L)
STD 8 7.5 ng	75 µL of TDA-3 (100 ug/L)
STD 9 10 ng	100 µL of TDA-3 (100 ug/L)

Calibration Standard Concentration for Tissues in Cell 2	Amount of Standard to Deliver to Sample Boat
STD 9 10 ng	100 µL of TDA-3 (100 ug/L)
STD 11 20 ng	200 µL of TDA-3 (100 ug/L)
STD 13 50 ng	50 µL of TDA-2 (1 mg/L)
STD 14 100 ng	100 µL of TDA-2 (1 mg/L)
STD 15 200 ng	20 µL of TDA-1 (10 mg/L)
STD 16 400 ng	40 µL of TDA-1 (10 mg/L)

7. SAMPLE ANALYSIS PROCEDURE

7.1 Open the oxygen supply.

7.2 Turn the NIPPON MA-3000 on with the switch on the front panel of the instrument.

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

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

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

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, go to standard page. Clear the old calibration (do not delete) using the blank page icon and save the new one in the calibration folder.

7.5.2 Analyze each calibration standard twice.

7.5.3 Push START to start analyzing calibration standards.

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

7.5.5 Go to “Calibration” and choose fit calibration in every cell. Save the results. The calibration curve is linear.

7.5.6 NIPPON MA-3000- calculates deviation in % for every point in calibration.

7.6 Sample Analysis:

7.6.1 Under ‘Sample’ create a new file for the analysis.

7.6.2 Select the appropriate calibration in STD page.

7.6.3 Select the method..

7.6.4 For analyzing tissue samples, choose ORGANISM (SOLID Method).and for analyzing sediment samples, choose SOIL&SLUDGE Method .

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 1 daily calibration check – STD 4 (0.5 ng) and STD 8 CCV (7.5 ng).

7.6.5.2 Cell 2 daily calibration check – STD 9 CCV (10 ng) and STD 14 (100 ng) for sediments and STD 15 (200 ng) for Tissues.

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

7.6.6.1 Cell 1 daily calibration check – STD 4 (0.5 ng) and STD 8 CCV (7.5 ng).

7.6.6.2 Cell 2 daily calibration check - STD 9 CCV (10 ng) and STD 14 (100 ng).

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

7.6.7 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.

7.6.7.1 Cell 1 second source check – TDA-CA (3.0 ng).

7.6.7.2 Cell 2 second source check – TDA-CB (20 ng).

7.6.8 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 ceramic boat. Record the exact weight transferred.

7.6.9 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 ceramic boat 0.05 – 0.4 g of sample. Record the exact weight.

7.6.10 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 NIPPON MA-3000, both the instrument and computer should be turned off and disconnected from the power supply. Turn off the oxygen supply. Allow the instrument to cool to room temperature before beginning maintenance.

8.2 Refer to the NIPPON Operator Manual for replacement of the catalyst and the amalgam trap.

8.3 Document all instrument maintenance in the instrument maintenance logbook.

9. DATA ARCHIVAL

The NIPPON MA-3000 instrument software does not automatically save the results from the analytical run. To distinguish files between the two NIPPON instruments, a suffix is used. The ‘NIPPON-1’ suffix is for S/N 2174-0758. The’NIPPON-2’ suffix is for S/N 2174-0759. See below for details:

9.1 NIPPON MA-3000-1 (SN 2174-0758): After measurements are complete, click File > Save and save the instrument software file on the hard drive of the

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

instrument computer with the format 20190805t1-NIPPON-1. 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 'NIPPON-1' appended to the file name, for example, 20190805t1-NIPPON-1.txt. The text file is saved to NIPPON-MA-3000-1.

9.2 NIPPON MA-3000-2 (S/N 2174-0759): 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-NIPPON-2. 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 'NIPPON-2' appended to the file name, for example, 20190805t2-NIPPON-2.txt. The text file is saved to NIPPON-MA-3000-2.

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

10.1 One method blank per batch of 20 samples. Place empty ceramic 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 0.0050 g of DORM-5 for tissue batches. Weigh approximately 0.015 g of SRM 2706 for sediment batches). 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 a spike solution. The acceptable recovery limits for the matrix spikes is 80 – 120 %. The RPD should be below 20 %.

10.3.1 Sediment Matrix Spikes – Duplicate matrix spikes are prepared by weighing two aliquots of the same sample and spiking with 30 µL of TDA-3. The acceptable recovery limits for the matrix spikes is 80 – 120 %. The RPD should be below 20 %.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

10.3.2 Tissue 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 %.

10.4 Continuous Calibration Verification (CCV) - Every 10 samples, standards, STD 7, and STD 14 are analyzed to verify the calibration. The STD 7 CCV is used for cell 1. The STD 14 CCV 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 (L-Cysteine in 0.2 % HNO_3) in an empty ceramic boat 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 is calculated by the instrument. The % Relative Error for calibration Standards (0.15 ng) and (0.3 ng) must be lower than 30% and for all other standards must be lower than 20%.

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 NIPPON operators manual.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

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.

APPENDIX A

Example Sample Sequence

STD 4
TDA-CA
STD 8
STD 9 **Initial Calibration Verification**
TDA-CB Completed at the start of each run.
STD 15 * for tissues STD 14 for Sediments Requires 90-110% recovery.

STD 14 CCVC * CCB must be below the MDL.
STD 7 CCVC

CCB

Method Blank
Sediment/Tissue PQL
SRM: DORM-5 (tissue) or SRM 2706 (sediment)
Sample 1
Sample 1 Matrix spike
Sample 1 Matrix spike duplicate
Sample 2
Sample 3
Sample 4
Sample 5

STD 14 CCV * **Continuous Calibration Verification / Blank**
STD 7 CCV All CCVs & CCB must be analyzed every 10 samples.
CCVs require 80-120% recovery; CCBs must be below the MDL.
CCB

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

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

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.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.