1.0 TITLE

Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation and Atomic Absorption Spectrophotometry.

2.0 LOCATION

2.1 Metals Laboratory.

3.0 SCOPE & APPLICATION

3.1 This method is applicable to solids, aqueous samples, and digested solutions in both the laboratory and field environments. Integration of thermal decomposition, sample preparation, and atomic absorption detection reduces the total analysis time of most samples to less than five minutes in either the laboratory or field setting. Total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type material as well as in aqueous wastes and ground waters can be determined without sample chemical pretreatment using this method, except as noted. Alternatively, this method can be used for the detection of total mercury from total decomposition sample preparation methods, such as method 3052 or for detection of extracted or leached mercury compounds or species from methods such as the SW-846 3000 series methods.

NOTE: For unique circumstances when mercury could be bound in silicates or other matrices that may not thermally decompose, validation of direct analysis of the solid should be confirmed with total decomposition with an EPA approved method (such as Method 3052) and analysis with this method

4.0 SUMMARY

4.1 Controlled heating in an oxygenated decomposition furnace is used to liberate mercury (Hg) from solid and aqueous samples in the instrument. 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. Here oxidation is completed, and the halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.7 nm as a function of mercury concentration. The mercury vapor is first carried through a long path length absorbance cell and then a short path length absorbance cell (the lengths of the first cell and the second cell are in a ratio of 10:1 or another appropriate ratio). The same quantity of mercury is measured twice, using two different sensitivities resulting in a dynamic range that spans at least four orders of magnitude.

4.2 **METHOD MODIFICATIONS and/or DEVIATIONS.**

4.2.1 Method 7473 specifies to prepare fresh standards daily, with nitric acid. The manufacturer recommends using a 100mg/L L-Cysteine solution as a stabilizer for the mercury standards. The L-Cysteine, if properly stored is good for up to 6 months. ACZ confirms each lot to be free from mercury using method 245.1/7470A.

5.0 REFERENCE

5.1 EPA method 7473 (2007): Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation and Atomic absorption Spectrophotometry.

5.2 NIC MA-3000 Instruction Manual, Nippon Instruments Corporation.

6.0 SAMPLE COLLECTION, HANDLING & PRESERVATION

6.1 According to Method 7473 samples should be collected in pre-cleaned or tested/certified containers.

6.2 Samples must be shipped, received, and stored at 0-6.0°C. Data should be appropriately qualified if thermal preservation conditions are not maintained.

6.3 The Hold Time is for all solid matrices is **28 days** from time of sampling if thermal preservation criteria are met.

Table 6.1: Hold Times

Product	Matrix	Hold Time Starts – Ends With
HG-7473	Solids	28 days from collection to analysis

6.4 Solid sample types:

6.4.1 **'As received'** condition is non-homogenized, un-dried, and not separated for particle size.

6.4.1.1 **'As received'** sediment (SD), sludge (SL), and soil (SO) samples are stored in either the Inorganics, Organics, or Sludge fridges at 0-6.0°C. Samples not properly stored should be appropriately qualified.

6.4.1.2 **'As received'** samples use percent solid data when calculating results. Percent solid data is found in SAGE → Sample Results → Type in L# → Select sub sample # → PCNT SOLID (Total solids for SL) if not on bench sheet.

6.4.2 Sediment (SD), sludge (SL), and soil (SO) samples that are large sized solid particles or rock cores, can be crushed, sieved to <2000, and dried at 40°C; this is a **'prepped solid'**. Client's may also request their samples to be prepped prior to analysis.

6.4.2.1 **'Prepped solid'** samples are stored in the soils department, are not cold, and should be qualified appropriately.

6.4.2.2 **Residual moisture** is used to calculate results in place of percent solid. Data is found in SAGE → Sample Results → Enter L# → Select sub-sample # → X-3050 → air dried solids.

NOTE: Occasionally percent solids data is generated from the prepped fraction rather than the 'as received' – in this case, it may be used for calculations in place of air-dried solids. The fraction used will be noted on the percent solids WG bench sheet.

6.4.3 Prepped **'Biota'** samples are fish (FI) and animals (AN) that are mechanically homogenized and re-frozen.

6.4.3.1 Prepped **'biota'** samples are stored at -10°C to -24°C in the fish fridge.

6.4.3.2 **'Biota'** samples are analyzed on a wet weight basis. Results are calculated using 100 percent solid.

6.4.4 Prepped '**plant'** (PL) samples are homogenized and dried at 40°C.

6.4.4.1 Prepped **'plant' (PL)** samples are stored at room temperature in the soils department.

6.4.4.2 **Residual Moisture** is used to calculate results in place of percent solid. Data can be found through SAGE → Sample Results → Enter L# → Select sub-sample # → X-3050 → air-dried solids.

7.0 APPARATUS & SUPPLIES

7.1 NIC Fully Automated Thermal Vaporization Mercury Analysis System MA-3000.

7.2 Ceramic boats

7.3 Graduated, HDPE, 50mL digestion tubes with caps, volume certified by manufacturer.

7.4 10-100µL adjustable pipette and pipette tips. Verify accurate delivery before use, see Qualtrax ID: 1522.

7.5 100-1000µL adjustable pipette and pipette tips. Verify accurate delivery before use, see Qualtrax ID: 1522.

7.6 Analytical balance, capable of weighing to 0.001g. Verify accurate delivery, see Qualtrax ID: 1522.

7.7 M102-Silent oxygen generator

7.8 Oxygen gas supply and regulator, purity ≥90% and pressure 0.1MPa to 0.5MPa.

7.9 Type I water system, >18.0 MΩ resistance.

7.10 Desktop PC with MA3Win Software installed

8.0 REAGENTS & STANDARDS

NOTES:

- Prepare and store standards using Class A certified containers. Clean with 1:1 HNO_3 and rinse with Type I (>18.0MΩ) water if needed. Store at room temperature.
- Volumes dispensed with verified mechanical pipettes.
- SCNs used for SAGE calculations must be entered using the 'Special SCN' function and have their true value reported in ng/g.

8.1 Ottawa Sand: Bake for at least 10 minutes at 800°C prior to use. Store in a sealed container. Observe manufacture's expiration date.

8.2 Standard Reference Materials (SRMs) of various matrices; plant, fish, soil, etc. Concentration is variable and manufacturer's expiration date applies.

8.2.1 The reference material needs to be purchased at a concentration where the laboratory can prepare MS/D and LCSS/D at an Hg value of 3–100 ng using no less then ~ 0.025 g of material.

8.3 L-cysteine (100mg/L): Add 0.1g L-Cysteine + 2mL HNO_3 to ~800mL Type I H_2O. QS to ~1L. Prepare every 6 months or at manufacture's expiration date. Store in cool dark place.

8.3.1 The L-cysteine solution and the mercury standard solutions prepared can be used for 6 months if they are stored in a cool dark place. Label with the date prepared.

8.3.2 The stability of the solutions will deteriorate as they age or if kept anywhere warm.

8.4 1:1 HNO_3: Used for cleaning purposes. Prepared in metals laboratory. Observe manufacturer's expiration date.

8.5 Mercury stock solution, 1000mg/L. Observe manufacturer's expiration date.

8.6 Mercury stock solution 2nd source, 1000mg/L. Observe manufacture's expiration date.

8.7 **10mg/L (10,000ng/g) Mercury Calibration Stock Intermediate**: Add 0.5mL of mercury stock solution to ~40mL of the 100mg/L L-Cysteine solution. QS to 50mL with the L-Cysteine solution. Prepare every 6 months or at manufacture's expiration date, whichever is sooner.

8.8 **10mg/L (10,000ng/g) Mercury 2nd Source Stock Intermediate:** Add 0.5mL of 2nd source mercury stock solution to ~40mL of the 100mg/L L-Cysteine solution. QS to 50mL with the L-Cysteine solution. Prepare every 6 months or at manufacture's expiration date, whichever is sooner.

8.9 **1.0mg/L (1000ng/g) Mercury Calibration Intermediate:** Add 5mL of the 10mg/L mercury calibration stock intermediate to ~40mL of the 100mg/L L-Cysteine solution. QS to 50mL with the L-Cysteine solution. Prepare every 6 months or at manufacture's expiration date, whichever is sooner.

8.10 **0.1mg/L (100ng/g) Mercury Calibration Intermediate:** Add 0.5mL of the 10mg/L mercury calibration stock intermediate to ~40mL of the 100mg/L L-Cysteine solution. QS to 50mL with the L-Cysteine solution. Prepare every 6 months or at manufacture's expiration date, whichever is sooner.

9.0 SAFETY

9.1 HAZARDS

9.1.1 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 reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedure.

9.2 SAFETY TECHNIQUE

9.2.1 Safety glasses are required, and the use of gloves and lab coat is strongly recommended. Shorts and open-toed shoes are not allowed in the lab.

9.2.2 Use care when pouring and pipetting reagents. Always add acid to water. Use the proper method when washing glassware.

9.2.3 Do not eat or use tobacco products in the lab.

9.2.4 Wipe up ALL spills immediately. Implement the Emergency Response Plan if necessary. Qualtrax ID: 1551.

9.2.5 Do not conduct "experiments" unrelated to the analysis.

9.3 PROTECTIVE EQUIPMENT

9.3.1 Use a fume hood when there is a potential for strong fumes.

9.3.2 A fire extinguisher is in each analytical laboratory.

9.3.3 An emergency shower and eye wash station are in the metals prep lab.

10.0 INTERFERENCES

10.1 In areas where mercury contamination is an existing problem, the background signal may be significantly increased.

10.2 Memory effects between analyses may be encountered when analyzing a sample of high mercury content prior to analyzing one of low content. If there is an over-calibration (OCAL), or carry-over is suspected, re-run the following sample for confirmation. PURGES can be inserted following samples of known high Hg concentrations, if possible.

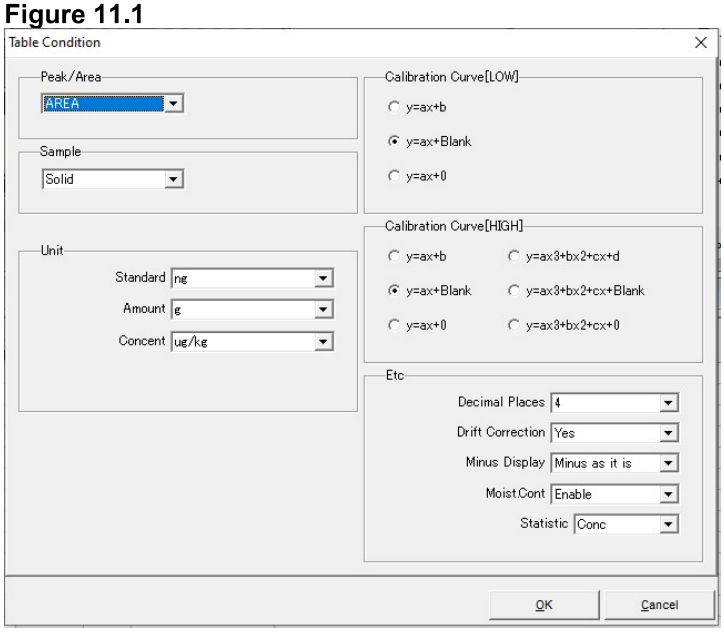
10.3 Co-absorbing gases, such as free chlorine and certain organics (as indicated in Method 7470 and 7471), should not interfere due to the release of decomposition products by the decomposition furnace, removal of some decomposition products by the decomposition catalyst, and the selective entrapment of mercury vapor on the amalgamator.

11.0 PROCEDURES

11.1 Instrument Setup

11.1.1 The table conditions are set and should not be changed. The instrument is set up to measure absorbance using peak area. Any changes must be approved by the supervisor. See Figure 11.1

Figure 11.1



11.1.2 Check humidifier to make sure the water line is at least between the 30mL and 40mL lines; refill with Type I H_2O if needed.

NOTE: If the humidifier is not sealed well enough, it can cause the leak check to fail. If humidifier was filled and leak occurs, ensure that it is tightly sealed then preform the leak check again.

11.1.3 Turn on M102-Silent oxygen generator to begin flow into the MA-3000. Check the drain tank for any liquid, and drain, if necessary.

11.1.4 Open MA3Win software.

11.1.5 Turn ON the main power switch for the MA-3000.

11.1.6 Software will prompt a “Check of flow path” select YES

11.1.6.1 The instrument will check the flow rate of oxygen, perform a leak check, and check the operation of the V1, V2, and V3 valves.

11.1.6.2 Once everything has passed, the instrument will begin the conditioning and warm up the heaters.

11.1.6.3 If the check fails, turn OFF the power and check for loosened joints, insufficient tightening of the sample inlet screw, or damage on the flow path and the humidifier, which is the most common reason for failure.

11.1.7 Run one to two purges to clear the system. There are two ways to purge the system.

11.1.7.1 To run a single purge without getting any results, click the purge button.  This method of purging does not use a boat.

11.1.7.2 To run a single, or multiple purges at once, navigate to the SMP tab and select 'PURGE' from the dropdown menu in the method column. Results will be displayed, and an empty boat is used.

11.1.8 Continue to the primary calibration or daily calibration, whichever is appropriate.

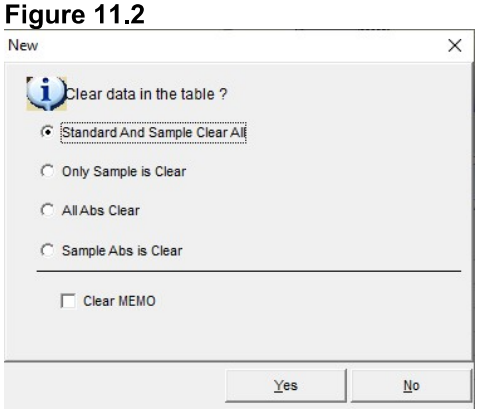
11.2 Primary Calibration

NOTE: A primary calibration must be performed when any significant instrumental parameters are changed, for example replacing the catalyst and amalgamator, or when the daily calibration results are not acceptable (See §11.3).

11.2.1 Click on the "New" icon on the top 

11.2.2 Select "Standard and Sample Clear All". See Figure 11.2

Figure 11.2

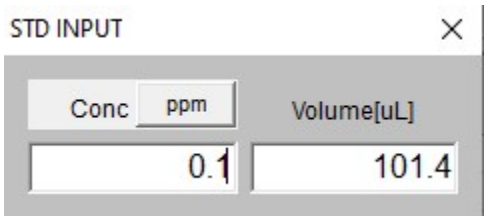


11.2.3 Make sure the STD tab in the bottom left is selected.

11.2.4 Click "STD" to open the "STD INPUT" box or by clicking on the desired cell. See Figure 11.3

11.2.5 Enter the concentration of the standard solution in ppm, and the volume of standard for each point in µL, as indicated in Table 11.2. **Analyze each calibration point twice.**

Figure 11.3



11.2.5.1 For the 0ng points, leave the first two boats empty on the tray.

11.2.5.2 For each standard, load an empty boat on to the balance, tare the balance, and pipette appropriate volume into boat; once stabilized, enter the weight in **µL manually** into the program. Make sure the location of the boats in the tray correspond with the position in the software.

NOTE: Trays are numbered in groups of ten from 1-100. The numbers on the tray may not match the number in the software. The instrument knows that position 1 is the top left of the top tray no matter what number the tray has.

Table 11.1: Primary Calibration

Calibration Target Value (Hg ng)	Volume (mL)/(g)	Standard Concentration (mg/L/ppm)	Cell
0	0	0	Low
1*	0.01	0.1	Low
5	0.05	0.1	Low
10	0.1	0.1	Low/High
20	0.2	0.1	High
100	0.1	1.0	High
500	0.05	10.0	High
1000	0.1	10.0	High

*The lowest non-zero point in the calibration must be ≤ PQL.

11.2.6 Load the trays into the instrument.

11.2.7 Click the 

icon or select 'Start' from the dropdown menu under Run. The system will ask for a file name. Name Primary Calibrations in the format Cal_YYMMDD. Ex. Cal_200710 to the documents folder for This PC.

11.2.8 The  icon allows the operator to toggle between viewing the calibrations under the profile screen, and the control screen.

11.2.8.1 Both the Low and High cell curves utilize a linear fit and are quantified as a function of peak area and must have a R^2 value ≥ 0.995.

11.2.8.2 Letters shown in red and "WARNING" indicate the calibration has a problem. Check the set standards value in the system setup to the

values from the calibration. See section 5.7.4.6 in the user manual for more details.

11.2.8.3 It is possible to ignore erroneous data and exclude it from the calculation and printing by clicking the OX column on TABLE window and selecting "X". Data can only be excluded if a valid reason can be documented for a sporadic point such as incomplete standard delivery. It can be unselected from the calibration and re-analyzed.

11.2.9 If subsequent samples are run on the same day as the Primary Calibration, the second source ICV4 must be analyzed at **100mg/by adding 0.01mL of the 10 mg/L ICV Intermediate.** Recovery must be within ±10 %. If the ICV4 fails, it can be reanalyzed one time. If it fails again, the Primary Calibration must be re-run. It is acceptable to run purges between the calibration and the ICV4 due to the high concentration of the final calibration standards.

11.2.10 If Calibration and initial QC are acceptable, continue to section 11.4, Sample Preparation and Analysis.

11.3 Daily Calibration

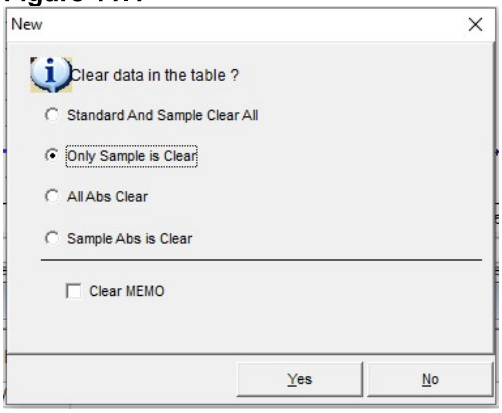
NOTE: If no significant instrument parameters are changed (i.e. replacing the catalyst and/or amalgamator), a daily calibration can be performed. **Recovery for each standard must be within ±10%.** Each daily calibration point can be attempted twice before corrective action is necessary.

11.3.1 A series of QC checks to ensure the primary calibration is valid. One high and one low point are tested for each calibration range. See Table 11.3.

11.3.2 Open the current calibration file by clicking on the Open button at the top of the screen and selecting the current calibration from the documents folder on This PC. This will ensure that the most current calibration is being used.

11.3.3 Click on the New icon  and select "Only Sample is Clear", this clears data only in the SMP table and STD table remains with the current calibration. See Figure 11.4.

Figure 11.4



11.3.4 Click on the 'SMP' tab of the table.

11.3.5 In the METHOD column, select STD from drop-down menu.

11.3.6 Click 'Name' column and select 'ICV1'. Weigh out appropriate volume according to Table 11.2 and click on the appropriate cell in the 'SVOL' column. Once the scale has stabilized, push the print button on the scale to enter the weight into the cell.

11.3.6.1 Repeat for remaining 3 ICVs.

11.3.6.2 Load sample boats into designated spots in the sample tray.

11.3.7 Click the boxes of the samples you want to run in the 'MEASURE' column.

11.3.8 Press 

. The Daily Calibration will run the selected samples. Once completed, make sure all ICVs are within the acceptance range listed in Table 11.2 before proceeding to sample analysis.

11.3.9 Purge system due to possible carryover from high standard. Proceed to sample preparation and analysis once purge reads < 0.2ng.

Table 11.2: Daily Calibration

NAME	INTERMEDIATE	VOLUME/WEIGHT (mL)/(g)	CONCENTRATION (µg/kg)	ACCEPTANCE RANCE (µg/kg)	Hg (ng)
ICV1	0.1mg/L Hg Cal Int.	0.03	100	90-110	3
ICV2	0.1mg/L Hg Cal Int.	0.08	100	90-110	8
ICV3	1.0mg/L Hg Cal Int.	0.1	1000	900-1100	100
ICV4	10mg/L Hg ICV Int.*	0.08	10,000	9000-11000	800

*The 10mg/L ICV Intermediate is made from a mercury stock that is a second source from that used to make the other calibration intermediates.

11.4 Sample Preparation and Analysis

11.4.1 Create a workgroup in SAGE with up to 20 client samples. Enter appropriate SCN's and PCN's for QC samples.

11.4.1.1 It is acceptable to mix different matrices within the same workgroup if each unique matrix has its own MS, DUP and LCSS/D.

11.4.2 Make sure current calibration is open in the STD tab of the software. If not, refer to section 11.3.2 and 11.3.3.

11.4.3 Using the SMP tab, enter the sample name (PBS, LCSS/D, CCV, or L#) into the 'NAME' column, using the bench sheet for sequence reference, starting with the PBS, including the work group number.

11.4.4 Place a clean boat on the holder on the balance and press '→T←' on the balance to tare. Add the appropriate weight to the boat and press the printer icon on the balance to print to the software. Make sure the cell you want to print to is selected in the SVOL column. Enter weight onto the bench sheet, making sure to record all decimal places. Refer to Table 11.3.

11.4.5 Repeat for each sample on the bench sheet, including CCVs every ten samples, as indicated on the bench sheet.

11.4.5.1 For the designated spiked sample (MS), weigh out the sample into the boat and enter weight into the SVOL column. Once recorded, tare the balance with the sample and boat still on the scale. Select the corresponding cell in the ADD.STD column for the sample and add ~0.02mg/L of the 1mg/L calibration standard. Press print on the balance to transfer weight and record on bench sheet in the spike weight column.

NOTE: The actual weight of the spike should not be applied in the SVOL column.

NOTE: The μg/Kg result for Matrix Spike samples is not applicable because there are different aliquots of different components (sample + spike) that the software cannot distinguish. Spike recoveries are calculated using sample weights, spike weights, and the "ng Hg" results. See section 13.2.4.3 for the spike recovery calculation.

11.4.5.2 The CCV is prepared at 50ng by pipetting 0.05mL of the 1mg/L calibration intermediate. Record the weight on the bench sheet.

11.4.5.3 If the sample is a filter, carefully, cleanly, and accurately cut a fraction of the filter (typically, 1/8–1/4 of the filter). Fold it into a sample boat for analysis. Instead of weighing the filter, enter the portion of the total filter used as a decimal in the sample weight field (i.e., if 1/8 of the filter is used, enter 0.125). Results are reported in ng/Filter. If the sample is a filter, but run under a 'MI' matrix, results units will need to be manually updated to ng/Filter.

NOTE: Confirm results are reported in ng/Filter during WG review - especially if the matrix is 'MI'.

11.4.6 Select the appropriate method from the dropdown menu of the 'METHOD' column for each sample. Refer to Table 11.3.

11.4.7 Make sure that the sample location in the trays matches the number in the SAMPLE No. column.

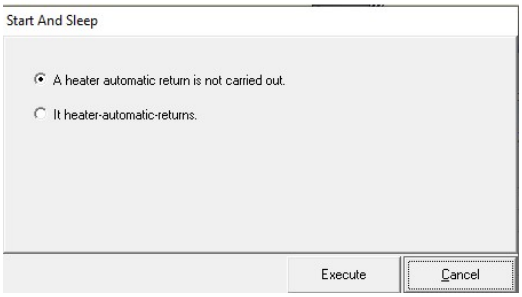
11.4.8 Click the box in the 'MEASURE' column for each of the samples to be run.

11.4.9 Press 

to begin analysis.

NOTE: To begin an analysis and have the heaters automatically turn off when the run completes, select 'Start and Sleep' from the 'Run' dropdown menu, and select 'A heater automatic return is not carried out'. See Figure 11.5

Figure 11.5



11.4.10 Review the data for OCALs and suspected carry over. Rerun OCALs using a lower sample weight to obtain results within the calibration range.

Table 11.3: QC Sources, Sample Weights, and Methods

SAMPLE TYPE	RECCOMMENDED LCSS/D Source* Weight	SAMPLE WEIGHT**	RECOMMENDED METHOD***
Aqueous Standards	Calibration and 2nd Source Standards prepared with L-Cysteine	Varied	STD
Soil, Sediment, and dry Sludges	MESS-4 Marine Sediment ~0.05-0.1g	~0.05-0.25g	SOIL
Aqueous Sludge	MESS-4 Marine Sediment ~0.05-0.1g	~0.1-0.25g	ORGANISM(SOLID)
Fish and Animal Tissue	NIST1566b Oyster Tissue ~0.05-0.1 g OR NRC Canada DORM4 ~0.03-0.08 g	~0.1-0.2g	ORGANISM(SOLID)
Plant Tissue	NIST1573a Tomato Leaves	~0.025-0.15g	SOIL

	~0.025–0.05 g		

*General recommendations, solid reference materials have variable mercury concentrations. The analyst should do their best to match the analytical matrix. Other sources with certified Hg in the appropriate range are acceptable.
**Use the smallest size aliquot in this range where a representative, homogenous sample can be attained. The more material that is used the greater the wear and tear on the catalyst and system. Extra precautions need to be taken and lower sample volumes used when samples contain high organic content.
*** Methods are determined by moisture and organic content of the sample. Other methods can be created and used for analysis.

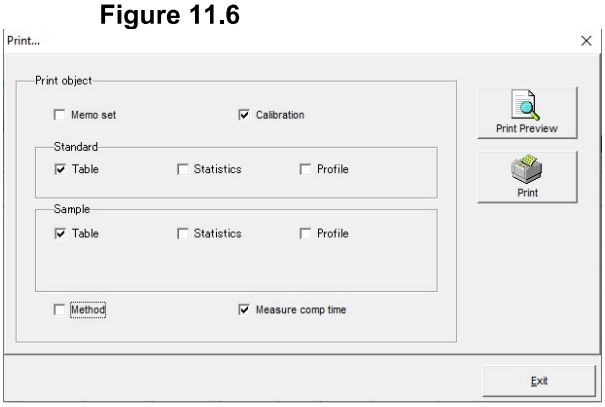
11.5 **Editing and Uploading Data:**

11.5.1 Click on the 'Table' containing all the data to make active. Make sure the whole date and time is visible in the STD tab.

11.5.2 Click 'File' and select 'Print" from the dropdown menu.

11.5.3 Make sure the Calibration, both tables, and the measure comp time are selected. See Figure 11.6

Figure 11.6



11.5.4 Click 'Print Preview' → Orientation should default to landscape → Print

11.5.4.1 Print to the PDF creator.
11.5.4.2 Enter work group number under the 'Filename:' Click 'Save'
11.5.4.3 Directory is set to save to P:\PDFMerge\MA3000.
11.5.4.4 The calibration and all the raw data are included.

11.5.5 While the 'Table' is still active, select 'Save as a Text File" from the "Edit' dropdown menu.

11.5.5.1 Save to U:\WaitLoad\MA3000 as the work group number. If there were multiple work groups run on the same day, save as the date, ex: 201013. Results will be saved as CSV file.

11.5.5.2 Open the file in Excel. Enter the appropriate percent solid, total solid or air dried solid into column G as a decimal. See section 6.4.

NOTE: The '0' assumes 100% solids.

11.5.5.3 If there are multiple work groups run on the same day, the file will need to be separated. Delete the data that is not needed from the other work group and save as the work group number. Each work group needs to contain the daily calibration and all the raw data for the work group. Be sure to include the closing/opening CCV between the work groups with each file.

11.5.5.4 Save the changes and move the file, named as the work group number to the U:\autoload\MA3000 to be uploaded into SAGE.

11.5.5.5 Review the work group in SAGE using the data review sheet, Qualtrax ID 1144. Document any problems, failures, and the corrective actions. Enter the work group number associated with the Primary Calibration in the AREV screen and on the review sheet.

NOTE: The SCNs included on the data review checklist should be the SCNs that were used for the associated Primary Calibration. SCNs for the daily calibration run with the work group itself are documented on the bench sheet.

11.6 Blank Treatment of Sample Boats

11.6.1 Accurate measurement is achieved by the sample boats being heat treated before measurement to remove any trace quantities of mercury.

11.6.2 At first use: Please use the sample boats after heat treatment.

11.6.2.1 Either run through the instrument using the 'PURGE' method or put into a 750°C oven for 1 hour.

11.6.3 Daily work:

11.6.3.1 Heat in 750°C oven for around 3 hours, or repeat measurements using the instrument.

11.6.4 Sample boats must be cooled down after the blank treatment and stored in an airtight container.

11.6.5 If contamination is suspected on the sample boats:

11.6.5.1 Immerse them in a solution of neutral detergent to soak and clean with ultrasonic vibrations for at least 30 minutes.

11.6.5.2 Scrub away any residue with a brush.

11.6.5.3 Immerse the boats in a ~1% nitric acid solution.

11.6.5.4 Rinse thoroughly in distilled water

11.6.5.5 Dry at 100°C for 2 hours.

11.6.6 The boat tray can get contaminated if any liquid splashes on it or a powder sample spills on it affecting results. Use trays in clean condition and wash with water if contaminated.

11.7 **Routine Maintenance**

11.7.1 The mercury collection tube (amalgamator) and sample heating tube (catalyst) should be changed periodically. There is no specific timeframe associated with replacement, but their degradation is generally associated with poor instrument response and an inconsistent or elevated baseline. Removal and replacement are described in section 6 of the operator's manual. Additionally, there is a video that goes through the process located in P:\Departments\Metals\MA3000.

11.7.2 Grease the sample changer if any unusual noise is heard when running.

11.7.2.1 Apply grease to the horizontal shaft, vertical shaft, sample inlet shaft, slide guides of the lift, and trapezoid screw threads. Refer to section 6.4.8 of the user's manual for a diagram.

11.7.2.2 Use only the grease specified for the system. Any other type of grease may not adhere well and cause failure.

12.0 QUALITY CONTROL

12.1 To ensure data validity and quality, a series of QC samples are analyzed with each analytical run; they are required by the methods published by the EPA and other regulatory agencies and are not optional unless otherwise indicated.

12.2 Perform either a Primary Calibration or Daily calibration at the beginning of each working day as described in section 11.2.

Table 12.1: QC Types, Limits, and Corrective Action

Type	Definition	Analysis	QC Limits	QC Limits and Corrective Action
Primary Calibration	A complete calibration of the instruments working range.	Analyze when any significant instrumental parameters are changed or ICV's continue to fail.	Low Cell: r^2>0.995 High Cell: r^2>0.995	Recalibrate
ICV1	Part of the daily calibration. Low range verification of the low cell.	First ICV run for daily calibration.	±10% of True Value	Re-run if fails. If re-run fails, remake standard and run at most two more times. If continues to fail, recalibrate.
ICV2	Part of the daily calibration. High range verification of the low cell.	Second ICV run for daily calibration.	±10% of True Value	Re-run if fails. If re-run fails, remake standard and run at most two more times. If continues to fail, recalibrate.

ICV3	Part of the daily calibration. Low range verification of the high cell.	Third ICV run for daily calibration.	±10% of True Value	Re-run if fails. If re-run fails, remake standard and run at most two more times. If continues to fail, recalibrate.
ICV4	Part of the daily calibration. High range verification of the high cell.	Fourth ICV run for the daily calibration.	±10% of True Value	Re-run if fails. If re-run fails, remake standard and run at most two more times. If continues to fail, recalibrate.
PBS	Preparation Blank Soil. Reagent blank carried through entire prep process to confirm absence of systematic contamination.	Run one for every 20 samples or less. Analyzed at the beginning of each workgroup sequence.	< 3 x MDL or < 10% Sample Concentration, whichever is greater.	Re-run. If re-run fails, reprep and reanalyze all associated samples.
LCSS/D	Laboratory Control Sample Soil and Duplicate. A matrix matched standard of known concentrations of mercury.	Run one set every 20 or less client samples, and one set for each matrix in work group.	±20% Recovery ≤ 20% RPD	Re-run. If re-run fails, reprep and reanalyze all associated samples.
MS	Matrix Spike. A client sample to which known concentrations of mercury is added. Carried through process and estimates accuracy of method and matrix effects.	Run one every 20 or less client samples, and one for each matrix in work group.	±20 % Recovery	Appropriately qualify associated samples.
DUP	Matrix Duplicate. A second aliquot of client sample prepped and analyzed as a sample. Demonstrates the precision of the procedure.	Run one every 20 or less client samples, and one for each matrix in work group.	≤ 20% RPD	Appropriately qualify associated samples.
CCV	Continuing Calibration	Run every ten samples, and at		Reanalyze associated samples.

	Verification. A mid-range standard used to verify system performance.	the end of each work group.	±20% of the True Value	

13.0 DATA CALCULATIONS, DATA REPORTING & ARCHIVING

13.1 The Method Detection Limit (MDL) for this method is 0.4 ng. The Practical Quantification Limit (PQL) is 2.0 ng.

13.2 Linear Calibration Equation

A=Bx+ C

Where: A = absorbance
C = intercept
B = slope
x = concentration of standards or samples

13.2.1 To calculate the intercept:

$$\text{Intercept (C)} = \frac{(n)\sum c_i^2 \sum a_i - \sum c_i \sum c_i a_i}{(n)\sum c_i^2 - (\sum c_i)^2}$$

13.2.2 To calculate the slope:

$$\text{Slope (B)} = \frac{(n)\sum c_i a_i - \sum c_i \sum a_i}{(n)\sum c_i^2 - (\sum c_i)^2}$$

13.2.3 To calculate the correlation coefficient:

$$\text{Correlation Coefficient (r)} = \frac{(n)\sum c_i a_i - \sum c_i \sum a_i}{\sqrt{(n)\sum c_i^2 - (\sum c_i)^2} x \sqrt{(n)\sum a_i^2 (\sum a_i)^2}}$$

Where: c = concentration
a = absorbance
n = number of samples

13.2.4 Calculation for spike % recovery

13.2.4.1 The spike recovery is calculated off the 'ng Hg' result in the instrument software and SAGE.

13.2.4.2 The amount of spike added must be recorded independently of the sample weight used (they must not be summed). The spike concentration value (ug/Kg) in the results is not relevant because it contains different components (sample + spike) each with different concentrations.

13.2.4.3 Spike calculation:

Table 13.1: Spike Calculation

Sample ID	Spike Weight	Sample Weight	Hg(ng)
L100000-01		0.4675	5.747
L100000-01MS	0.1005	0.5015	47.595

1) Use a ratio to calculate the ng Hg in the identical sample weight as used in the MS using the sample's results:

$\frac{5.747ng}{0.4675g} = \frac{X}{0.5015}$ X = 6.165 ng Hg in 0.5015 g sample (MS)

2) Spike TV: [Spike] = 447.4 ng/g

3) MS calculation:

47.595 ng - 6.165 ng= 41.43 ng spike found
41.43 ng/0.1005 g spike wt.= 412.24 ng/g spike found
(412.24/447.4)*100= 92.1 % recovery

13.2.4.4 DUP RPD Calculation

13.2.4.4.1 Perform the RPD calculation by comparing the concentrations (ng/g) of the Sample and DUP using the following equation:

$$\frac{([sx] - [DUP])}{([sx] + [DUP])/2)} \times 100 = RPD$$

14.0 METHOD PERFORMANCE / DETECTION LIMITS

14.1 An MDL study is required as part of initial method development. Additionally, an MDL study must be performed whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions may impact the sensitivity of the instrument.

14.1.1 MDL_s: Spike at eight aliquots at 2–5 x MDL into sample boats and process as described in this SOP. Include a passing calibration, and instrument QC as dictated in this SOP.

14.1.2 MDL_b: Run eight blanks along with spiked MDLs samples.

14.1.3 Enter data into form 2267 in Qualtrax. Attach all raw data and supporting documentation and submit it to the department supervisor for review. Refer to Qualtrax ID 1518 for more detail.

14.2 Quarterly QA MDL Samples: Each quarter, QA samples will be logged in for Mercury Analysis. Prep and analyze according to the method and this SOP, by spiking reagent blank at the PQL or the agreed upon spiking level determined by QA and the Supervisor. These samples can be pulled into workgroups containing other client samples and passed through SAGE as a normal workgroup. Refer to SOP 1518 in Qualtrax for additional information.

14.3 A successful initial DOC (IDOC) must be completed and approved by the QA/QC department for each analyst prior to independent generation of client data. A continuing DOC (CDOC) must be performed on an annual basis. The average percent recovery of the DOC replicates must be within the LCSS/D limits (± 20%) as defined in Table 18.1. RSD between the 4 replicates must be less than 20%.

14.3.1 Prepare and analyze a calibration curve (a new calibration is required for IDOCs only) and associated Instrument QC as outlined in §11.3.

14.3.2 Analyze four individual aliquots of the LCSS (Marine Sediment NIST2702) or a similar solid SRM. Each DOC should be prepared using an appropriate sample weight to bring the result within the instrument's analytical range.

14.3.3 Enter the results on the DOC form (FRMAD023), attach all raw data, all supporting documentation, and turn in to the department supervisor for review. Refer to SOPAD001 for additional information.

15.0 DOCUMENTATION

15.1 Record the appropriate information for all reagents in LIMS database and the department Standard/Reagent Log.

15.2 Make sure the following information is included with the Workgroup:

15.2.1 Analysis date.
15.2.2 Analytical method used.
15.2.3 Analyst's initials.
15.2.4 Calculated QC data results.
15.2.5 Any remarks about analysis or samples.
15.2.6 Data review/checklist form.
15.2.7 *ANY OTHER PERTINENT INFORMATION*

16.0 WASTE MANAGEMENT/POLLUTION PREVENTION

16.1 All standards that contain > 2µg/L (0.002 mg/L) should be poured into an appropriately labeled container. When container is full, put it in the appropriate Hazardous Waste Satellite Accumulation Area until it can be collected by the Hazardous Waste Officer.

16.2 Refer to ACZ's Waste Management Plan: Qualtrax ID 1520 for further details regarding disposal for this method.

17.0 DEFINITIONS

17.1 Units – Several forms of concentration units are mentioned in this SOP, SAGE, and the instrument software. The units, **mg/L** and **mg/Kg** are synonymous and indicate a concentration in **parts per million (ppm)**. The units, **µg/L, ng/g, and µg/Kg** are synonymous and indicate concentration in **parts per billion (ppb)**. ppb = ppm x 100

17.2 Thermal Decomposition – Partial or complete degradation of sample components using convection and conduction heating mechanisms resulting in the release of volatile components such as water, carbon dioxide, organic substances, elements in the form of oxides or complex compounds and elemental gases.

17.3 Amalgamation - the process by which mercury forms a metal alloy with gold.

17.4 Mercury Collection Tube (Amalgamator) - A system composed of gold particles at high surface area to volume ratio for the purpose of amalgamating mercury vapor.

17.5 Primary Calibration - A complete calibration of the instruments working range and is performed initially and when any significant instrumental parameters are changed.

17.6 Daily Calibration - A calibration performed with minimal standards to ensure that the primary calibration is valid.

17.7 Initial Calibration Verification 1 (ICV1) - Low Range test of the low cell analyzed at a concentration of 3ng. Recovery of ICV1 must be ± 10%. If it fails it can be reanalyzed one time. If the reanalysis fails a Primary Calibration must be performed.

17.8 Initial Calibration Verification 2 (ICV2) - High range test of the low cell analyzed at a concentration of 8ng. Recovery must be ± 10%. If it fails it can be reanalyzed one time. If it fails again, a Primary Calibration must be performed.

17.9 Initial Calibration Verification 3 (ICV3) - Low range test of the high cell analyzed at 100ng. Recovery must be ± 10%. If it fails it can be reanalyzed one time. If it fails again, a Primary Calibration must be performed.

17.10 Initial Calibration Verification 4 (ICV4) - High range test of the high cell analyzed at 800ng. Recovery must be ± 10%. If it fails it can be reanalyzed one time. If it fails again, a Primary Calibration must be performed.

17.11 Memory Effects – Mercury vapor may remain in the decomposition tube, amalgamator or absorbance cells and be released in a subsequent analysis resulting in a positive bias.

17.12 Sample boat – The non-amalgamating thermally stable vessel used for containment and transport of the sample for thermal decomposition.

18.0 TABLES & DIAGRAMS

Table 6.1: Hold times
Table 11.1: Primary Calibration
Table 11.2: Daily Calibration
Table 11.3: QC Sources, Sample Weights, and Methods
Table 12.1 QC Types, Limits, and Corrective Action
Table 13.1 Spike Calculation

19.0 CORRECTIVE ACTION

19.1 For QC samples that do not meet the method acceptance criteria, refer to Table 12.1. For retests that will occur past the method hold time, check first with the department supervisor to determine if the reanalysis should be conducted.

19.2 For any SOP/method deviation fill out section 1 of a corrective action report, Qualtrax ID: 2296. If necessary, the department supervisor and/or project manager may provide additional information in the appropriate sections; however, QA does not need to close a minor corrective action. Attach a copy of the minor corrective action report to all workgroups affected. A minor corrective action is for documentation purposes –any SOP or method deviation may be noted on the data review checklist or on the workgroup bench sheet in lieu of using Qualtrax ID: 2296.

19.3 For any system failure a major corrective must be opened, and the problem investigated. Consult the QA department to open a major corrective action. The corrective action will be assigned a unique tracking number by the QA Officer (or designee) and will be closed by the QA Officer (or designee) once the failure has been resolved. Use Qualtrax ID: 2296.