	Alaska Department of Environmental Conservation Environmental Health Laboratory 5251 Dr. Martin Luther King, Jr. Avenue, Anchorage, AK 99507 Standard Operating Procedure
SOP Title:	Determination of Total Mercury by EPA 7473
Version/Revision Date:	04-2011
Supersedes:	02-2007
Reference Method:	EPA 7473

STANDARD OPERATING PROCEDURE

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1.0 Scope and Application

1.1 This method is applicable to the determination of total mercury in various environmental matrices including biota, sediments, and soil samples.

2.0 Summary of Method

2.1 Controlled heating in an oxygenated decomposition furnace is used to liberate mercury 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 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 253.7nm as a function of mercury concentration.

3.0 Health and Safety Warnings

3.1 Before performing this SOP, the pertinent MSDS for each chemical should be read.

3.2 Proper personal protective equipment (PPE) should be worn at all times while handling reagents, standards, and samples.

3.3 Use care in handling hot quartz boats that have recently gone through the analysis or cleaning procedures.

3.4 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. All expired Hg stock and working standards must be disposed of per the EHL Chemical Hygiene Plan.

3.5 Use acceptable procedures for handling the compressed oxygen gas. When moving and replacing the oxygen bottle, ensure that the valve has been covered with the protective cap. Never "blow out" the valve of a new tank when replacing the regulator. Never use Teflon™ tape. The tank valve should only be on when the instrument is on. After installing a new oxygen bottle, check for leaks. Always transport new and used tanks with an approved bottle cart.

3.6 Even though the amount of mercury exiting the instrument is small, a mercury trap should be employed in a vented fume hood

4.0 Interferences

4.1 Carryover (memory effects) between analyses may be encountered when analyzing a sample of high mercury concentration (400ng) prior to analyzing one of low concentration (25ng or less). Typically, to minimize memory effects, analyze the samples in batches of low and high concentrations, always analyzing those of low concentration first. If this batching process cannot be accomplished, a blank analysis with an extended decomposition time may be required following the analysis of a highly concentrated sample to limit memory effects, or several empty boats or empty slots are analyzed until the result is below the MDL.

5.0 Personnel Qualifications

5.1 This procedure may only be performed by an analyst trained in using the DMA-80 and has run four passing IDC's. Analysts who have not completed an Initial Demonstration of Capability may perform the method only under the direct supervision of the Chemistry Supervisor or other qualified staff.

6.0 Sample Collection, Handling and Preservation

6.1 Solid samples should be submitted in pre-cleaned glass jars (I-Chem, Eagle Picher, or equivalent) and are stored at 4°C until analysis.

6.2 Biota samples are stored in wide mouth jars in the freezer at ≤ -10°C until the day before analysis.

6.3 Fish tissue samples are thawed overnight at 4°C and homogenized with a small, stainless spatula by stirring; then loaded onto quartz sample boats of the DMA-80 automatic mercury analyzer.

7.0 Equipment and Supplies

7.1 Milestone Model DMA-80 Direct Mercury Analyzer, or equivalent.

7.2 Analytical balance, capable of weighing to 0.1mg.

7.3 Milestone quartz sample boats, or equivalent.

7.4 A muffle furnace capable of maintaining a temperature of 800° C.

7.5 Stainless steel tongs.

7.6 A gravity convection drying oven with thermostatic control capable of maintaining 110°C.

7.7 Desiccator.

7.8 Glassware – volumetric flasks, class A, 10mL.

7.9 Porcelain crucibles for quartz boat storage.

7.10 Assorted calibrated pipettes.

7.11 Teflon coated weighing spatula.

7.12 Stainless stirring spatula.

7.13 Small cleaning brush.

7.14 Squeeze bottle with DI water.

8.0 Reagents and Standards

8.1 Reagent Water, ASTM Type II, Milli-Q or equivalent.

8.2 1% Nitric Acid (HNO_3)

Add 20mL concentrated HNO_3 solution to approximately 1500mL Milli-Q (reagent) water. Mix well and dilute to 2000mL with Milli-Q (reagent) water.

8.3 Stock Mercury (Hg) Standard, 1000mg/L Hg (Inorganic Ventures, catalog #CGHG1-1 or equivalent).

8.3.1 10mg/L Mercury (Hg) Intermediate Calibration Standard: Dilute 0.1mL (100µL) of 1000 mg/L Stock Mercury (Hg) Standard to 10mL with 1% nitric acid.

8.3.2 1.0mg/L Mercury (Hg) Working Calibration Standard: Dilute 1mL of the 10mg/L Mercury (Hg) Intermediate Calibration Standard to 10mL with 1% nitric acid.

8.3.3 0.1mg/L Mercury (Hg) Working Calibration Standard: Dilute 1mL of the 1.0mg/L Mercury (Hg) Intermediate Calibration Standard to 10mL with 1% nitric acid.

8.4 Certified Reference Material: Dogfish Muscle Certified Reference Material for Trace Metals, DORM-3, National Research Council Canada. This CRM is used for the Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) (NRC-CNRC, catalog #DORM-3 or equivalent).

8.5 Oxygen, Ultra High Purity (UHP) grade.

9.0 Instrument Setup, Calibration and Standardization

9.1 Set instrument parameters according to the conditions listed in Table 1.

9.2 Calibration.

9.2.1 Login as the administrator to perform calibrations.

9.2.2 On the main DMA-80 desktop page, select the DMA-80 Measurement. Click the **Calib.** tab and press the "diskette" icon to save the current calibration to a new data file (Example: "010511a"). Clear the calibration points by pressing the "blank paper" icon and resave the data file.

9.2.3 Return to the **Meas.** tab and click the "magic wand" icon to add a new line. In the Sample Name field type the ICAL standard name. Under the Weight column, enter the volume in mL of the working Hg standard that will be used for calibration (see Table 4). Under the State drop-down menu select calibration. "C" will appear in the State column, indicating that the current process is calibration.

9.2.4 Select the **Links** tab and choose the correct calibration and method files.

9.2.5 Place the sample quartz boat into the position indicated in the "Pos" column, and then pipette into the sample boat the proper volume of Hg calibration standard solution as in Table 4. Each standard solution is analyzed twice.

9.2.6 Select the **Result** tab, and press the **Start** button to begin calibration. Once finished running all the calibration points, press the "diskette" icon to confirm the name of the data file and save. Select the **Calibration** tab. Press the **Cell 1** tab, select "linear calibration algorithm with $R^2 \geq 0.990$." Repeat the same procedure for **Cell 2**. Press the "diskette" icon to confirm the name of the data file and save.

9.2.7 If there is difficulty meeting the linear or quadratic calibration algorithm with $R^2 \geq 0.990$, the instrument will require recalibration and/or replacement of the catalyst/amalgamator system and maintenance. Consult the DMA-80 operating manual for the details of the other two calibration approaches.

10.0 Sample Preparation

10.1 Samples: Transfer approximately 0.2g ± 0.02g of sample into a quartz boat.

10.2 Method Blank: Place an empty quartz boat in the DMA-80.

10.3 Calibration Blank: Pipette 20µL of 1% nitric acid into a quartz boat. **Calibration only!**

10.4 Continuing Calibration Verification: The CCV's are analyzed in tandem using the DORM-3 CRM: Transfer 0.04g ± 0.004g of Dorm-3 CRM into a sample quartz boat for the low level cell CCV and 0.2g ± 0.02g for the high level cell CCV.

10.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) set: Weigh out two separate 0.2g ± 0.02g aliquots of a sample from the batch for the MS/MSD set. Spike the MS/MSD samples with 50µL of 1.0mg/L Mercury (Hg) Working Calibration Standard.

11.0 Sample Analysis

11.1 Power up the DMA-80 Mercury Analyzer (switch at right front of instrument).

11.2 Turn on the oxygen supply at the tank and adjust the low pressure side of the regulator to 60 psi and 600 psi to the high pressure side (the DMA-80 must be on prior to this step).

11.3 Perform a calibration check of the balance in accordance with the appropriate SOP (5, 1, 0.2, and 0.005 grams).

11.4 After letting the DMA-80 warm up for at least 30 minutes, log on under your name with the appropriate password. Select DMA-80 Measurement and click on the **Meth.** tab to select the appropriate method. Verify that the instrument settings are correct (see Table 1 and Table 2). Click on the **System** tab to verify all levels are red.

11.4.1 Be sure the Transcend memory card is inserted in the instrument prior to running a batch on the DMA.

11.5 Under the **Meas.** tab select the **Sample** tab and click the 'blank page" icon. Click the "diskette" icon. Save the data file as the date of analysis followed by an "a" (Example: "020310a"). Additional runs can be saved as the date of analysis and the next letter in the alphabet. This is to identify different runs if there are multiple runs in a single day (Example: "100810a, 100810b, 100810c,"etc).

11.6 Initially, there must be two or three blank analyses (with or without a boat) to ensure that there are no mercury residue effects and that the system is stabilized. Click the "magic wand" icon on the bottom left of the screen to add sample lines. Under the sample name column, enter "eb" for empty boat. For blank analyses 0.2g is manually entered in the weight column. Confirm that the correct calibration and method are being used by selecting the **Links** tab. Switch back to the **Sample** tab and press the green **Start** button on the bottom right of the screen. Sample weights can be entered manually or automatically by the balance interface with the DMA-80.

11.6.1 Result values should be < ½ MRL. If they are not, run more empty boats. Choose the **Result** tab to view results.

11.7 Run low level CCV. Place a clean quartz boat on the scale, tare the scale, and weigh out 0.04g ± 0.004g of DORM-3 into the boat. Enter the weight in the DMA. Place the boat in the DMA-80 in the appropriate "POS" slot (number not in parenthesis). Enter this as batch number-SRM1 (Example: "P104035-SRM1") into the sample name column.

11.7.1 Note: When not actually running, the sample tray will always index to the front center position represented by the highlighted sample line on the screen. An arrow was marked on the instrument chassis to indicate this position.

11.7.2 A Remarks Column is available in this window for any individual comments for each sample line.

11.8 Run high level CCV. Weigh out 0.2g ± 0.02g of DORM-3 into the boat, enter this as batch number-SRM2 (Example: "P104035-SRM2").

11.9 Run CCB. Place an empty boat in the next slot and add as batch number-BLK1 (Example: "P104035-BLK1").

11.9.1 Verify CCV's and CCB are within range (see Table 3). If they are not, run another CCV/CCB set.

11.10 Run samples. Weigh out 0.2g ± 0.02g of homogenized fish tissue into a tared quartz boat. Enter the weight and sample number into the DMA-80. Wipe spatula with a Kimwipe between each sample. See Table 3 for example sample queue with QC guidelines.

11.10.1 If there is difficulty meeting the QA requirements, the instrument will require recalibration and/or replacement of the catalyst/amalgamator system and maintenance.

11.11 Quartz Boat Cleaning

11.11.1 Turn the muffle furnace on to 800˚C. The warm up usually takes about 45 minutes.

11.11.2 Remove any ash in boats by running Milli-Q water and scrubbing with a small test tube brush, taking care not to crack the boat. Rinse the boats thoroughly and place them face down on dry paper towels. Allow the boats to air dry or place the ceramic bowl and boats into a drying oven for 30 minutes or until dry at 105-110°C.

11.11.3 When the muffle furnace is up to temperature, place the ceramic bowl and quartz boats in the furnace using the long handled tongs (46 cm long), leave in the furnace for about an hour. Remove the porcelain dish using the tongs and carefully pour the quartz boats onto a sheet of asbestos for cooling, set bowl on asbestos as well. Let cool for at least 15 minutes, return boats to ceramic bowl and cover container to keep dust out.

11.12 Instrument Maintenance

11.12.1 Ensure the low pressure side gauge is at 60 psi and the high pressure is above 500 psi. When the high pressure gets down to 500 psi, the tank is empty. Replace it with a full oxygen tank.

11.12.2 Ensure all heaters are ready before starting an analysis. Click the **System** tab on the screen and check for the 3 OK labels at the bottom of the schematic.

11.12.3 Keep the autosampler tray clean. Wipe up spills immediately.

11.12.4 Maintain a complete and current maintenance log.

11.12.5 During routine maintenance of the DMA-80, both the unit and the lab terminal should be turned off and disconnected from the power supply. The oxygen supply must be turned off at the tank. Change the internal consumables only after the unit has cooled to room temperature.

12.0 Data Analysis and Calculations

12.1 When run is complete, click the "diskette" icon to save the results. Click "yes" to overwrite data. Log out and eject the Transcend memory card from the top of the DMA-80 monitor. Place memory card in easy-doc reader, and plug into a PC loaded with easy doc software.

12.2 The folder should automatically open, select the correct file and open it. If it does not open automatically, open the driver called "PIO" under My Computer, open the "Data" folder, and select the correct file. Click the **Print/Export** button to print the Results Page.

12.3 Click the **green X** (excel) icon. Save the file onto the G-drive exactly as the DMA file name was saved in *G:\EH\Eh-Lab\DataCapture\DMA_DataFiles\DMA-80\New DMA-80\(year)*

Leave excel file open, minimize.

12.4 Click the "diskette" icon and save a copy of the text file to the G-drive in *G:\EH\Eh-Lab\Data Capture\DMA_DataFiles\DMA-80\New DMA-80\Text\Text(year).* Close file. Safely remove the easy doc from the PC and return the memory card to the DMA-80 monitor.

12.5 Open the Element Database and go into the bench sheet of the batch to be reported. Click **Export** and save into "HgWeights". Replace file. *C:\ELMNT\UserFiles\ Hgweights.*

Open the "Hgweights" file. Using the Excel file created earlier from the DMA results, copy and paste the values from the weight column (J), in the DMA file to the "Hgweights" file. Column J weights must be copied into Column G (initial weight) and Column H (final weight) of the "Hgweights" file. The initial and final weights must match. Click on **Save** to save the "Hgweights" file.

Return to element database and re-open the batch's bench sheet. Select **Open** at the bottom of the window and open the "Hgweights" file. The new weights should upload into the bench sheet.

12.6 Highlight all samples, right click and change status from "batched" to "analyzed." While all samples are highlighted, right click, select "Prepared" and enter the date and time the DMA began analyzing. Be sure the analyst's initials are correct (Prepared by). Do the same for the QC's. Right click each SRM separately, select "Spike amount", multiply SRM weight x 1000 (ie. 0.2003g = 200.3) Save. Print the Bench Sheet.

12.7 Under the main Element window, click on "Laboratory" and select **Data Entry/Review.** An "Enter/Edit Data" window will appear. Click on the batch number. Select the **Data Entry** tab then **Create** to upload the data into the window below. Select the **Data Tool** button.

12.8 Select the correct file and double click on it; the samples will appear in the upper left window. Highlight the samples and QC's run, click **Include**, and select **Done**. (There will be a sample file added to the end of the list by Element that was not run. Do not include this file.) **Merge** the files.

12.9 Verify that the number of samples on the **Merge Upload** tab and the **Instrument Data** tab correlate. Rename any samples that are not named as they are in the Element batch under the **Instrument Data** tab. Click the **Refresh** button. Click on **Save**, choose the Element folder *C:\ELMNT\UserFiles*, and select the "gg" spreadsheet. Answer "Yes" to replace the existing data. Click **Done** and close the Data Tool window.

12.10 In the **Enter/Edit Data window**, change the analyst initials from ZZZ to the analyst's initials by clicking the Analyst column header, right-clicking, and selecting "Fill cells." Use the drop-down menu to select the analyst's initials.

12.11 Click **Save** in the Enter/Edit Data window to save the merged files. Click done. Under the Data Review tab select **Query.**

12.12 The test results will now appear. Lock the page by clicking on the Lock column header and selecting Lock. Click the Printer icon to print the Data Review report.

12.13 Calculations

12.13.1 Sample Concentration

$$\text{Concentration (mg/kg)} = \frac{\text{Mercury (Hg) (ng)}}{\text{Sample Weight (g)}} \times \frac{1000\text{g}}{1\text{kg}} \times \frac{1\mu\text{g}}{1000\text{ng}} \times \frac{1\text{mg}}{1000\mu\text{g}}$$

or

$$\text{Concentration (mg/kg)} = \frac{\text{Mercury (Hg) (ng)}}{\text{Sample Weight (g)}} \times \frac{1\text{mg}}{1000\text{kg}}$$

12.13.2 Percent Drift (%D)

$$\text{Drift (\%)} = \frac{|C_c - C_t|}{C_t} \times 100\%$$

where:
C_c= Calculated concentration
C_t= Theoretical concentration

12.13.3 Duplicate Relative Percent Difference (RPD)

$$\text{RPD} = \frac{|X_1 - X_2|}{(X_1 - X_2)/2} \times 100\%$$

where:
X_1 = Concentration of sample
X_2 = Concentration of duplicate

Significant figures: final results are rounded using EPA rules to 2 significant figures.

13.0 Data and Records Management

13.1 Assemble a data package consisting (in order):

13.1.1 Element bench sheet with uploaded weights.

13.1.2 Results report from element database.

13.1.3 Completed data review checklist.

13.1.4 Non-conformance details report (if applicable).

13.1.5 Calibration curve copy/absorbance vs. time graphic plots.

13.1.6 DMA-80 run log.

13.2 Place data package in an end tab manila folder with a label denoting the date of analysis *G:\EH\Eh-Lab\Chemistry\Label Files\AnalysisFolders\EPA 7473.LWL* and give completed file to chemistry supervisor for review.

14.0 Quality Control

14.1 QC requirements are summarized in Table 5.

14.2 <u>IDC/MDL Studies:</u> A set of 4 passing IDC's must be conducted by each new analyst; these are low-level CCV's. An MDL study must be conducted annually. If appropriate, the IDC and MDL studies may be combined.

14.2.1 An MDL study is conducted annually and/or when significant changes in instrument occur, or when a new instrument is purchased for the analysis.

14.3 Reporting Limit (RL): Reference Element for the current MRL for mercury in fish and shellfish tissue.

14.4 The R^2 of the calibration curve must be greater than or equal to 0.990.

14.5 Initial Calibration Verification (ICV): The ICV must be obtained from a second source other than that of the calibration standard. The DORM-3 CRM is used as the ICV and analyzed after calibration.

14.5.1 The ICV acceptance criterion is +/-10%. If recovery falls out, one rerun is allowed. If recovery remains outside of the allowable range, recalibration is required.

14.5.2 The DMA-80 has two cells in series for testing low and high level Hg. The low range cell can measure Hg from 0 to 35 ng and the high range cell can test Hg from 35 to 600 ng. After calibration, both low and high ranges ICVs are required to run.

14.5.3 If samples contain mercury concentration higher than the low range cell limit, then the high range cell ICV must be run with same acceptance criterion. Otherwise, only the low range cell ICV is required.

14.6 Continuing Calibration Verification (CCV): The DORM-3 certified reference material (CRM) is used as working CCV and analyzed at the beginning of a run, after every 10 samples and at the end of the run.

14.6.1 The initial CCV acceptance criterion is +/-10%. The following pairs of CCV's have an acceptance criterion of +/-20%. If recovery falls out, one rerun is allowed. If recovery remains unacceptable, recalibration is required with rerun of all samples analyzed after last acceptable CCV.

14.6.2 If samples contain mercury concentration higher than the low range cell limit, then the high range cell CCVs must be run with same acceptance criterion. Otherwise, only the low range cell CCVs are required.

14.7 Method Blank/Calibration Blank (MB/CB): A calibration blank must be analyzed after each pair of CCV's.

14.7.1 The level of total Hg in the MB must be ≤ ½MRL.

14.7.2 When MB/CB contamination is apparent, samples associated with the MB/CB may require a rerun.

14.7.3 If the measured sample concentration is greater than 10 times the MB/CB contamination, the sample does not need reanalysis. If the sample has a concentration < MRL, the sample does not need to be rerun. All other associated samples will require reanalysis.

14.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD). An MS/MSD pair is performed with every sample batch of 20 samples or less, or at the frequency requested by the client.

14.8.1 The MS/MSD aliquots are spiked with calibration standard as described in section 10.4.

14.8.2 The acceptance limits are 80%-120% recovery.

14.8.3 If the spiking value is less the 5x the concentration of native concentration of Hg in the sample, the acceptance limits are advisory only.

14.8.4 If recoveries are outside acceptance limits then the data is flagged as estimated (J qualifier).

14.9 Sample Duplicate: A sample duplicate is performed with every sample batch of 20 samples or less, or at the frequency requested by the client. One duplicate for every 10 samples are run for fish tissue.

14.9.1 The advisory RPD for a sample duplicate is $\leq 20\%$.

14.9.2 A reanalysis will be required when the allowable Relative Percent Difference (RPD) limit is exceeded. If the rerun batch has a RPD > 20%, the sample will be flagged as non-homogeneous.

15.0 References

15.1 USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW8-46, 3rd Edition; Method 7473.

15.2 "*Guidance for Preparing Standard Operating Procedures (SOPs)*", United States Environmental Protection Agency, EPA QA/G-6, March 2001.

15.3 Milestone DMA-80 Direct Mercury Analyzer User Manual – Revision 3/2004

15.4 EPA 7473, Revision 0, February 2007.

Table 1
Temperature Program for DMA-80

Pos	t	T
1	00:01:00	200
2	00:03:00	650

Table 2
Analytical Parameters for DMA-80

Parameter	Value
Max Start T	200°C
Purge time	60s
Amalgamator heating time	12s
Signal recording time	30s

Table 3
Example Sample Queue

Sample Name	Quality Control	Notes
Element batch#-SRM1 (ie. P103006-SRM1)	Low level Initial Calibration Verification (ICV)	0.3438-0.4202 mg/kg (±10% of 0.382 true value)
Element batch#-SRM2	High level Initial Calibration Verification (ICV)	0.3438-0.4202 mg/kg (±10% of 0.382 true value)
Element batch#-BLK1	Initial Calibration Blank (ICB)	< ½ MRL
Batch Samples 1-10	Element sample number (*ie. 1010003-40*)	Each set of 10 must have a sample duplicate.
Element batch#-DUP1	First sample duplicate	Randomly selected sample is measured and run again.
Element batch#-MS1	Matrix Spike (MS) 80-120% recovery	Same sample source as DUP1 or DUP2; but run w/ 50µL spike
Element batch#-MSD1	Matrix Spike Duplicate (MSD) 80-120% recovery	Same sample source as DUP1 or DUP2; but run w/ 50µL spike
Element batch#-SRM3	Low level Continuing Calibration Verification (CCV)	0.3056-0.4584 mg/kg (±20% of 0.382 true value)
Element batch#-SRM4	High level Continuing Calibration Verification (CCV)	0.3056-0.4584 mg/kg (±20% of 0.382 true value)
Element batch#-BLK2	Continuing Calibration Blank (CCB)	< ½ MRL
Batch Samples 11-20	Element sample number	Each set of 10 must have a sample duplicate.
Element batch#-DUP2	Second sample duplicate	Another randomly selected sample is measured and run again.
Element batch#-SRM5	Low level Continuing Calibration Verification (CCV)	0.3056-0.4584 mg/kg (±20% of 0.382 true value)
Element batch#-SRM6	High level Continuing Calibration Verification (CCV)	0.3056-0.4584 mg/kg (±20% of 0.382 true value)
Element batch#-BLK3	Continuing Calibration Blank (CCB)	< ½ MRL

Table 4
Mercury (Hg) Standard Volumes for Calibration Curve

Name	Standards Size	ng of Hg	Software Weight Entry	Software Concentration Entry
ICAL 1	20µl 1% Nitric Acid	0ng	0.0001	0.0001
ICAL 2	10µl 0.1mg/L Mercury (Hg) Working Calibration Standard	1ng	0.01	0.1
ICAL 3	20µl 0.1mg/L Mercury (Hg) Working Calibration Standard	2ng	0.02	0.1
ICAL 4	50µl 0.1mg/L Mercury (Hg) Working Calibration Standard	5ng	0.05	0.1
ICAL 5	10µl 1.0mg/L Mercury (Hg) Working Calibration Standard	10ng	0.01	1
ICAL 6	15µl 1.0mg/L Mercury (Hg) Working Calibration Standard	15ng	0.015	1
ICAL 7	20µl 1.0mg/L Mercury (Hg) Working Calibration Standard	20ng	0.02	1
ICAL 8	50µl 1.0mg/L Mercury (Hg) Working Calibration Standard	50ng	0.05	1
ICAL 9	10µl 10mg/L Mercury (Hg) Working Calibration Standard	100ng	0.01	10
ICAL 10	20µl 10mg/L Mercury (Hg) Working Calibration Standard	200ng	0.02	10
ICAL 11	50µl 10mg/L Mercury (Hg) Working Calibration Standard	500ng	0.05	10

Table 5
Quality Control Requirements

Parameter	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	As required	5 points minimum for both low and high range. $R^2 \geq 0.990$	Rerun initial calibration
Initial Calibration Verification (ICV)	At beginning of sequence and every 10 samples	ICV ±10% of the true value	Rerun once. If ICV still out after re-analysis then re-calibrate.
Continuing Calibration Verification (CCV)	After every 10 samples	CCVs ±20% of the true value	Rerun once. Re-analyze samples analyzed after the last acceptable CCV. If CCV still out after re-analysis then re-calibrate.
Method Blank (MB)	Once per batch of 20 samples or daily, whichever frequency is greater.	< ½ MRL	Rerun once. Investigate source of contamination. Re-analyze associated samples if results are > RL or < 10X MB level.
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	Once per batch of 20 samples or daily, whichever frequency is greater.	Recovery ±20%	Rerun once. If MS/MSD recovery is >120% and samples are >RL, then report results with J qualifier.
Sample Duplicate (DUP)	Once per batch of 20 samples or daily, whichever frequency is greater.	RPD ≤ 20%	Rerun once. If RPD still not within acceptance criteria qualify sample results.

Table 7
Data Review Checklist – EPA Method 7473

	Alaska Department of Environmental Conservation Environmental Health Laboratory 5251 Dr. Martin Luther King, Jr. Avenue, Anchorage, AK 99507 Standard Operating Procedure
SOP Title:	Determination of Total Mercury by EPA 7473
Version/Revision Date:	04-2011
Supersedes:	02-2007
Reference Method:	EPA 7473

Date of Analysis: _____ Project Name: _____

Calibration

Review Item	Analyst	Reviewer	Comments
1. Initial Calibration performed at high and low level, with at least 3 points per level?			
2. Initial Calibration $r^2 \geq 0.990$ for high and low level?			

Batch QC

Review Item	Analyst	Reviewer	Comments
1. Initial Calibration Verification (ICV) within ±10% of the true value?			
2. CCV every 10 samples and closing?			
3. Continuing Calibration Blank (CCB) after every CCV?			
4. CCB ≤ ½MRL?			
5. Closing CCV within ±20% of the true value?			
6. MS/MSD pair analyzed every 20 samples?			
7. MS/MSD recovery 80%-120%?			
8. Samples duplicate every 10 samples?			
9. Sample duplicate RPD ≤ 20%			

Samples

Review Item	Analyst	Reviewer	Comments
1. Results within calibration range?			
2. Data entry spot checked at least 10%?			

Reviewer_____ Date:_____

Table 8
Catalyst Tube Conditioning Procedure

Introduction:
Every time a new catalyst or amalgamater tube is replaced a new calibration curve is required, but at first the following conditioning procedure must be followed.

This process is not necessary for DMA80 units delivered directly from Milestone because this was already done during final quality control testing.

Note: Before starting the procedure, be sure that the catalyst/amalgamator are correctly installed and the DMA80 unit is ready to operate (alignment of actuators, stability of Oxygen flow). For more details see the operator manual.

DMA80 procedure for conditioning new catalyst/amalgamator tubes:

Step	Reagent/Sample Type	Sample Amount	DMA80 Program		
			Drying Time and Temperature[1][2]	Decomposition Time and Temperature	Purging/Waiting Time
1	Common white flour	100mg	IR: 60sec/300°C	IR: 180sec/850°C	60sec
			ATC: 60sec/200°C	ATC:180sec/650°C	
2	HNO_3, 5%[3]	0.1mL	IR: 60sec/300°C	IR: 180sec/850°C	60sec
			ATC: 60sec/200°C	ATC: 180sec/650°C	

[1] The program has to be set according to the type of temperature control on the drying/decomposition furnace: external infrared (IR) or internal thermocouple (ATC) sensor.

[2] In case of T640/T1640 controller the reported temperature and time refer to the "holding" step.

[3] Quartz sample boat required. In case of metal boat usage, they must be deeply cleaned and a stability test run.

Repeat the above procedure at least five times, or until the blank absorbance is <0.0030.

After condition a stability test must be run. Analyze a fresh aqueous 100ppb standard five times. The RSD must be <1.5%. For this analysis the recovery is not as important as the DMA stability.