

STANDARD OPERATING PROCEDURE

For USEPA METHOD 7473

MERCURY IN SOLIDS AND SOLUTIONS BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY USING THE MILESTONE DMA-80 MERCURY ANALYZER

SOP #: METHOD # EPA7473

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1.0 SCOPE AND APPLICATION

- 1.1 This method is for the determination of the following RCRA analytes in solids, biological tissue, aqueous samples and digested solutions in the lab using a Milestone DMA-80 mercury analyzer.

<u>Analyte</u>	<u>Chemical Abstract Services Registry Numbers (CASRN)</u>
Mercury total (Hg) (organic and inorganic)	7439-97-6

Integration of thermal decomposition sample preparation and atomic absorption detection reduces the total analysis time of most samples to 5 minutes in the laboratory. Total mercury (organic and inorganic) in soils, sediments, biological tissue, bottom deposits, and sludge-type materials as well as in aqueous wastes and ground waters can be determined without sample chemical pretreatment using this method. Alternatively, this method can be used for the detection of total mercury from total decomposition sample preparation methods, such as Method 3052.

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. 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 253.7 nm as a function of mercury concentration.

3.0 DEFINITIONS

- 3.1 Amalgamation: The process by which mercury forms a metal alloy with gold.
- 3.2 Amalgamator: A system composed of gold particles at a high surface area to volume ratio for the purpose of amalgamating mercury vapor.
- 3.3 Amalgam Heater Time: The period of time required for the amalgamator to be rapidly heated in order to release all of the collected mercury into the absorbance cells.
- 3.4 Analytical Sample: Any sample in which mercury is being determined, except for standards, method blanks, or QC reference samples.
- 3.5 Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the instrument.
- 3.6 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to mercury concentration.



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- 3.7 Concentrate Sample: An instrument function which allows for the use of multiple determinations of a sample to address difficulties related to low amounts of mercury.
- 3.8 Consumables: Specific items for the DMA-80 that must be replaced to maintain the machine. See Appendix 1
- 3.9 Continuing Instrument Calibration Verification (CCV): A mercury standard which is analyzed after every 20 samples and at the end of the analytical run to verify the accuracy of the analysis and monitor instrument drift.
- 3.10 Daily Calibration Verification: A calibration performed with minimal standards, either solid or liquid, to ensure that the primary calibration is valid. This is performed prior to a sample run. For example, when two standards within the range of interest are analyzed and agree within +/-10% of their true values the primary calibration is assumed to be valid.
- 3.11 Decomposition Temperature: A component of the instrument process that decomposes or ashes the sample destroying the matrix.
- 3.12 Decomposition Time: The time during which the sample is treated at a high temperature.
- 3.13 Drying Time: The amount of time a sample is dried as part of the instrument process.
- 3.14 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.
- 3.15 Laboratory Duplicates (Sample and Sample Duplicate) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of the sample and the sample duplicate indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.16 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which a known quantity of mercury is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
- 3.17 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which a known quantity of the mercury is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for background concentrations.
- 3.18 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if mercury is present in the laboratory environment, reagents, or apparatus.
- 3.19 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.
- 3.20 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. For



example, this may result when a low concentration sample is analyzed after a sample of high mercury content.

- 3.21 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.22 Minimum Reporting Limit (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the MRL check standard for that analyte and can only be used if acceptable quality control criteria for the analyte at this concentration are met.
- 3.23 MRL Check Standard – Low-level standard with concentration 3 to 5 times the MDL value. The standard is analyzed at the beginning of each analytical run before the samples are run.
- 3.24 Primary calibration: A complete calibration of the instrument's working range. This calibration is performed initially and when any significant instrumental parameters are changed.
- 3.25 Purge Time: The time required for the flow of oxygen to flush out all the pyrolysis products from the system before the start of the mercury measurement.
- 3.26 Quality Control Sample (QCS) - A solution of mercury of known concentration, which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
- 3.27 Quality Control Sample - Standard Reference Material (QCS-SRM) - A sample of a matrix similar to the sample being analyzed, which contains mercury of a known or accepted concentration. The QCS-SRM is obtained from a source external to the laboratory and contains the analyte of interest at certified concentrations for the method of interest. The QCS-SRM is processed in the same manner as the sample, unlike the QCS in 3.26, and is used to check method performance.
- 3.28 Recording Time: The period of time required by the software to record the signal from the mercury vapor traveling through the absorption flow cells.
- 3.29 Sample boat: The non-amalgamating thermally stable vessel used for containment and transport of the solid or liquid sample for thermal decomposition. Quartz and nickel boats are used for the DMA-80.
- 3.30 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.31 Total Recoverable Analyte - The concentration of an analyte determined either by "direct analysis" of an unfiltered acid-preserved drinking water sample with turbidity of < 1 NTU or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.
- 3.32 Weights (class 1): Weights meeting the National Institute of Standards & Technology Acceptance Tolerances and used to verify the operation of the analytical balance.
- 3.33 Working Standards: Lower concentration standards prepared by diluting liquid stock standards.



4.0 INTERFERENCES

- 4.1 Interference may result from sample cross-contamination, using contaminated equipment, solvents, acids, reagents or sample containers. All acids used are trace metal grade. All sample containers used are metal-free. All glassware used for this method are separate and dedicated to this method. Sample cross-contamination problems can be eliminated or minimized through the use of dedicated sampling equipment and/or proper cleaning of the equipment each time it is used to process a new sample. All sample boats are cleaned by running them through a cleaning run on the DMA-80 and then stored in covered containers.
- 4.2 Memory effects between analyses may be encountered when analyzing a sample with a high mercury level (>300ng) prior to analyzing a low level sample (<25ng). To minimize memory effects, analyze low level batches before high level batches. This is not always possible, a blank analysis with an extended decomposition time maybe required following the high level samples or a set of blank analyses are run until the memory effect is no longer present. These blank analyses are not counted as an analysis sample in the sample run.
- 4.3 Interferences caused by a sample matrix are possible. Monitoring of this type of interference is performed through the analysis of a lab fortified matrix sample. If the results do not meet recovery criteria, results will be flagged accordingly.
- 4.4 A continuous calibration blank (CCB) is analyzed after calibration, after every 10 samples, and at the end of the analytical run; the analyst monitors the concentration of the CCB.

5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. All laboratory personnel are trained on the laboratory safety procedures applicable to, and the OSHA and other regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. These reagents are used in a fume hood and if skin or eye contact occurs, large volumes of water are applied to flush the area of contact. An emergency shower and eyewash station are located in the laboratory. Safety glasses are used for eye protection, and protective clothing is worn.
- 5.2 Acidification of samples is done in a fume hood to prevent the inhalation of toxic gases, such as cyanide or sulfide.
- 5.3 All personnel handling potentially infectious environmental samples are immunized against known disease causative agents.
- 5.4 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Exhaust or carrier gases should be passed through a mercury trap and be vented to a fume hood or snorkel. The analyst should use proper PPE i.e. lab coat, chemical resistant gloves and eye protection when handling mercury standard reagents used for this analysis.
- 5.5 All laboratory personnel fully comply with all relevant federal, state, and local waste management and disposal regulations. (Sect 14.0 and 15.0)



6.0 EQUIPMENT AND SUPPLIES

- 6.1 Milestone DMA-80 Direct Mercury Analyzer and labTERMINAL 1024
- 6.2 General Maintenance Procedure for the DMA-80 is performed by the lead analyst. Service calls are placed to the company only when the lead analyst is not capable of performing the required maintenance. Annual service maintenance is performed by the Milestone field technician.
- 6.3 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, for determining dissolved solids in digests or extracts and weighing boats for the DMA-80. The Precisa balance (XB 220A) is used and has a direct data input into the DMA-80 labTERMINAL 1024.
- 6.4 Oxygen tank – High purity
- 6.5 Assortment of air displacement pipetters capable of delivering volumes ranging from 0.1 to 2500 μ l with corresponding metals-free disposable pipet tips.
- 6.6 Mortar and pestle, ceramic or nonmetallic material.
- 6.7 Polypropylene sieve, 5-mesh (4-mm opening).
- 6.8 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area is designated for trace element sample handling. Field sample containers used in the determination of trace elements are purchased as pre-cleaned glass or HDPE containers. Laboratory containers for sample handling and storage are bought trace metal-free or pre-cleaned. Volumetric flasks and other glassware used to make standards, etc., are cleaned as follows: glassware is washed with a detergent solution made from Citranox, rinsed with tap water, soaked for four or more hours in 20% (v/v) nitric acid or hydrochloric acid, rinsed with reagent water, and stored in a clean cabinet.
 - 6.8.1 Glassware – Type A Volumetric flasks and centrifuge tubes (glass and/or metal-free plastic).
 - 6.8.2 Assorted glass calibrated Type A volumetric pipettes.
- 6.9 Flour for conditioning the catalyst tube when a new tube is installed.
- 6.10 Cotton swabs for cleaning the DMA-80.
- 6.11 Quartz and nickel sample boats
- 6.12 Maintenance grease for pneumatic cylinders
- 6.13 Bent tip stainless steel tweezers
- 6.14 Stainless steel micro spatulas
- 6.15 Set of Class 1 analytical balance weights
- 6.16 Kimwipes



7.0 REAGENTS AND STANDARDS

- 7.1 Only high-purity reagents suitable for trace metal analysis are used. All acids used for this method are equivalent to trace metal purity grade.

See links to the Reagent-Standard Preparation Bench Sheets for this method in the Forms Section on the last page of this SOP

- 7.2 Hydrochloric acid, concentrated (sp. gr. 1.19) - HCl.
- 7.3 Nitric Acid, concentrated (sp. gr. 1.41) - HNO₃
- 7.4 Reagent water - ASTM Type I reagent-grade water
- 7.5 Standard Stock Mercury Solutions - Stock 1000mg/L mercury standards are purchased. They are replaced when expiration dates are exceeded.
- 7.6 Preparation of Working Calibration Standard Solutions: Calibration standard solutions are prepared as necessary .
- 7.6.1 Standard Stock Solutions: 1,000 mg/L single element certified standard (s) are purchased. From this stock, prepare the following standards using the appropriate acid (HCl). See Mercury standards preparation for curve for DMA80 EPA 7473 (Form 1) and Mercury Standards preparation for EPA 7473 (Form 2.)
- 7.7 Blanks - Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve; the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure; the laboratory fortified blank is used to assess routine laboratory performance; and a rinse blank is used to flush the instrument to reduce memory effects.
- 7.7.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards.
- 7.7.2 Laboratory reagent blank (LRB) contains all the reagents in the same volumes as used in the processing of the samples. The LRB is carried through the same entire preparation scheme as the samples including sample digestion.
- 7.7.3 Laboratory fortified blank (LFB) is prepared by spiking an aliquot of the laboratory reagent blank with a single element or multi-element standard solution. The LFB must be carried through the same entire preparation scheme as the samples, including sample digestion.
- 7.7.4 Rinse Blanks are run through the machine to clear out the Hg memory effect from highsamples.
- 7.8 Quality Control Sample (QCS) - Analysis of a QCS (3.17) is performed for initial verification of calibration standards in order to verify instrument performance. The QCS is obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Appropriate preservation and pretreatment steps are performed on all samples analyzed by this method. The pH of all aqueous samples is tested immediately prior to the direct analysis of any sample (pH is recorded on a pH log sheet that is included with the sample reports).



- 8.2 For the determination of the dissolved elements, the sample is filtered through a 0.45- μ m pore diameter membrane filter at the time of collection or as soon thereafter. The sample is acidified with (1+1) nitric acid immediately following filtration to pH < 2.
- 8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH < 2. The sample is held for sixteen hours, and then verified to be pH < 2 just prior to analysis.
- 8.4 Solid samples do not require preservation other than storage at 4°C.
- 8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user.
- 8.6 Fish/biological tissue samples should be stored at -10°C to -30°C.

9.0 QUALITY CONTROL

- 9.1 The quality control program for this method consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and quality control standards as a continuous check on laboratory performance. Records of these data are maintained and kept on file.
- 9.2 Initial Demonstration of Performance
- 9.2.1 Initial demonstration of performance was conducted immediately after instrument installation. LDR, MDL, and IDL were produced prior to any analysis of environmental samples. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.
- 9.2.2 Linear Dynamic Range (LDR) (also referred to as the Linear Calibration Range – LCR) was established for each wavelength utilized and was determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR was determined by analyzing increasingly higher standard concentrations of the analyte until the observed analyte concentration was no more than 10% below the stated concentration of the standard. The LDRs are documented and kept on file. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit are diluted and reanalyzed. The LDRs are verified annually or whenever a change in analytical or instrument performance occurs, which would then dictate that the LDRs be re-determined.
- 9.2.3 Quality control sample (QCS) - The QCS (3.26) is analyzed with every analytical run to verify the calibration standards. To verify the calibration standards, the mean concentrations from the QCS must be within $\pm 10\%$ of the stated values. If the calibration standards are not verified, performance is unacceptable and the determination of analytes is not continued. The source of the problem is identified and corrected before proceeding with any analyses.
- 9.2.4 Quality Control Sample-Standard Reference Material (QCS-SRM) (Sect. 3.27)
QCS-SRM is analyzed with every analytical run to verify the method performance. The QCS-SRM recovery must be within the manufacturer's specifications or the stated specification for the sample matrix recoveries.
- 9.2.5 Method detection limit (MDL) - MDLs are established for the wavelength utilized, (see Table 3), using reagent water (blank) fortified at a concentration of two to five times the MDL (Table 3). To determine MDL values, seven replicate aliquots of the fortified



reagent water are processed through the entire analytical method or a set standard will be processed through the entire analytical method during a sample run. Seven results from these set standard samples will constitute the data set for the MDL study. The results may be from at least three different days and no more than three results from any one day will be used. Two data points are determined on each of two days; three data points are determined on a third day. No data points are dropped. Another method for obtaining the MDL values is to take the results from the method reporting level (MRL) standards that are run before each ICP sample run. Collect seven days' worth of runs and use those MRL values for the data points for the MDL study.

Calculation of the MDL is as follows:

$$MDL = (t) \times (S)$$

Where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

s = standard deviations of the replicate analyses.

MDLs determined for this method are sufficiently low to detect analytes at the required levels.

9.3 Assessing Laboratory Performance

9.3.1 Laboratory reagent blank (LRB) - The laboratory analyzes one LRB with every batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination.

9.3.2 Laboratory fortified blank (LFB) - The laboratory analyzes one LFB with each batch of samples. The LFB accuracy is calculated as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{S} \times 100$$

Where:

R = Percent recovery

LRB = Laboratory reagent blank.

LFB = Laboratory fortified blank.

S = Concentration equivalent of analyte added to fortify the LRB solution.

If the recovery of the analyte falls outside the required control limits of 85 - 115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

An example of an LFB used in the lab would be as follows:

LFB is prepared by adding 0.1 mL of 10 mg/L standard and QS to 10 mL with reagent water. LFB is acidified in the same manner as samples and standards.

The concentration of the LFB is calculated as follows:



$$0.10\text{mg} / \text{L} = \frac{0.100 \text{ mL} \times 10 \text{ mg} / \text{L standard}}{10 \text{ mL of reagent water}}$$

Higher or lower LFBs are prepared to correspond with the range of the sample concentrations.

- 9.3.3 The LFB analysis data are used to assess laboratory performance against the required control limits of 85-115%. When sufficient internal performance data become available (usually a minimum of twenty to thirty analyses), optional control limits are developed from the mean percent recovery (\bar{x}) and the standard deviation (S) of the mean percent recovery. These data are used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{x} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \bar{x} - 3S$$

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits are calculated using the most recent twenty to thirty data points. The standard deviation (S) data are used to establish an on-going precision statement for the level of concentrations included in the LFB. These data are kept on file and available for review.

9.4 Assessing Analyte Recovery and Data Quality

- 9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Separate aliquots from the sample are taken for replicate and fortified analyses to assess the effect. Laboratory fortified matrix (LFM) samples and duplicate samples are processed to assess matrix effects.
- 9.4.2 The laboratory adds a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot is a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples and solid samples the concentration added is expressed as mg/kg.

$$\frac{(\text{amount of spike added in L})(\text{concentration of spike in } \frac{\text{mg}}{\text{L}})}{\text{Kg of sample used}} = \frac{\text{mg}}{\text{kg}} \text{ spike added.}$$

Sect. 12.3).

- 9.4.3 Percent recovery for each analyte is calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

Where:

R = Percent recovery

C_s = Fortified sample concentration.

C = Sample background concentration.

s = Concentration equivalent of analyte added to fortify the sample.



- 9.4.3.1 The analyst will spike a sample with a concentration above the MRL but not above the LDR of calibration. If normal spike concentrations do not meet this criterion, on-line spikes will be prepared and analyzed.
- 9.4.3.2 A 1 mg/L Hg standard spiking solution is used for the LFM. (See Form 2). Depending on the Hg concentration of the sample, a 20 μ L, 40 μ L, 60 μ L or larger aliquot of Hg spiking solution is added to the LFM aliquot sample.
- 9.4.3.3 The above LFM's spike amount for a 20 μ L LFM sample is calculated as follows:

$$\frac{0.02 \text{ mL} \times 1 \mu\text{g} / \text{mL Hg std.}}{\text{amount of sample in grams}} = \text{True value (TV) of spike } \mu\text{g} / \text{g} = \text{mg} / \text{kg}$$

- 9.4.4 If the recovery of the analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user will be informed of the matrix effect.
- 9.4.5 Reference materials are utilized for every analytical run. They are analyzed to provide additional performance data, and demonstrate the ability to perform the method on a particular matrix.

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Set up a calibration curve using the procedure from the Milestone User Manual found on pages 57 to 60 – 4.2 Calibration process using aqueous Hg Standard. The Milestone user manual is located on the shelf above the instrument. Use Calibration type B method starting on page 59. See Form 2 for Hg standards preparations. The correlation coefficient for the curves for cell 1 and cell 2 are > 0.995. The daily calibration verification standards acceptance criteria is $\pm 10\%$.
- 10.2 The DMA 80 must be recalibrated when there has been a major change to supplies or consumables (e.g. catalyst tube), or when valid QC samples no longer meet acceptance criteria. See Form 1 for Hg standards preparations.

11.0 PROCEDURE - Instrument Operating Procedure & Daily Maintenance – DMA-80

Maintenance is listed in the Milestone User Manual found on page 72 to 93. All maintenance performed is logged in the DMA-80 maintenance logbook. Catalyst tube conditioning procedure comes with the catalyst tube from Milestone. Always condition a new catalyst tube, it may have to be done more than once.

11.1 Gas Supply:

- 11.1.1 Turn on Oxygen supply lever on the bench behind the machine. It is set at 60 psi. (The oxygen tank is in the mechanics room and stays on all the time.)
- 11.2 Turn on DMA-80 - switch on lower right front corner of the machine. The labTERMINAL 1024 will activate when the DMA-80 is turned on. Go to Administrator line. Enter 123456 in the password
- 11.3 Turn on Precisa balance. Use class "1" weights to calibrate the balance. Record the weights in the balance log book located behind the balance.



- 11.4 Go to Panel Administration – go through the top tabs Access, Settings (check save of data after one measurement -the automatically box should be checked.), Regulations, Format (check for eraseable sectors, if red is present then hit optimize box)

- 11.5 Go to Balance set up

Manufacturer of balance – Precisa

Baudrate (to balance) – 960 Baud

Databits (to balance) – 7 Bits

Parity (to balance) - Even

These settings will allow the data in the balance to be connected to the DMA-80 and enter the weight values of the samples into the sample data files.

- 11.6 If there is a valid calibration curve, daily calibration is not required. Insure that the correct calibration curve is in use. 11.7 Set up sample runs by using the procedure from the Milestone User Manual found on pages 64 to 67.

Program set up

1. Drying temp. (°C) 300
2. Drying Time (sec) (10 blanks) (60 for most samples) (80 - 100 for fish)
3. Decomposition Temp.(°C) 850
4. Decomposition Time (sec) 180 (200 for fish)
5. Purge (sec) 60
6. Amalgam time (sec) 12
7. Recording time (sec) 30

- 11.8 Trouble shooting messages are listed in the Milestone User Manual found on pages 68 to 93.

- 11.9 Load samples into tray according to the following sequence list:

Typical Analytical Sequence

Sequence Sample ID

- | | |
|---|--|
| 1 | Blank |
| 2 | Blank |
| 3 | Blank |
| 4 | Lab Reagent Blank (LRB) |
| 5 | MRL Minimum Reporting Level Standard |
| 6 | LFB 20 (IPC checks cell1) (90 to 110%) |
| 7 | LFB 40 (IPC checks cell 2) (90 to 110%) |
| 8 | QCS 20 (quality control standard to check cell 1) (90 to 110%) |
| 9 | QCS 40 (quality control standard to check cell 2) (90 to 110%) |



- 110%)
- 10 Blanks are run to check for memory effect
- 11 Sample 1
- 12 Sample 2
- 13 Sample 3
- 14 Sample 5
- 15 Sample 6
- 16 Sample 7
- 17 Sample 8
- 18 Sample 8 Duplicate
- 19 Sample 8 Laboratory Fortified Matrix (LFM)
- Blank
- 20 SRM (70 to 130%)
- 21 Blank
- An additional set of no more than 10 samples, including one or more Laboratory Fortified Blank (LFB), LFM's, Matrix QCS(s), and duplicates as required by the method. An IPC B and blank must be at the start of a sample set of 10 and at the end. If there are fewer than 10 samples in the last set of samples, the following sequence finishes the sample run.
- 22
- 23 SRM (QCS Performance Check Standard)
- 24 LFB (85 to 115%), Performance Check Standard(s)
- 25 Blank

Note: Memory effect from high samples may come into the run at any time. Analyst must watch for this and put blanks in after high samples to clear out the system.

Note: Quartz boats are used for liquid samples and standards. LFM samples are not spiked until right before the metal or quartz boat goes into the furnace.

12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 Sample data are reported in units of mg/L for aqueous samples and mg/kg wet weight for solid samples.
- 12.2 For dissolved aqueous analytes, report the data generated directly from the instrument with allowance for sample dilution. Concentrations below IDL and MDL are not reported.
- 12.3 For total recoverable analytes in solid samples, the (C) concentration in mg/kg is calculated, manually or by the DMA 80 software, as follows:

$$\text{Sample Conc. (mg / kg) wet weight basis} = \frac{C \times V \times D}{W}$$

Where:



- C = Concentration in extract (mg/L)
- V = Volume of extract (L)
- D = Dilution factor (undiluted = 1)
- W = Weight of sample aliquot extracted (kg)

13.0 METHOD PERFORMANCE

Listed in Table 5 are the MDLs for total recoverable metals determined for the wavelength used in this method. The MDL was determined in reagent water blank matrix.

14.0 POLLUTION PREVENTION

- 14.1 Refer to the WES Environmental Management System (EMS) policy and SOPs regarding pollution prevention.
- 14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.0 WASTE MANAGEMENT

- 15.1 WES laboratories fully comply with all applicable federal, state, and local environmental regulations. WES is also committed to protecting the air, water, and land by minimizing and controlling all chemical releases from fume hoods, biological safety cabinets, and bench operations. Refer to the WES EMS policy and SOPs regarding waste management.
- 15.2 All chemical waste is collected in sealed waste containers. Once the waste containers reach capacity, they are transferred to the WES hazardous waste storage room where they are emptied into a waste drum (organic or inorganic). Within 180-days of waste accumulation, the waste drum is transported off the premises by a licensed hazardous waste management contractor. Under the WES EMS, a chemical inventory database has been developed to track purchases and use of chemicals and other hazardous materials, and the waste generated by the use of these chemicals.

16.0 REFERENCES

- 16.1 EPA Method 7473. Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry, February 2007.
- 16.2 EPA New England Region 1. ECASOP- MilestoneSOP1 Revision #0, January 20, 2008
- 16.3 USEPA Region 9 Laboratory Richmond, California, Standard Operation Procedure 535 Analysis of Mercury in Solids by Thermal Decomposition and AAS
- 16.4 Milestone DMA-80 User Manual – Revision 3/2004



17.0 TABLES AND VALIDATION DATA

TABLE 1. Quality Control Tests and Acceptance Limits for the Analysis of Mercury by EPA Method 7473

Accuracy			Precision		
QC Test	Acceptance Limits (% Recovery)	Frequency	QC Test	Acceptance Limits (RPD ^a)	Frequency
LFB ^b	85 – 115 ^f	≥ 10%	Duplicates	≤ 20 ^g	≥ 10%
LFM ^c	70 – 130 ^f	≥ 10%			
QCS ^d	90 – 110 ^f	≥ 10%			
SRM ^e	70 – 130 ^f	≥ 10%			

^a RPD = relative percent difference among duplicates.

^b LFB = laboratory fortified blank sample.

^c LFM = laboratory fortified matrix sample

^d QCS = quality control sample from source outside of the laboratory run after ICP 1 and 2.

^e SRM = standard reference material – freeze dried material with known amount of mercury, run after every 10 samples

^f Based on ± 3 standard deviations (SD) of the mean % recovery of a 30-sample set.

^g Based on ± 3 standard deviations (SD) of the mean RPD of the 30-sample set.



TABLE 2. Quality Control Elements and Acceptance Limits for EPA Method 7473

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Linear Dynamic Range (LDR)	Every year and according to the judgment of the analyst.	Six standards, two of which are close to the upper limit of the LDR with an observed analyte conc. no more than 10% below the stated conc. of the standard.	Check/service instrument.
Instrument Stability	20-minute warm-up	Machine will not go to sample mode before the warm-up is complete	
Initial Calibration	Initial start up of the DMA-80 and whenever there is a major change to any of the consumables of the DMA-80	$r^2 > 0.995$	Recalibrate with new standards
Quality Control Samples (QCS-MS)	Quality control samples run between every 10 sample analyses. Standard Reference Materials are used.	70 to 130% recovery	
Instrument Performance Check Sol. IPC A Initial Performance Calibration Check(s) (Daily calibration verification standards.)	Run these solutions at the start of each daily run to test cell1 and cell 2.	IPC 1 & 2 (± 10)	Reanalyze IPC, if outside range, make new solutions, reanalyze. If outside range, recalibrate, and repeat analysis. Re-analyze sample since last successful IPC B, or discontinue & recalibrate instrument if necessary.
Calibration Blank (CCB)	Immediately following each calibration, after every tenth sample and at the end of the run	< MDL, but > a negative signal in concentration units equal to the MDL	Reanalyze. Determine cause, or recalibrate instrument.
Quality Control Sample (QCS)	After calibration	+/- 10%	Acceptable range must be met before continuing with sample analysis. Recalibrate and repeat.
Laboratory Reagent Blank (LRB)	One with each batch of 20 or fewer samples	< MRL	Determine and eliminate the source of contamination & then repeat sample analysis. If reanalysis is not possible, the data may be qualified.
Laboratory Duplicate	Every 10 or fewer samples	RPD $\leq 20\%$	Repeat using fresh sample. If failure



TABLE 2. Quality Control Elements and Acceptance Limits for EPA Method 7473

QC Elements	Frequency	Acceptance Criteria	Corrective Action
	or less		continues, check sample for non-homogeneity and system for problems. If the sample is not homogeneous, note this with the Duplicate's results.
LFM	Every 10 or fewer samples or less	70 – 130% Note: Recovery calculations are not required if the concentration added is less than 25% of the unfortified sample concentration	If laboratory performance shown to be in control, LRB and LFB or QCS within acceptance criteria, problem is a matrix effect – qualify data.
LFB	One with each batch of 20 or fewer samples	85 – 115%	The source of the problem must be identified and resolved before continuing analysis
MDL determination (USEPA, 1997)	Annually or a new operator, or judgment of the analyst	Target analyte concentration spiked into the blank matrix must not exceed 10 times (approximately) the experimentally determined MDL (7 spiked blanks) if RSD from analysis of 7 aliquots is < 10%, conc. used to determine MDL is too high.	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte
MRL Check Standard	At the beginning of every analytical run	± 20%	Acceptable range must be met before reporting data. If not acceptable, then rerun MRL if not acceptable remake standard. If not acceptable remake curve. If problem persists suspect the MDL and MRL are too low for the analysis conditions.



TABLE 3. Method Detection Limits (MDLs) for Trace Metal Analysis in Reagent Water by EPA Method 7473 (8/22/12 to 9/13/12)

Analyte	Wavelength	MDL (mg/L)	Spike Concentration (mg/L)
mercury	254	0.0025	0.006
Based on seven determinations spiked at the concentrations shown and run on 8/22/12, 9/6/12, 9/7/12, 9/10/12, 9/11/12, 9/12/12, 9/13/12 . The MDL is based upon a sample size of 100 μ L.			



FORM 1. Mercury Standards Preparation for Curve for DMA80 EPA 7473

[Mercury Standards Prep for curve for DMA80 EPA7473](#)

FORM 2. Mercury Standards Preparation for EPA 7473

[Mercury Std Prep for EPA 7473](#)

APPENDIX 1. Consumables

The following table lists the main consumables for the instrument and estimated lifetimes. The lifetime estimates are based on regular/daily use. The listed components would need to be replaced when, after corrective action, calibration checks and analytical QC limits continue to be exceeded.

Consumable	Lifetime	Comment
Amalgamator	4 to 6 months	The stated lifetime is when the samples analyzed are mostly organic tissue such as fish, otherwise, longer lifetime is possible. When amalgamator is to be replaced, other associated hardware, such as the decomposition tube and connecting joints will likely need to be changed.
Catalyst	4 to 6 months	The catalyst, like the amalgamator, is impacted by organic tissue such as fish.
Charcoal trap	About 1 year	For every two changes of the Amalgamator and catalyst one change of the trap would be needed.
Boats	Varies with use and handling	When boats show Hg levels greater than zero after 4 to six scrubblings and cleaning with soap and RO water, they need to be discarded as solid Hg waste.
Maintenance grease	Based on usage	Lubrication of pneumatic actuator
Fuses	Variable	Instrument will not operate with bad fuse. Access to fuses is above the power cable at the rear panel.