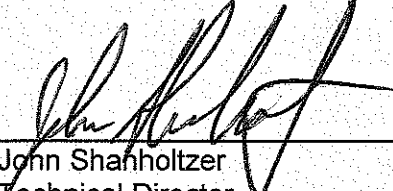
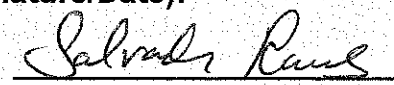
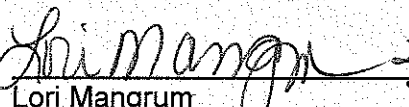
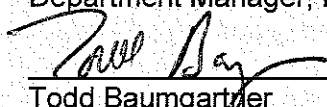
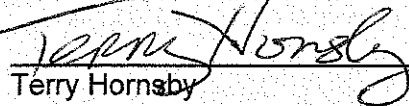


## Title: DIGESTION & ANALYSIS FOR MERCURY BY AUTOMATED COLD VAPOR ATOMIC ABSORPTION

Method: EPA 245.1 and SW 846 7470A, 7471A

Approvals (Signature/Date):	
 John Shahholtzer Technical Director	<u>2-24-10</u> Date
 Salvador Ramos Health & Safety Manager / Coordinator Department Manager, Metals	<u>2/24/10</u> Date
 Lori Mangrum Quality Assurance Manager	<u>2/24/10</u> Date
 Todd Baumgartner Laboratory Director	<u>2/24/10</u> Date
 Terry Hornsby Operations Manager	<u>2-24-10</u> Date

### Copyright Information:

This documentation has been prepared by TestAmerica Laboratories, Inc. and its affiliates ("TestAmerica"), solely for their own use and the use of their customers in evaluating their qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to TestAmerica upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use it for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

THIS DOCUMENT CONTAINS VALUABLE CONFIDENTIAL AND PROPRIETARY INFORMATION. DISCLOSURE, USE OR REPRODUCTION OF THESE MATERIALS WITHOUT THE WRITTEN AUTHORIZATION OF TESTAMERICA IS STRICTLY PROHIBITED. THIS UNPUBLISHED WORK BY TESTAMERICA IS PROTECTED BY STATE AND FEDERAL LAW OF THE UNITED STATES. IF PUBLICATION OF THIS WORK SHOULD OCCUR THE FOLLOWING NOTICE SHALL APPLY:

©COPYRIGHT 2010 TESTAMERICA LABORATORIES, INC. ALL RIGHTS RESERVED.

Facility Distribution No. \_\_\_\_\_

Distributed To: \_\_\_\_\_

## **1.0 Scope and Application**

### **1.1 Analytes, Matrix(s), and Reporting Limits**

The purpose of this SOP is to describe the procedures used to analyze water, solid, and sludge samples for the determination of mercury prior to the analysis through cold vapor atomic absorption by methods SW 846 7470, 7471 and EPA 245.1.

The routine target analyte lists, current Reporting Limit (RL), Method Detection Limit (MDL) and precision and accuracy limits associated with this procedure are given in the Method Limit Group (MLGs) in LIMS. The applicable range of this method is 0.2µg/L – 10µg/L.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 20 in the Quality Assurance Manual.

## **2.0 Summary of Method**

- 2.1 This method is a cold-vapor atomic absorption method and is based on the absorption of radiation at the 253.7nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.
- 2.2 A known volume of the well-mixed sample is transferred to a suitable digestion vessel. The sample is digested with aliquots aqua regia, reagent water and potassium permanganate. After digestion and cooling, the sample is mixed with sodium chloride-hydroxylamine sulfate and analyzed by cold vapor atomic absorption.
- 2.3 Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (253.7nm) is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

## **3.0 Definitions**

Refer to SOP TP-AN-005: Definitions, Terms, and Acronyms and to the current revision of the Tampa's Quality Assurance Manual (TP-QAM) for a complete listing of applicable definitions.

#### 4.0 Interferences

- 4.1 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.
- 4.2 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.
- 4.3 Physical interference affects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.
- 4.4 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.
- 4.5 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on the recovery of mercury from spiked samples.
- 4.6 Chlorides can cause a positive interference. Sea water, brines and industrial effluents high in chlorides require additional permanganate (as much as 25mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

**NOTE:** Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

- 4.7 Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

- 4.8 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. Reducing the volume of original sample used can eliminate the problem.
- 4.9 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7nm) are confirmed interferences. The concentration levels for interferants are difficult to define.
- 4.10 Volatile materials (e.g., chlorine) which absorb at 253.7nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the digestion vessel should be purged before addition of stannous chloride solution.
- 4.11 Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if performed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as Total Kjeldahl Nitrogen (TKN) or chemical oxygen demand (COD).

## **5.0 Safety**

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

### **5.1 Specific Safety Concerns or Requirements**

- 5.1.1 The samples are digested in strong acid solutions and contain acid concentrations of 10-20% by volume. The analyst must wear protective clothing such as a lab coat or apron. The acids used in this procedure will destroy unprotected clothing. The analyst must wear proper eye protection such as lab glasses or face shield. Acid can be splashed into the eyes from many sources. Gloves must be worn to protect hands from acid burns.
- 5.1.2 The acid digestion procedures must be performed under a properly functioning fume hood. The acid fumes from the digestion can cause mild to severe respiratory problems if inhaled.
- 5.1.3 Each analyst should be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds. The following specific hazards are known:

5.1.3.1 The following materials are known to be corrosive:

Hydrochloric acid, Sulfuric acid, Nitric acid and Aqua Regia.

5.1.3.2 The following materials are known to be oxidizing agents:  
Nitric acid and Potassium Permanganate.

- 5.1.4 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.
- 5.1.5 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.
- 5.1.6 Care must be taken when handling the digestion beakers. Before handling a vessel that has been in use, check the temperature to make sure that it is not hot. Make sure that the digestion vessels are placed on a stable platform during and after the digestion. Vibrations from the hood or an unstable platform can cause the beakers to move and possibly to fall and splatter an analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.
- 5.1.7 Acid / peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.
- 5.1.8 Do not look directly into the beam of the Hg lamp. The UV radiation that this lamp emits is harmful to the eyes.
- 5.1.9 The CVAA device must be properly vented to remove potentially harmful fumes generated during sample analysis.

## 5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

Hydroxylamine Hydrochloride	Corrosive	2 Mg/M3-TWA	Extremely destructive to mucous membranes and upper respiratory tract. Symptoms may include burning sensation, coughing wheezing, laryngitis, shortness of breath nausea, vomiting. Skin irritant and sensitizer, may cause burns.
Stannous Chloride	Corrosive Oxidizer Acidic	2 Mg/M3-TWA	Can cause irritation of respiratory tract; symptoms include ongoing coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Nitric Acid	Corrosive Oxidizer Poison	2ppm-TWA 4ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

## 6.0 Equipment and Supplies

### 6.1 Instrumentation

- 6.1.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95°C+/-3°C. The temperature of the hot plate or digestion block must be



monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

**NOTE:** The use of hot plates is listed in the preparation steps but a digestion block may be used if the same general procedures are employed. The hot plate or digestion block settings must be recorded in the maintenance log or other suitable log.

- 6.1.2 Analytical balance capable of accurately weighing to the nearest 0.01g.
- 6.1.3 Cold vapor atomic absorption instrument: Cetac M-6100 or Leeman PS200II or equivalent

## 6.2 Supplies

- 6.2.1 Digestion vessels: Disposable 50mL digestion cups with volumetric graduations. Cups must come with analysis report per case of digestion cups. The lot number must be entered in the digestion sheet and the analysis report must be saved for future reference.
- 6.2.2 Watch glasses, "ribbed", to fit over digestion vessels (not required for block digestion vessels)
- 6.2.3 Class A Volumetric flasks- 100mL or appropriate volume
- 6.2.4 Graduated cylinders- 50mL
- 6.2.5 Pipettes, repipetors, and Class A glass volumetric pipettes
- 6.2.6 Whatman 0.45µm (pore size), polypropylene, syringe filter
- 6.2.7 Thermometer that covers a temperature range of 80°C-120°C
- 6.2.8 pH indicator strips (pH range 0 – 6)
- 6.2.9 Plastic spoons and/or transfer pipettes
- 6.2.10 Plastic digestate storage bottles

## 7.0 Reagents and Standards

All reagents and standards are to be labeled with their unique TALS ID, including the name of the reagent, the concentration, the date prepared, analyst initials, and the expiration date. Reagent preparation is documented in TALS according to SOP TP-AN-004: *Standard Materials and Reagent Traceability*. General guidance on the preparation of standards is given in SOP TP-AN-011: *Standard Preparation*.

The expiration date of the intermediate spiking solutions is 1 month from the date of preparation or the expiration date of the stock(s) used to prepare the spiking solution (the expiration date of the stock is 1 year). The lab should prepare standards from neat materials only if a certified solution is not available.

- 7.1 Reagent water: Lab generated de-ionized water, ASTM Type I or Type II. The conductivity monitored in accordance with Tampa's most current revision of SOP TP-AN-009 *Conductivity Checks for Laboratory Deionized Water*.
- 7.2 Nitric acid (HNO<sub>3</sub>): reagent grade

7.3 Aqua regia:

- 7.3.1 Prepare daily by carefully adding three volumes of concentrated HCl to one volume of concentrated  $\text{HNO}_3$ .

**Caution!** This reagent **MUST** be prepared and used under a working fume hood.

**NOTE:** Use immediately after preparing and prepare only amount needed.

## 7.4 Hydrochloric Acid (HCl) concentrated: reagent grade

7.5 10% Hydrochloric acid:

- 7.5.1 Slowly add 200mL of concentrated HCl to approximately 1500mL of reagent water. Bring to volume at 2L.

**Caution!** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.6 Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), concentrated: reagent grade7.7 Sulfuric acid, 0.5N:

- 7.7.1 Dilute 14mL of concentrated  $\text{H}_2\text{SO}_4$  to 1L with reagent water.

**Caution!** When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.8 Stannous Chloride solution:

- 7.8.1 Add 50g of stannous Chloride to 500mL of DI water plus 100mL of HCL. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

7.9 Sodium chloride-hydroxylamine hydrochloride solution:

- 7.9.1 Add 120g of sodium chloride and 120g of hydroxylamine hydrochloride to 1000mL of reagent water.

**NOTE:** Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.10 Potassium permanganate, 5% solution (w/v):

- 7.10.1.1 Dissolve 5g of potassium permanganate for every 100mL of reagent water.

7.11 Potassium persulfate 5% solution (w/v):

- 7.11.1 Dissolve 5g of potassium persulfate in 100mL of DI water.

## 7.12 Calibration Standards



7.12.1 Mercury stock solutions, purchased at 1000ppm ( $\mu\text{g/mL}$ ), in 2%  $\text{HNO}_3$ . [Primary Source (Calibration curve/CCV) mehgcalsto and Secondary Source (ICV/LCS/MS/MSD) mehgicvsto].

7.12.2 Intermediate mercury standards (10ppm):

7.12.2.1 These solutions are prepared monthly by diluting 1.0mL of the mercury stock solutions to 100mL with 2%  $\text{HNO}_3$  in a volumetric flask. (Exp: 1 month) [Primary Intermediate (mehgcalint) and Secondary Intermediate (mehgicvint)].

7.12.3 Working mercury standards (50ppb):

7.12.3.1 These intermediate solutions are prepared weekly by diluting 0.50mL of the intermediate mercury solution to 100mL with 2%  $\text{HNO}_3$  in a volumetric flask. (Exp: 1 week). [Primary Working (mehgcalw) and Secondary Working (mehgicvw)].

7.12.4 Initial calibration curve:

7.12.4.1 Prepare the solid initial calibration curve by diluting the primary working mercury standard to the following concentrations: 0.2, 0.5, 1, 5, and  $10\mu\text{g/L}$ . Add 0.3g of boiling chips to the digestion tube, spike each tube with correct amount of standard, dilute volume to 10mL's with reagent water. Final volume will be 50mL.

7.12.4.2 Prepare the aqueous initial calibration curve by diluting the Primary working mercury standard to the following concentrations: 0.2, 0.5, 1, 5, and  $10\mu\text{g/L}$  with reagent water to a final volume of 25mL.

7.12.4.3 Calibration curve standards **MUST** be digested with the sample batch.

7.12.5 Initial calibration verification standards ( $2.5\mu\text{g/L}$ ):

7.12.5.1 Add 2.5mL of (mehgicvw) (50ppb) to a final volume of 50mL. It is similar to the calibration standards, but from a completely different source.

7.12.6 CCV ( $5\mu\text{g/L}$ ):

7.12.6.1 Add 5.0mL of (mehgcalw) (50ppb) to a final volume of 50mL. From the same source as the initial calibration curve and the concentration.

7.12.7 Laboratory Control Sample, MS/MSD spike ( $5\mu\text{g/mL}$ ):

7.12.7.1 For Solid Samples: Add 1.0mL of (mehgicvw) (50ppb) to a final volume of 50mL. The spiking standard is prepared using 2%

HNO<sub>3</sub> as the solvent.

7.12.7.2 For Aqueous Samples: Add 0.5mL to a final volume of 25mL.

**NOTE:** For solid matrices, the ICV, CCV and spiking standards are prepared with 0.3g boiling chips in the digestion tube and the correct amount of standard, diluted to a volume of 10mL's with reagent water. For aqueous matrices, the ICV, CCV and spiking standards are diluted to a final volume of 25mL's.

## 8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time <sup>1</sup>	Reference
Aqueous (water) and TCLP leachates	HDPE	250mL	Ambient HNO <sub>3</sub> to pH <2	28 Days	N/A
Solids, Soils, Sludges	HDPE	500mL	Cool ≤ 6°C None	28 Days	N/A

<sup>1</sup>Inclusive of digestion and analysis.

8.1 Sample holding time for metals included under this SOP is 28 days from the date of collection to the date of analysis.

8.2 Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered. The samples should be filtered through a 0.45µm filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

**NOTE:** If a sample being analyzed for dissolved metals is found to contain sediment, the analyst should contact their supervisor. The client should be notified of the problem to decide how to treat the sample.

8.3 The pH of all preserved samples must be checked and documented upon arrival in the lab. If the pH is not within the proper range, additional acid is added to the sample to bring the pH below 2.

8.3.1 Place a piece of pH paper (wide range or narrow range can be used) on a watch glass or other inert surface.

8.3.2 Transfer a few drops of the sample to the pH paper and note the color change. If the pH <2, record this in the log and transfer the sample to the storage area.

- 8.3.3 If the pH is greater than 2, contact the Project Manager to get approval to adjust the pH and document via a NonConformance Memo (NCM). If the Project Manager approves the pH adjustment, move the sample under a hood. Add 1:1 nitric acid to the sample in 1mL aliquots, checking the sample pH after each addition, until the pH <2. The volume of 1:1 nitric acid added to the sample should not exceed 1% of the total volume of the sample. For a 500mL sample, the maximum volume of 1:1 nitric is 5mL. If more acid is required, contact the supervisor for further guidance.

**NOTE:** Samples that are not at pH <2 upon arrival in the lab may contain cyanide or sulfide or may be highly buffered. Working under a hood minimizes the hazard that may be caused by the evolution of hydrogen cyanide or hydrogen sulfide upon acidification of the sample. Be aware that acid/base neutralization reaction may be violent and evolve a good deal of heat.

## 9.0 Quality Control

Please refer to Appendix 4 of the laboratory QAM and Appendix A of this SOP for additional information relating to the QC associated with this method.

### 9.1 Sample QC

- 9.1.1 Tampa's most current revision of SOP TP-AN-006: *Analytical Batching and Evaluation of Data* provide guidance on evaluating QC and sample data, including recommended corrective actions.

- 9.1.2 Each analytical batch may contain up to 20 environmental samples. Every 20 or fewer samples, a Method Blank (MB), Laboratory Control Standard (LCS), Matrix Spike (MS), and Matrix Spike Duplicate (MSD) are required.

9.1.2.1 Method 245.1 requires MS/MSD for every 10 samples.

Quality Controls	Frequency	Control Limit <sup>2</sup>
Method Blank (MB)	1 in 20 or fewer samples	< MDL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	80-120%
Laboratory Control Sample (LCSD)*	1 in 20 or fewer samples	80-120%
Matrix Spike (MS) <sup>1,3</sup>	1 in 20 <sup>3</sup> or fewer samples	80-120%
MS Duplicate (MSD) <sup>1,3</sup>	1 in 20 <sup>3</sup> or fewer samples	80-120%

LCSD Duplicate (LCSD) is performed only when there are samples for a TMDL project included in the batch.

<sup>1</sup> The sample selection for MS/MSD is randomly selected, unless specifically requested by a client.

<sup>2</sup> Statistical control limits are updated annually and are updated into TALS

<sup>3</sup> Method 245.1 require MS/MSD every 10 samples

### 9.2 Instrument QC

- 9.2.1 Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument.

- 9.2.2 A calibration curve is performed daily, followed by an Initial Calibration Verification (ICV), an Initial Calibration Blank (ICB), and a RL standard.

9.2.3 A Continuing Calibration Verification (CCV) and Calibration Verification Blank (CCB) are analyzed every 10 or fewer samples.

Step	Standards	Type	Control Limit	Frequency
Initial Cal	10ppb, 5.0ppb, 1.0ppb, 0.50ppb, 0.20ppb	Linear cal	>0.995	Daily
ICV	2.5ppb	Linear cal	90-110%	After calibration
ICB	0ppb	Linear cal	<MDL	After ICV
RL	0.20ppb	Linear cal	50-150%	After ICV
CCV	5.0ppb	Linear cal	90-110%	Every 10 samples
CCB	0ppb	Linear cal	<MDL	After CCV
LCS	3.0ppb	Linear cal	80-120%	Every 20 samples
MS/MSD	3.0ppb	Linear cal	80-120%	Every 20 samples

**NOTE:** ICV, LCS, and MS/MSD are required to be from a different source standard than the calibration and CCV standards

9.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include re-preparation of samples unless the results indicate that a spiking error may have occurred.

9.2.4.1 If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.2.4.2 The TCLP matrix spike sample is prepared by spiking a 25mL aliquot of a leachate with 0.5mL of the working LCS/MS spike solutions.

**NOTE:** The TCLP matrix spike must be added prior to preservation of the leachate.

9.2.5 Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the

analytical method SOPs, the blank and all associated samples in the batch must be re-digested.

9.2.5.1 Aqueous method blanks are prepared by taking 25mL of reagent water.

9.2.5.2 TCLP method blanks are prepared by taking 25mL of leachate fluid blank.

9.2.5.3 Solid method blanks are prepared by adding 0.3g boiling chips to a 10mL of reagent water. The final volume will be 50mL.

9.2.6 Laboratory Control Samples (LCS) -One LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy and precision of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be re-preparation and reanalysis of the batch.

9.2.6.1 The aqueous LCS is prepared by spiking a 25mL aliquot of reagent water with 0.5mL of the working LCS/MS spike solutions.

9.2.6.2 The TCLP LCS is prepared by spiking a 25mL aliquot of leachate fluid blank with 0.5mL of the working LCS/MS spike solutions.

9.2.6.3 The solid LCS is prepared by adding 0.3g boiling chips to a 10mL aliquot of reagent water. It is then spiked with 0.5mL of the working LCS/MS spike solutions. The final volume will be 50mL.

9.2.7 The accuracy (% Recovery) and precision (% RPD) for the lab spike and matrix spikes should be checked against the limits listed in the method. The lab spikes must meet these accuracy and precision limits. If limits are not met, investigate the cause and either reanalyze or re-extract. The matrix spike recoveries are used to evaluate the matrix effect on the analysis and are advisory.

9.2.8 Linear Calibration Range

9.2.8.1 It must be determined from a linear calibration prepared from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The LCR should be determined by analyzing successively higher standard concentrations of mercury until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The determined LCR must be documented and kept on file. The LCR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. All samples reported are either within or diluted to be within the calibration range. The LCR should be verified annually or whenever, in the judgment of the analyst, a change in analytical

performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined. Since the initial calibration is performed almost every analytical run, and the initial calibration satisfies the requirement for the LCR, the ICAL will be considered to have fulfilled the LCR requirement.

## 10.0 Procedure

### 10.1 Sample Preparation

This SOP is applicable to the preparation of solid samples for the determination of Mercury as defined by SW846 Method 7471A.

#### 10.1.1 Solid Samples

10.1.1.1 Transfer a 0.3g aliquot of a well-mixed sample to a clean 50mL digestion tube or other suitable digestion vessel.

**NOTE:** If there is not sufficient volume to use a 0.3g aliquot, the lab can use a smaller amount of sample; the amount of sample should be accurately weighed and recorded on the digestion log form. This weight should be used in the calculation of the final concentration.

10.1.1.2 Add 0.3g of Teflon chips to a 50mL digestion tube that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

10.1.1.3 Add 1.0mL of the appropriate spiking solutions to a 0.3g aliquot of teflon chips designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 0.3g aliquot of Teflon chips with 1.0mL of the appropriate spiking solutions.

10.1.1.4 Add 1.0mL of the appropriate spiking solutions to each of two 0.3g aliquots of the client sample designated as the matrix spikes sample (MS and MSD).

10.1.1.5 Record the following information on the digestion log sheet:

- date
- analyst's initials
- sample identification
- the amount of sample digested
- batch identification
- temperature of the digestion block (daily)
- the reagent log numbers of the acids used for the digestion
- the standard log numbers of the spiking solutions
- the time that the digestion was started
- the SOP/method number

**NOTE:** A digestion batch consists of twenty field samples and the associated QC items. The batch is not to exceed 20 field samples. Every digestion batch will have a method blank, a laboratory control sample (LCS), a matrix spike and a matrix spike duplicate (if there



is sufficient sample for the MS/MSD). If there is not sufficient sample for MS/MSD, the LCS is prepared in duplicate (LCSD).

- 10.1.1.6 Add 10mL of DI water to each sample.
- 10.1.1.7 Add 2.0mL of DI water to LCS, MS/MSD, before spiking with 1.0mL of spike standards. Bring to final volume of 10mL.
- 10.1.1.8 Add 2.5mL of aqua regia to each 50mL digesting tube.
- 10.1.1.9 Heat for 2 minutes in water bath at 95°C and then cool.
- 10.1.1.10 Add 25mL of reagent water to each 50mL digesting tube.
- 10.1.1.11 Add 7.5mL of  $\text{KMnO}_4$  to each 50mL digestion tube. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. An additional 3 portions may be added. If the color does not persist, a smaller sample size may be required.
- 10.1.1.12 Cap the 50mL digesting tube and shake well.
- 10.1.1.13 Heat for 30 minutes in a water bath at 95°C +/- 5°C.
- 10.1.1.14 Cool the samples.
- 10.1.1.15 Add 3mL of sodium chloride-hydroxylamine sulfate to reduce the excess  $\text{KMnO}_4$ .
- 10.1.1.16 Bring up to a final volume of 50mL with DI water and shake well.
- 10.1.1.17 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the prep batch in TALS. The sample is now ready for analysis by CVAA.

#### 10.1.2 Aqueous Samples

- 10.1.2.1 Transfer a 25mL aliquot (or an appropriate volume diluted to 25mL with reagent water) of a well-mixed sample to a clean 50mL digestion tube.

**NOTE:** If there is not sufficient volume to use a 25mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 12.5mL of sample is digested, one half of the routine volumes of reagent are used and the final volume of the digestate is brought back to 12.5mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely. This shall be completely documented using a Nonconformance Memo that has been discussed with the supervisor and Project Manager. The NCM must be filed in the project file.

- 10.1.2.2 Add 25mL of reagent water to a 50mL digestion tube that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for

contamination that may be due to glassware, reagents, or sample handling.

10.1.2.3 Add 0.5mL of the appropriate spiking solutions to a 25mL aliquot of reagent water designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 25mL aliquot of reagent water with 0.5mL of the appropriate spiking solutions.

10.1.2.4 Add 0.5mL of the appropriate spiking solutions to each of two 25mL aliquots of the client sample designated as the matrix spikes sample (MS and MSD).

10.1.2.5 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the volume of sample digested
- batch identification
- the lot number of the acids used for the digestion
- the lot number of the Hg spiking solutions
- the time that the digestion was started
- the SOP/method number

**NOTE:** A digestion batch consists of twenty field samples and the associated QC items. The batch is not to exceed 20 field samples. Every digestion batch will have a method blank, a laboratory control sample (LCS), a matrix spike and a matrix spike duplicate (if there is sufficient sample for the MS/MSD). If there is not sufficient sample for MS/MSD, the LCS is prepared in duplicate (LCSD).

**NOTE: Method 245.1 requires MS/MSD every 10 samples.**

10.1.2.6 Add 0.62mL of concentrated  $\text{HNO}_3$  to each sample.

10.1.2.7 Add 1.25mL of concentrated  $\text{H}_2\text{SO}_4$  to each 50mL digestion tube.

10.1.2.8 Add 3.75mL of  $\text{KMnO}_4$  to each 50mL digestion tube. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. An additional 3 portions may be added. If the color does not persist, sample dilution may be required.

10.1.2.9 Add 2mL of potassium persulfate to each sample.

10.1.2.10 Cap the 50mL digestion tube and shake well.

10.1.2.11 Heat for two hours in a water bath at  $95^\circ\text{C} \pm 5^\circ\text{C}$ .

10.1.2.12 Cool the samples.

10.1.2.13 Add 1.5mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess  $\text{KMnO}_4$ .

- 10.1.2.14 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the prep batch in TALS. The sample is now ready for analysis by CVAA.

## 10.2 **Calibration**

**NOTE:** The calibration must be done daily. This SOP is not meant to be a replacement for the manufacturer's instrument manual. The analyst must read the instrument manual or receive full hands on training before operating the instrument.

- 10.2.1 Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument.

### 10.2.2 Initial startup of the instrument

- 10.2.2.1 Before analysis begins inspect the system (pump tubes, mixing coil, gas/ liquid separator) to see if any parts need to be cleaned or replaced.

- 10.2.2.2 Fill the rinse bottle with 10% HCl solution.

- 10.2.2.3 If the lamp is not already on and warmed up, turn on the lamp and allow it to warm up for at least 30 minutes.

- 10.2.2.4 If the lamp is already on and warmed up, fill the reductant bottle with the stannous solution. Turn the pump and gas on using the instrument control panel in the software. Allow a minimum of 20 minutes of pump time for the pump tubes to break in each day.

### 10.2.3 Autosampler setup

- 10.2.3.1 Fill the standard tubes with the appropriate calibration curve standards.

- 10.2.3.2 Fill the sample test tubes with the samples in the applicable order. An example order is as follows: The preparation blank will be analyzed first. The LCS will follow immediately after the preparation blank. The samples, matrix spikes and duplicates will then follow with a maximum of 10 analyses between CCVs/CCBs.

- 10.2.3.3 Enter the sample/QC IDs into the autosampler table giving each sample a unique name. Remember to set the first CCV/CCB to run after the first 9 samples, as the PQL standard counts toward the maximum 10 samples between CCV/CCB's.

- 10.2.3.4 Load the rack(s) onto the autosampler.

#### 10.2.4 Calibration of the mercury analyzer.

10.2.4.1 Call up the required protocol, if necessary.

10.2.4.2 Open a new batch using the day's date as follows: YMDDA, where Y is the last number in the current year, M is the current month written using a letter from the table below, DD is the day as two digits and A is the instrument designation-"H" for the Hydra AA, and "P" for the PS200II. For example, the first run of the day on July 16, 2004 on the Hydra AA would be batch # 4E16H.

January	A	July	G
February	B	August	H
March	C	September	I
April	D	October	J
May	E	November	K
June	F	December	L

10.2.4.3 Enter the operator ID (e.g., J.Smith).

10.2.4.4 Reset the calibration for a new calibration in the standards tab on the Hg runner program.

10.2.4.5 Select standards 1 through 6 and select Rep 1 and click on the Stand Auto button.

10.2.4.6 When all calibration standards have been analyzed, go to the Cal Curve in the database program. If the calibration is within acceptable limits (correlation > 0.995) accept the linear calibration and print the calibration curve.

### 10.3 **Sample Analysis**

10.3.1 After calibration, analyze the ICV, ICB and PQL standard.

10.3.2 Select the racks to be analyzed and the number of positions on each rack to be analyzed. Click on the Run Auto Key.

10.3.3 If the concentration of a sample is above the calibration range of the Hg analyzer, the sample digestate must be diluted and reanalyzed. Samples should be diluted with digested blank solution.

10.3.4 Carryover from high concentration samples usually affects only the next two samples in the sequence. If the results for the two samples following an "off-scale" sample are greater than the RL, these two samples must be reanalyzed to verify the presence and quantitation of mercury. It is recommended that all positive samples (greater than the RL) after the "off-scale" sample be reanalyzed. It is the responsibility of the analyst to clearly

demonstrate that all mercury results are accurate and free from carry-over contamination.

### 10.3.5 Serial Dilution (Analytical Spikes)

10.3.5.1 A serial dilution is performed to verify that samples of similar matrix types are free from interferences from each batch.

10.3.5.2 Select one sample from within a batch for the serial dilution.

10.3.5.3 Dilute the sample by a factor of 5 greater than the original sample.

10.3.5.4 Analyze the diluted sample and an undiluted sample immediately after.

10.3.5.5 If both the serial dilution and original sample are above the RL, calculate the percent difference of the serial dilution.

10.3.5.6 If the results of the dilution are within 10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than 10%, matrix interference should be suspected.

## 11.0 Calculations / Data Reduction

### 11.1 Difference of the serial dilution

$$\%Diff = \frac{|(C_{sd} \times DF_{sd}) - (C_s \times DF_s)|}{C_s \times DF_s} \times 100\%$$

Where:

$C_s$  = concentration of the original sample ( $\mu\text{g/L}$ )

$C_{sd}$  = concentration of serial dilution ( $\mu\text{g/L}$ )

$DF_s$  = dilution factor of the original sample ( $\mu\text{g/L}$ )

$DF_{sd}$  = dilution factor of the serial dilution ( $\mu\text{g/L}$ )

### 11.2 Spiking Solution

$$V_i = \frac{C_f \times V_f}{C_i}$$

Where:

$V_i$  = volume of stock standard needed to prepare the spiking solution (mL)

$C_i$  = concentration of stock solution ( $\mu\text{g/mL}$ )

$C_f$  = concentration of spiking solution to prepare ( $\mu\text{g/mL}$ )

$V_f$  = volume of spiking solution to prepare (mL)

The concentration can be expressed in whatever terms the analyst finds most convenient -  $\mu\text{g/L}$ ,  $\mu\text{g/mL}$ ,  $\text{mg/L}$ , etc. The units must be the same for  $C_i$  and  $C_f$ .

### 11.3 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$$

### 11.4 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

### 11.5 Concentration (mg/kg or L) = $\frac{C \times V \times D}{W}$

Where:

C = sample concentration in extract (ppm)

V = Volume of extract (mL)

D = Dilution Factor

W = Weight/Volume of sample aliquot extracted (grams or mL's)

**NOTE:** All dry weight corrections are made in LIMS at the time the final report is prepared.

### 11.6 Aqueous and Leachate Samples

The concentration of mercury in liquid samples is routinely reported as µg/L and is calculated as follows:

$$C(\text{sample}) = C(\text{curve}) \otimes DF$$

Where:

C(sample) = concentration of sample (µg/L)

C(curve) = concentration from curve (µg/L)

DF = dilution factor

The RL (in µg/L) is calculated as follows:

$$RL(\text{sample}) = RL(\text{qam}) \otimes DF$$

Where:

RL(sample)<sub>e</sub> = reporting limit of sample (µg/L)

RL(qam) = reporting limit from QAM (µg/L)

DF = dilution factor (The RL in the QAM assumes that DF=1)

The reporting limit (RL) may also be reported in mg/L. Results in mg/L are reported by dividing the result in µg/L by 1000.

### 11.7 Soil/Solid Samples

The concentration of mercury in soil and solid samples is routinely reported as mg/kg on a dry weight basis and is calculated as follows:



$$C_{sample} = C_{curve} \times \frac{F \times DF}{W \times \%solids} \times \frac{1mg}{1000ug}$$

Where:

$C(sample)$  = concentration of sample (mg/kg dw)

$C(curve)$  = concentration of digest from curve (µg/L)

F = final volume of digest (L)

W = weight of sample digested (kg)

solids = (percent solids)/100

DF = dilution factor

The reporting limit (RL) for soil/solid samples is calculated as follows:

$$RL(sample) = RL(qam) \otimes DF \otimes \frac{1.0g}{W \otimes solids}$$

Where:

$RL(sample)$  = reporting limit of sample (mg/kg dw)

$RL(qam)$  = reporting limit from QAM (mg/kg)

W = weight of sample digested (kg)

solids = (percent solids)/100

DF = dilution factor

RL is based on a 1-gram sample with a percent solids of 100 (solids =1).

This equation assumes that all digests are taken to the same final volume as the standards.

## 12.0 Method Performance

12.1 Method Detection Limit Study (MDL) - The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined accordance with 40 CFR, Chapter 1, Part 136, Appendix B and with reference to the laboratory's MDL procedure in Section 20 of the Quality Assurance Manual. An MDL reflects a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.1.1 The method detection limit (MDL) is determined annually in accordance with Tampa's most current revision of SOP TP-CA-090 Procedure for the Determination of Method Detection Limit

12.2 Demonstration of Capabilities - Each analyst must perform an Initial Demonstration of Capability (IDOC) in accordance with the procedure outlined in Section 20 of the Quality Assurance Manual. The evaluation of the IDOC data should be completed prior to the analysis of samples. A Continuing Demonstration of Capability (CDOC) must be performed annually or whenever there is a significant change in the instrument parameters or the associated method.

- 12.3 Training Requirements – Each analyst's required employee training (such as orientation to the laboratory's policies and procedures and in-house method training) are outlined in Section 18 of the Quality Assurance Manual.

### 13.0 Data Assessment And Acceptance Criteria For Quality Control Measures

- 13.1 The following represent data assessment for samples and acceptance criteria for QC measures. Corrective actions for any failure in QC measures are shown in Section 14.

#### 13.2 QC sample acceptance criteria

- 13.2.1 **Method Blank.** No target analytes may be present in the method blank above the reporting limit.

- 13.2.2 **Laboratory Control Sample (LCS).** The analyte must be within established control limits for accuracy (%Recovery) and precision (RPD). Exceptions are allowed only with QA and project management approval.

- 13.2.3 **Matrix Spike/Matrix Spike Duplicate (MS/MSD).** The analyte should be within established control limits for accuracy (%Recovery) and precision (%RPD). Deviations from this may be the results of matrix effects, which are confirmed by passing LCS/LCSD. No specific corrective actions are required in the evaluation of the MS/MSD results provided that the batch LCS is in control. Analysts should use sound judgment in accepting MS/MSD results that are not within control limits, especially if the LCS results are borderline. Check with supervisor, Lab Manager and or Project Manager on reporting out of control limits QC.

#### 13.3 Sample result evaluation

- 13.3.1 **Dilutions:** If the response for any compound exceeds the working range of the analytical system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit in the upper half of the calibration range. The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

### 14.0 Corrective Actions For Out Of Control Data

- 14.1 **Method Blank.** The samples in the batch associated to the defective method blank are evaluated. If the analyte found in the method blank is confirmed to not be present in one or more of the associated samples at any level, the contamination did not affect those samples. This represents a non-impact situation and no specific corrective action is taken. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements. If the analyte found in the method blank is confirmed to be present in one or more of the associated samples, the concentrations are compared. If the concentration in

the method blank exceeded 10% of concentration found in one or more samples, the prescribed corrective action is to re-analyze all affected samples. If the concentration in the method blank was less than 10% of the concentration found in one or more samples, the sample can be reported by qualifying the affected analytes. A nonconformance memo (NCM) is written and discussed with the laboratory supervisor and Project Management for evaluation against project requirements.

- 14.2 **Laboratory control sample.** If the analyte is out of control for accuracy, the associated samples are evaluated. If the recovery is biased high and the associated samples have no positive results for that analyte, a non-impact situation ensues. A nonconformance memo (NCM) is written to notify project management of the situation for evaluation against project requirements. If the recovery is biased high and the associated samples have positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the recovery is biased low and the samples have no positive results for that analyte, the prescribed corrective action is reanalysis of the affected sample(s). If the analyte is out of control for precision (RPD), the associated samples are evaluated. All decisions about corrective action(s) are made in consultation with the project manager. If there are no positive results in one or more samples, a non-impact situation ensues for those samples. A nonconformance memo is written to notify project management of the situation for evaluation against project requirements.
- 14.3 If there are positive results for one or more analytes, the likelihood of poor reproducibility increases and corrective action must be evaluated. A nonconformance memo is written and discussed with the laboratory supervisor and Project Management of the situation for a project decision on whether the affected sample(s) should be reanalyzed.

#### 15.0 **Contingencies For Handling Out Of Control Data Or Unacceptable Data**

- 15.1 **Method blanks.** If there is insufficient sample to perform re-analysis; the analyst must notify the project manager for consultation with the client. In this situation, all associated samples are flagged with an "I" qualifier and appropriate comments in the narrative.
- 15.2 **LCS/LCSD.** If the batch is not reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. Acceptable matrix spike recoveries are not sufficient justification to preclude re-extraction of the batch. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation. A NCM will have to be filled out stating this problem and or a solution.
- 15.3 **Insufficient sample.** If there is insufficient sample to repeat the analysis, the situation is discussed with the project manager for consultation with the client and documentation is provided in a NCM.
- 15.4 **Procedural Variation.** One time procedural variations are allowed only if deemed necessary in the professional judgment of the analyst to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any

variation shall be completely documented using a Nonconformance Memo and approved by the Supervisor and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

- 15.5 When QC results, unknown positives, or sample matrix present the analyst with questionable data, the spike results, sample matrix, and reported positives in the batch are all to be considered. Acceptability may be determined by citing historical data on a case by case basis. The project manager must be notified of any method anomalies, and can then advise the client on the usability of the data and any other necessary actions.

## **17.0 Pollution Control**

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

## **18.0 Waste Management**

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Tampa's current revision of SOP TP-HAZ-001 *Waste Management*).

The following waste streams are produced when this method is carried out.

- Acidic waste containing nitric and hydrochloric acid is generated by the digestion. Digested samples are neutralized and poured down the drain after analysis.
- Contaminated disposable materials utilized for the analysis. The materials used in this procedure are inert and are disposed into a waste receptacle following neutralization and disposal of the digested sample(s).
- Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.
- Excess samples, reagents, and digestates must be disposed in accordance with SOP TPA-HAZ-001: *Waste Management*

## **19.0 References / Cross-References**

- 19.1 Tampa's Quality Assurance Manual (TP-QAM), current revision.
- 19.2 Corporate Environmental Health and Safety Manual (CW-E-M-001), current revision.
- 19.3 TestAmerica Tampa SOP's:
- 19.3.1 TP-HAZ-001 *Waste Management*

19.3.2 TP-AN-004: *Standard Materials and Reagent Traceability.*

19.3.3 TP-AN-005: *Definitions, Terms, and Acronyms*

19.3.4 TP-AN-009: *Conductivity Checks for Laboratory Deionized Water.*

19.3.5 Methods 7471: *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

## **20.0 Method Modifications:**

- Reduced volumes for samples and standards are used for both solids and liquid samples. Reagents and molar ratios are the same as the published methods.
- Samples are digested through the use of a digestion block with plastic digestion cups in place of 300mL BOD bottles.
- Samples, calibration curves, and QC samples are analyzed through the use of an auto analyzer.

## **21.0 Attachments**

- 21.1 Appendix A: SOP SUMMARY
- 21.2 Appendix B: Contamination Control Guidelines
- 21.3 Appendix C: Soil and Sludge Digestion Summary
- 21.4 Appendix D: Aqueous Digestion Summary
- 21.5 Figure 1: Sample Preparation Flowchart.
- 21.6 Figure 2: Sample Analysis Flowchart

## **22.0 Revision History**

- Revision 4, dated 01 March 2010
  - Incorporated TP-ME-013: *Digestion Procedure for Mercury: Digestion of Aqueous Samples for Mercury Analysis* and TP-ME-014: *Digestion Procedure for Mercury: Digestion of Solid and Sludge Samples for Mercury Analysis*.
  - Changed from 7470 and 7471B to 7470A and 7471A.
  - Added to Sections 14 through 16
  - Defined the LCR more clearly
- Revision 3, dated 15 May 2009
  - Updated to TestAmerica format, removed all STL logo's, nomenclature, etc.
  - Updated references, added TestAmerica SOP's to reference section.
  - Added revision history section
  - Added method modifications section, listed reduced volumes, digestion block & cups and use of autoanalyzer.

## Appendix A: SOP SUMMARY

### Collection, Preservation, and Hold Times

<b>Container</b>	<b>Aqueous:</b> Minimum 250mL plastic or glass bottle with a plastic or Teflon-lined lid. <b>Soils:</b> Minimum 250mL plastic or glass bottle with a plastic or Teflon-lined lid. If other metals are being tested, the aliquot form mercury may be taken from the same container
<b>Preservation</b>	<b>Aqueous:</b> HNO <sub>3</sub> to pH <2 in the field. If dissolved mercury is required, filter the samples before preservation. <b>Soils:</b> No chemical preservation required
<b>Storage</b>	<b>Aqueous:</b> Room temperature if properly preserved <b>Solids</b> should be stored at 4°C (<6°C, but not frozen) from collection until preparation.
<b>Hold Time</b>	<b>Aqueous and Soils:</b> Aqueous and Soils: Samples must be analyzed within 28 days of collection.

Wastes are treated in the same manner as soils.

ANALYTICAL SEQUENCE	
Instrument Startup	Turn on the mercury analyzer according to the instrument manufacturer's recommendations. Allow the mercury lamp Proper warm-up time. Inspect and change pump tubes and drying tubes as needed. Check and align lamp and cell According to the instrument manufacturers recommendations.
Initial Calibration	Beginning with the blank, calibrate with the blank and 5 standards. One standard must be at or below the RL.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the analysis run. The ICV Solution must come from a source other than the calibration source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with a concentration at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run. The CCV and ICV may be the same solution. Analyze a calibration blank after every CCV.
Detection Limit Check Solution	At the beginning of the analysis run, verify the accuracy at the RL by analyzing a standard with a concentration at or below the required RL.
Serial dilution	At a minimum of once per analytical batch, verify the absence of matrix interference by analyzing a serial dilution.



**Appendix A: SOP Summary (cont.'d) - QC Criteria**

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 blank and 5 standards Correlation > 0.995	Recalibrate
Initial Calibration Verification Standard (ICV) Second Source	At the beginning of the analysis	SW846 = within +/- 10% 245.1 = within +/- 5%	Recalibrate
Continuing Calibration Verification Standards (CCV)	At the beginning and end of the analysis and every 10 samples.	SW846 = within +/- 20% 245.1 = within +/- 10%	Terminate the analysis, correct the problem and reanalyze all samples since the last compliant CCV.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less than the required RL.	SW846 = terminate the analysis, Correct the problem and reanalyze all samples since the last compliant CCB.
RL standard (detection limit standard CRA)	After every calibration but not before the ICV.	50-150% of true value	Recalibrate.
Laboratory control sample (LCS)	One per batch of twenty or fewer samples	SW846 = within +/- 30% 245.1 = within +/- 15%	Redigest and reanalyze batch
Preparation Blank - SW846	One per batch of twenty or fewer samples	Result < required RL.	Re-digest and reanalyze batch (if sample result >20X the blank, the sample does not have to be re-digested/reanalyzed)
MS/MSD - SW846	One set per batch of twenty or fewer samples	%Rec = 70 – 130% %RPD = < 30%	Flag and report data
MS/MSD - 245.1	MS added to a minimum of 10% of samples	%Rec = 70 - 130%	Flag and report data
Serial Dilution Analysis (1+4 dilution)	One per batch of twenty or fewer samples	If sample is at least 25 times the instrument detection limit the serial dilution, corrected for the dilution factor, should agree within +/- 10% of the undiluted sample. (Section 10.3.5)	Note Matrix interference.

## **APPENDIX B**

### **Contamination Control Guidelines**

#### **The following procedures are strongly recommended to prevent contamination:**

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

#### **The following are helpful hints in the identification of the source of contaminants:**

Reagents or standards can contain contaminants or be contaminated with improper use of a pipette. Never pipette directly from a stock standards bottle.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

## APPENDIX C

### Mercury Soil and Sludge Digestion SOP- Summary

#### Standards/QC Prep:

Final volume-	50mL
Blank-	0.0
Low (CRI)-	0.2ppb
	0.50ppb
	1.00ppb
Med. (CCV)-	5.0ppb
High-	10.0ppb

#### Sample/MS/MSD Prep:

- Step 1** Weigh 0.3g of sample into a 50mL plastic digestion cup (MS/MSD included as samples) For MB, LCS, and curve weigh 0.3g of Teflon boiling chips.
- Step 2** Add 10mL DI water to each sample bottle and 2.0mL DI water to the LCS, MS, MSD.  
Spike QC (working stock)  
Pipette 1.00mL of the ICV working stock solution into each of the LCS & MS/MSD samples. Bring to final volume of 10mL after spiking.
- Step 3** Add 2.5mL Aqua Regia to each bottle and heat at 95°C for 2 minutes. Remove samples from heat source and allow samples to cool.
- Step 4** Once samples have cooled, add 25mL of DI
- Step 5** Add 7.5mL of  $\text{KMnO}_4$  to each sample and to each standard. Cap and shake vigorously then let the samples equilibrate for 15 minutes.
- Step 7** Heat samples for **30 minutes** in a digestion block that has been heated to 95°C
- Step 6** Remove from digestion block, cool, add 3.0mL of hydroxylamine to samples and to standards.
- Step 8** Bring all samples up to a final volume of 50mL, cap and shake vigorously.

**Samples are now ready for analysis.**

#### **Reagents and Standards:**

Stannous Chloride – 25g to 250mL of DI plus 50ml of HCL.

Hg stock solution – 1000ppm; Intermediate Solution – 10.0ppm; Working Stock – (ICV & CAL) – 50.0ppb

Aqua Regia – 3:1 ratio of HCl:  $\text{HNO}_3$  (30mL HCl plus 10mL  $\text{HNO}_3$  for example)

$\text{KMnO}_4$  – Dissolve 5.0g of  $\text{KMnO}_4$  for every 100mL DI.

Hydroxylamine – Dissolve 12g NaCl and 12g of hydroxylamine hydrochloride for every 100mL.

## Appendix D

### Mercury Aqueous Digestion SOP Summary

#### Standards/QC Prep:

25mLs of DI water into a 50mL Hg digestion vial

Blank- 0.0

Low (CRI)- 0.2ppb

0.50ppb

1.00ppb

Med. (CCV)- 5.0ppb

High- 10.0ppb

#### Sample/MS/MSD Prep:

- Step 1** Shake well and pipette 25mL of each sample into a 50mL disposable digestion cup (MS/MSD included as samples)
- Step 2** Spike QC (working std.)  
Pipette 0.5mL of the ICV working std. solution into 24.5mL of the LCS & MS/MSD samples
- Step 3** Add 0.62mL of  $\text{HNO}_3$  to each sample and to each standard.
- Step 4** Add 1.25mL of  $\text{H}_2\text{SO}_4$  to each sample and to each standard.
- Step 5** Add 3.75mL of  $\text{KMnO}_4$  to each sample and to each standard. Cap and shake vigorously then let the samples equilibrate for 15 minutes.
- Step 6** Add 2mL of potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) to each sample and to each standard.
- Step 7** Heat samples and standards at  $95^\circ\text{C}$  in a hot block for 2hrs. Record the hot block temperature.
- Step 8** Remove from water bath, cool, add 1.5mL of hydroxylamine to samples and to standards.

**Samples are now ready for analysis.**

#### **Reagents and Standards:**

Stannous Chloride – 25g to 250mL of DI plus 50ml of HCL

Hg stock solution – 1000ppm; Intermediate Solution – 10ppm; Working Stock – (ICV & CAL) – 50.0ppb

Potassium Persulfate - Dissolve 5g of  $\text{K}_2\text{S}_2\text{O}_8$  for every 100mL DI

$\text{KMnO}_4$  – Dissolve 5g of  $\text{KMnO}_4$  for every 100mL DI

Hydroxylamine – Dissolve 12g NaCl and 12g of hydroxylamine hydrochloride for every 100mL.

Figure 1: Sample preparation flowchart

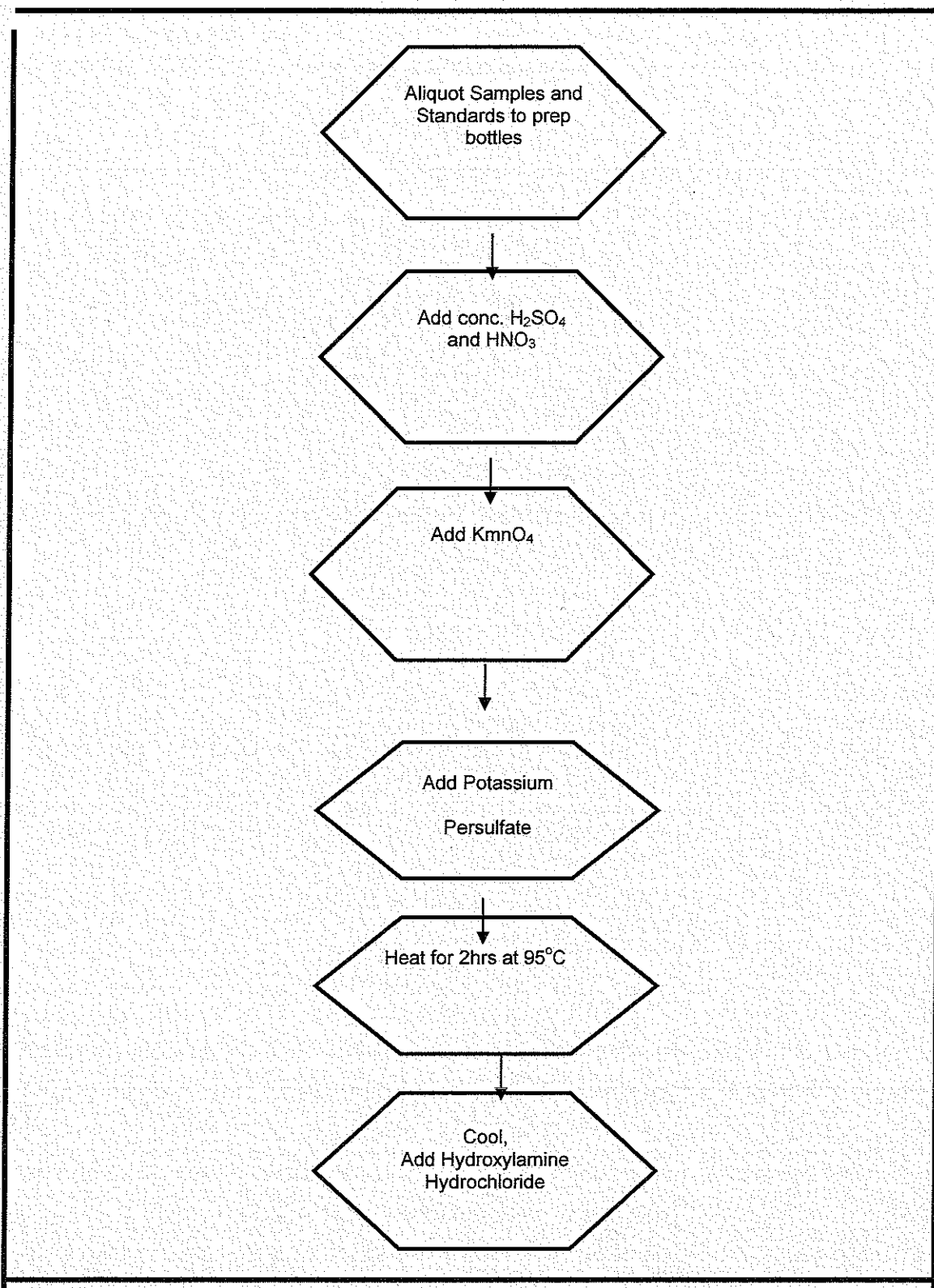


Figure 2: Sample analysis flowchart

