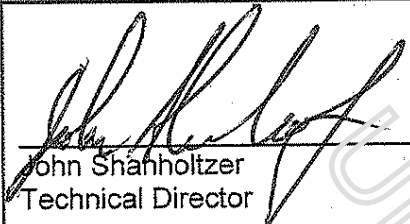
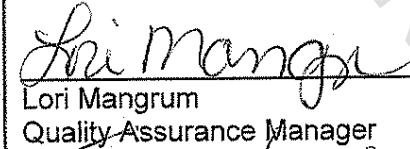
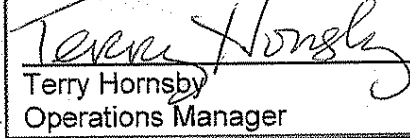
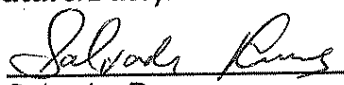
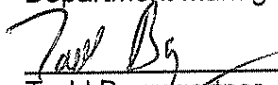


**Title: DIGESTION PROCEDURE FOR ICP: TOTAL METALS AND TOTAL RECOVERABLE METALS IN LIQUID SAMPLES**

**Methods: SW-846 EPA 3005A, 3010A, EPA 200.7**

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## 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 digest water, drinking water, wastewater, and leachate samples prior to the analysis by ICP (SOP TP-ME-001) using SW-846 Method 3005A, 3010A and MCAWW Method 200.7.

SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP.

SW-846 Method 3010A is used to prepare aqueous samples, TCLP leachates, and wastes that contain suspended solids for total metals analysis by ICP.

MCAWW Method 200.7 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

The SOP is based on the guidance in SW-846 Methods 3005A and 3010A and EPA Method 200.7. Note that EPA has promulgated two procedures as EPA 200.7—one for drinking water and one for NPDES. The digestion procedures for both 200.7 methods are performed in the same manner as 3005A for total recoverable metals and dissolved metals, and 3010A for total metals and dissolved metals.

The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in the Methods Limit Group (MLG) in TestAmerica Tampa's LIMS (EALS). The detection limits are also found in the SOP TP-ME-001: *Elements by ICP (200.7 and 3010B)*.

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

Total metals and TCLP leachates (Method 3010A / 200.7): A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with nitric acid at approximately 95°C. After sample has digested, as evidenced by a clear, pale yellow color, HCl is added and the sample is brought up to the original volume with reagent water.

Total recoverable metals (Method 3005A / 200.7): A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with dilute nitric acid and hydrochloric acid at approximately 95°C. After sample has evaporated to approximately 10-20mL, the sample is brought up to the original volume with reagent water.

Drinking water samples with a turbidity concentration of less than 1 NTU can be analyzed with no digestion if the required quantitation limits can be achieved with no sample preconcentration. The exception to this rule is silver, which requires sample digestion prior to analysis.

Samples filtered for the determination of dissolved metals do not require digestion if the sample:

- 1) has a low COD(<20mg/L);
  - 2) has a turbidity <1 NTU ;
  - 3) is colorless with no significant odor ; and
  - 4) is of one liquid phase and free of suspended particulates or precipitates after acidification
- (40 CFR Part 136 Table 1B-note 4)

### 3.0 Definitions

3.1 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.

3.2 Analytical Spike or Post-Digestion Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed

3.3 Digestate - The digested sample.

3.4 Dissolved metals – Those elements that pass through a 0.45µm membrane. (Sample is acidified after filtration).

3.5 Suspended metals – Those elements that are retained by a 0.45µm membrane.

3.6 Total metals – The concentration determined on an unfiltered sample following digestion.

3.7 Total recoverable metals – The concentration determined on an unfiltered sample following treatment with hot, dilute acid.

3.8 TCLP – Toxicity Characteristic Leaching Procedure

### 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 C for additional contamination control guidelines.

4.3 Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

- 4.4 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.
- 4.5 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.
- 4.6 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony and arsenic are easily lost by volatilization.
- 4.7 Precipitation of silver chloride ( $\text{AgCl}$ ) may occur when chloride ions and high concentrations of silver (i.e., greater than 1mg/L) are present in the sample.
- 4.8 Specific analytical interferences are discussed in each of the determinative methods.

## **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 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.1.2 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.
- 5.1.3 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 breathed.
- 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 cups. 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. On analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.
- 5.1.7 All work must be stopped in the event of a known or potential compromise to the health and safety of a Tampa associate. The situation must be reported **immediately** to a laboratory supervisor.
- 5.1.8 Always carry bulk concentrated acid bottles in appropriate impact proof containers.
- 5.1.9 Acid / peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.
- 5.1.10 Discard cracked or dirty digestion cups to prevent injury and or contamination. Dispose of the cracked or dirty vessels in the proper receptacle.
- 5.1.11 Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

## 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
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-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	5 ppm-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.
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

- Hot plate or digestion block-capable of maintaining a sample temperature of 95°C+/-5°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.

- Analytical balance capable of accurately weighing to the nearest 0.01 grams.

### 6.2 Supplies

- Digestion vessels: Teflon or Pyrex beakers, 150mL and 250mL, or comparable digestion vessels (250mL beakers are listed in the preparation steps but smaller digestion block vessels can be substituted)
- Watch glasses, "ribbed", to fit over digestion vessels (not required for block digestion vessels)
- Class A Volumetric flasks- 100mL or appropriate volume
- Graduated cylinders-50mL
- Pipettes, repipetors, and Class A glass volumetric pipettes.
- Funnels or equivalent filtration apparatus (i.e., 10cc syringe).
- Whatman No. 41 filter paper or equivalent.
- Thermometer that covers a temperature range of 0°C-200°C.
- pH indicator strips (pH range 0 – 6).
- Plastic digestate storage bottles.

## 7.0 Reagents and Standards

All reagents are to be labeled with their unique TALS ID, including name of the material, concentration, date prepared/received, expiration date, and analyst name, according to SOP TP-AN-004, *Standard Material and Reagent Traceability*. Calibration solutions are prepared from either certified stock solutions, from stock solutions purchased from vendors, or from stock standards prepared from neat materials. See SOP TP-AN-011: *Standard Preparation* for guidance in standard preparation. Certificates of analysis or purity must be received with all neat compounds and stock solutions and scanned into TALS.

The expiration date of the spiking solutions is 180 days from the date of preparation or the expiration date of the stock(s) used to prepare the spiking solution (if expiration date of the stock is less than 180 days). The lab should purchase certified solutions from TestAmerica-approved vendors, if available.

7.1 Reagents water-lab generated deionized 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>)-trace metal grade. The assay sheet of each lot of acid received

into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.3 Hydrochloric acid (HCl)-trace metal grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.4 Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking solutions. The following equation can be used:

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

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  $C_f$ .

7.5 Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased. The concentrations of the analytes in this solution are listed on the accompanying certificate of analysis. Store this solution at room temperature. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. (QC21 and QC7).

7.6 Working LCS / MS spike solutions: The LCS/MS working spike solutions are provided directly by the vendor, no further standard preparation is necessary.

7.7 The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom TA Tampa solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.8 TCLP Laboratory Control Sample and Matrix Spiking Solutions are purchased. The concentrations of the analytes in this solution are listed on the accompanying certificate of analysis. Store this solution at room temperature. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. (QC21 and QC7).

## **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	Reference
Waters <sup>2</sup> TCLP leachates	HDPE	250mLs 500mLs	HNO <sub>3</sub> , pH < 2;	180 Days	40 CFR Part 136.3

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

<sup>2</sup>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.

8.1 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.

8.2 All samples should be verified for proper preservation and residual chlorine upon arrival in the lab. If chlorine and/or pH are not appropriate, the samples will be marked for the deficiency. Appropriate steps must be taken by the analyst to adjust the pH and chlorine if samples are not properly preserved. If the pH is not within the proper range, additional acid is added to the sample to bring the pH below 2. Acid or sodium hydroxide can be added to samples to adjust the pH; and sodium thiosulfate is added for residual chlorine.

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

8.2.2 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.

8.2.3 If the pH is greater than 2, contact the Project Manager to get approval to adjust the pH. If approved, document the anomaly via a NCM. 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.

8.2.4 After pH adjustment, samples must be held for 18 hours prior to analysis. The pH is verified and documented at the 18 hour mark.

**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 for additional information relating to the QC associated with this method. Appendix A provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

Conditions must be the same for all standards, samples and QC samples.

### 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 Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.1.2.1 Sample Count - Laboratory generated QC samples (Method Blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as 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	Statistical Limits <sup>2</sup>
Laboratory Control Sample (LCSD)*	1 in 20 or fewer samples	Statistical Limits <sup>2</sup>
Matrix Spike (MS) <sup>1,3</sup>	1 in 20 or fewer samples	Statistical Limits <sup>2</sup>
MS Duplicate (MSD) <sup>1,3</sup>	1 in 20 or fewer samples	Statistical Limits <sup>2</sup>

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> For EPA 200.7 MS/MSD is required every 10 samples

9.1.3 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 redigested.

9.1.3.1 Aqueous method blanks are prepared by taking 50mL or 50g of reagent water through the appropriate procedure.

9.1.3.2 TCLP method blanks are prepared by taking 50mL or 50g of

leachate fluid blank through the appropriate procedure.

- 9.1.4 Laboratory Control Samples (LCS) - One aqueous 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. Ongoing 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.

9.1.4.1 The aqueous LCS is prepared by spiking a 50mL aliquot of reagent water with 0.50mL of QC 21 and QC 7 -LCS/MS spike solutions and 0.045mL of 1000 mg/L Na Stock Solution for the ICP.

9.1.4.2 The TCLP LCS is prepared by spiking a 50mL aliquot of reagent water with 0.50mL of QC 21 and QC 7 -LCS/MS spike solutions and 0.045mL of 1000 mg/L Na Stock Solution for the ICP.

- 9.1.5 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/MSDs. 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.

9.1.5.1 The aqueous MS/MSD sample is prepared by spiking a 50mL aliquot of reagent water with 0.50mL of QC 21 and QC 7 -LCS/MS spike solutions and 0.045mL of 1000 mg/L Na Stock Solution for the ICP.

9.1.5.2 The TCLP matrix spike sample is prepared by spiking a 50mL aliquot of reagent water with 0.50mL of QC 21 and QC 7 -LCS/MS spike solutions and 0.045mL of 1000 mg/L Na Stock Solution for the ICP.

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

9.1.5.3 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 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) and Initial Calibration Blank (ICB).

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

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

9.2.4 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.

9.2.5 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.

9.2.6 Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

## 10.0 Procedure

### 10.1 Sample Preparation

10.1.1 Unless otherwise requested, groundwater and surface waters will be prepared using the total recoverable metals procedure. TCLP samples must be digested for total metals.

10.1.2 Drinking water samples with a turbidity concentration of less than 1 NTU can be analyzed with no digestion if the required quantitation limits can be achieved with no sample preconcentration. The exception to this rule is silver, which requires sample digestion prior to analysis. The turbidity of drinking water samples can be checked using the procedures in SOP TP-GE-014: *Turbidity*. If the turbidity of the sample is not checked, the digestion procedure must be performed. If silver must be determined in a drinking water sample, the sample must be digested.

10.1.3 Samples filtered for the determination of dissolved metals do not require digestion if the sample (40 CFR Part 136 Table 1B-note 4):

10.1.3.1 has a low COD(<20mg/L)

10.1.3.2 has a turbidity <1 NTU

10.1.3.3 is colorless with no significant odor

10.1.3.4 is of one liquid phase and free of suspended particulates or precipitates after acidification

#### 10.1.4 Total Recoverable Metals: Aqueous Samples (Method 3005A and 200.7)

This digestion procedure is used for the preparation of aqueous samples for total recoverable metal determination by ICP (or flame AA).

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

**NOTE:** If there is not sufficient volume to use a 50mL 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 25mL 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 25mL. 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 Report and is approved by a Department Manager and QA Manager. The NCM shall be filed in the project file.

10.1.4.2 Add 50mL of reagent water to a digestion cup 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.

10.1.4.3 Add 0.50mL of the appropriate spiking solutions to a 50mL aliquot of reagent water designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

10.1.4.4 Add 0.50mL of the appropriate spiking solutions to each of two 50mL aliquots of the client sample designated as the matrix spikes sample (MS and MSD).

10.1.4.5 Record the following information on the digestion log:

10.1.4.5.1 date

10.1.4.5.2 analyst's initials

10.1.4.5.3 sample identification

10.1.4.5.4 the volume of sample digested

10.1.4.5.5 batch identification

10.1.4.5.6 temperature of the digestion block (daily)

10.1.4.5.7 the lot number of the acids used for the digestion

10.1.4.5.8 the lot number of the ICP spiking solutions

10.1.4.5.9 the time that the digestion was started

10.1.4.5.10 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).

10.1.4.6 Add 2.0mL of concentrated HCl and 2.0mL of concentrated HNO<sub>3</sub> to each sample.

10.1.4.7 Cover each beaker with a watch glass (a watch glass is not required for the digestion block). Gently heat the beaker until the sample refluxes.

**NOTE:** The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker.

10.1.4.8 Evaporate the sample until the volume is approximately 15mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

**NOTE:** If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.4.9 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50mL with reagent water.

**NOTE:** The digestate may be diluted to a volume less than the original volume if sample concentration is required to meet lower reporting limits. The pre-concentration must be limited to a factor of four (4).

10.1.4.10 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

#### 10.1.5 Total Metals: Aqueous Samples (Method 3010A and 200.7)

This digestion procedure is used for the preparation of aqueous samples for total metal determination by ICP (or flame AA). This digestion procedure is not suitable for samples that will be analyzed by graphite furnace atomic absorption (GFAA) because hydrochloric acid (HCl) can cause interferences during furnace atomization.

10.1.5.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a clean 250mL Teflon beaker or other suitable digestion vessel.

**NOTE:** If there is not sufficient volume to use a 50mL 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 25mL 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 25mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

10.1.5.2 Add 50mL of reagent water to a beaker 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.

10.1.5.3 Add 0.50mL of the appropriate spiking solutions to a 50mL aliquot of reagent water designated as the laboratory control spikes (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

10.1.5.4 Add 0.50mL of the appropriate spiking solutions to two 50mL aliquots of the client sample designated as the matrix spikes samples (MS and MSD).

10.1.5.5 Record the following information on the digestion log:

10.1.5.5.1 date

10.1.5.5.2 analyst's initials

10.1.5.5.3 sample identification

10.1.5.5.4 the volume of sample digested

10.1.5.5.5 batch identification

10.1.5.5.6 temperature of the hot plate or digestion block (daily)

10.1.5.5.7 the lot number of the acids used for the digestion

10.1.5.5.8 the lot number of the ICP spiking solutions

10.1.5.5.9 the time that the digestion was started

10.1.5.5.10 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).

10.1.5.6 Add 1.5mL of concentrated  $\text{HNO}_3$  to each sample.

10.1.5.7 Cover each beaker with a watch glass (a watch glass is not required for the digestion block).

10.1.5.8 Gently heat the beaker until the sample refluxes.

**NOTE:** The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker.

10.1.5.9 Evaporate the sample until the volume is approximately 5-10mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

**NOTE:** If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

- 10.1.5.10 Remove the beakers from the hot plate and cool the beakers to room temperature. Add another 1.5mL portion of concentrated  $\text{HNO}_3$ . Replace the watchglass and continue heating the sample on the hot plate. Again, at the proper temperature, the sample should gently reflux in the beaker-do not allow the sample to boil.
- 10.1.5.11 Continue heating the sample and adding additional 1.5mL portions of concentrated  $\text{HNO}_3$  until the digestate is light in color or does not change in appearance after subsequent additions of  $\text{HNO}_3$ . If a sample requires more than 6mL of acid to digest, contact the digestion lab supervisor for guidance.
- 10.1.5.12 Evaporate the digestate (covered with the watch glass) until the volume is approximately 5-10mL.
- 10.1.5.13 Remove the watch glass and add a 2.5mL of concentrated  $\text{HCl}$ . Replace the watchglass on the beaker and warm the sample digestate for 15 minutes.
- 10.1.5.14 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50mL with reagent water.

**NOTE:** The digestate may be diluted to a volume less than the original volume if sample concentration is required to meet lower reporting limits. The pre-concentration should be limited to a factor of four (4).

- 10.1.5.15 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

#### 10.1.6 Total Metals: TCLP Samples

This digestion procedure is used for the preparation of TCLP leachate samples for total metal determination by ICP. This digestion procedure is not suitable for samples that will be analyzed by graphite furnace atomic absorption (GFAA) because hydrochloric acid ( $\text{HCl}$ ) can cause interferences during furnace atomization. Note that the LCS is spiked with the routine analytes to allow the TCLP samples to be digested along with aqueous samples. A MS for TCLP must be analyzed for each waste type.

- 10.1.6.1 Transfer a 50mL aliquot of a well-mixed sample to a clean 50mL Teflon vial or other suitable digestion vessel. The volume of spike solution added should be adjusted proportionately.
- 10.1.6.2 Add 50mL of extraction fluid to a beaker 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. A blank for each type of extraction fluid must be digested and analyzed.
- 10.1.6.3 Add 0.50mL of the appropriate spiking solutions to a 50mL aliquot of extraction fluid. This is designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is

required, spike a second 50mL aliquot of extraction fluid with 0.50mL of the appropriate spiking solutions. Preparing a LCS with all of the target analytes eliminates re-digestion and provides QC for the requested analytes.

**NOTE:** If both extraction fluid I and extraction fluid II are included in the batch, use extraction fluid I for the LCS and LCSD.

10.1.6.4 Add 0.50mL of each ICP TCLP spiking solution to a separate 5.0mL aliquot of the client sample (diluted to 50mL) designated as the matrix spike.

10.1.6.5 Record the following information on the digestion log:

10.1.6.5.1 date

10.1.6.5.2 analyst's initials

10.1.6.5.3 beaker ID#

10.1.6.5.4 sample identification

10.1.6.5.5 the volume of sample digested

10.1.6.5.6 batch identification

10.1.6.5.7 temperature of the hot plate or digestion block (daily)

10.1.6.5.8 the lot number of the acids used for the digestion

10.1.6.5.9 the lot number of the ICP spiking solutions

10.1.6.5.10 the time that the digestion was started

10.1.6.5.11 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), and a matrix spike.

10.1.7 Add 1.5mL of concentrated  $\text{HNO}_3$  to each sample.

10.1.8 Cover each beaker with a watch glass (a watch glass is not required for the digestion block). Gently heat the beaker until the sample refluxes.

**NOTE:** The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker.

10.1.9 Evaporate the sample until the volume is approximately 15-20mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

**NOTE:** If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

10.1.10 Remove the beakers from the hot plate and cool the beakers to room temperature. Add another 1.5mL portion of concentrated  $\text{HNO}_3$ . Replace the watchglass and continue heating the sample on the hot plate. Again, at the proper temperature, the sample should gently reflux in the beaker-do not allow the sample to boil.



- 10.1.11 Continue heating the sample and adding additional 1.5mL portions of concentrated  $\text{HNO}_3$  until the digestate is light in color or does not change in appearance after subsequent additions of  $\text{HNO}_3$ . If a sample requires more than 6mL of acid to digest, contact the digestion lab supervisor for guidance.
- 10.1.12 Evaporate the digestate (covered with the watch glass) until the volume is approximately 5-10mL.
- 10.1.13 Remove the watch glass and add 2.0mL of concentrated HCl. Replace the watchglass on the beaker and warm the sample digestate for 15 minutes.
- 10.1.14 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50mL with reagent water.
- 10.1.15 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

## 10.2 Calibration

- 10.2.1 Samples are calibrated in accordance with TestAmerica Tampa SOP TP-ME-001 *Elements by ICP (EPA 200.7/6010C)*.

## 10.3 Sample Analysis

- 10.3.1 Samples are analyzed in accordance with TestAmerica Tampa SOP TP-ME-001 *Elements by ICP (EPA 200.7/6010C)*.

## 11.0 Calculations / Data Reduction

- 11.1 Calculations for the determination of metals by ICP are given in SOP TP-ME-001: *Elements by ICP (EPA 200.7/6010C)*.

## 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 in 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.
- 12.2 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 method detection 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 judgement 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.

- 14.2.1** 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 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. An 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 an NCM.

## 16.0 **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."

## 17.0 **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.

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

- Acidic waste containing nitric acid generated by the extraction: Acid waste is to be neutralized and poured down the drain.

## 18.0 **References / Cross-References**

18.1 Standard Methods for the Examination of Water and Wastewater, 21<sup>th</sup> edition, Method 3030C. 2005.

18.2 Tampa's Quality Assurance Manual (TP-QAM), current revision.

18.3 Corporate Environmental Health and Safety Manual (CW-E-M-001), current revision.

18.4 TestAmerica Tampa SOP's:

18.4.1 TP-HAZ-001 *Waste Management*

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

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

18.4.4 TP-AN-009 *Conductivity Checks For Laboratory Deionized Water*.

18.4.5 TP-ME-001 *Elements by ICP (EPA 200.7/6010C)*

#### **19.0 Method Modifications:**

Not applicable to this SOP.

#### **20.0 Attachments**

Appendix A: Summary of Quality Control Requirements  
Appendix B: Contamination Control Guidelines

#### **21.0 Revision History**

- Revision 3, dated 15 February 2010
  - Updated format
  - Added Sections 13 through 15
  - Added Operator's Manager
  - Updated dates to 2010
- Revision 2, 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

## APPENDIX A

### Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Lab control sample	One per batch of twenty samples or less	6010C: TP-QAM 200.7: 85-115%	Redigest and reanalyze batch
Preparation blank - SW846	One per batch of twenty samples or less	result  <RL or result <5% of the analyte level in the sample.	Redigest and reanalyze batch
Preparation blank - 200.7	One per batch of twenty samples or less	result  <RL or result <10% of the analyte level in the sample	Redigest and reanalyze batch
MS/MSD - SW846	One set per batch of twenty samples or less	TP-QAM	Flag and report data

## **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.

