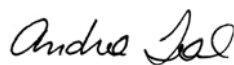



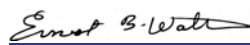
ELEMENTS BY ICP

(Methods: EPA 200.7, 6010B, and 6010C)

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1.0 **Scope and Application**

This SOP gives the procedures for the determination of metals (elements) by inductively coupled plasma (ICP) atomic emission spectroscopy.

The routine matrices for this procedure are waters and soils; however, this procedure may be adapted to accommodate other matrices as outlined in Section 16.1.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 **Summary of Method**

Prior to analysis by ICP, the sample must be digested/filtered using the sample preparation method appropriate to the analyte/matrix combination. Sample digestates/filtrates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT) or onto a charge-coupled device (CCD). The PMTs and CCDs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

Note: Drinking water samples (EPA 200.7) only require digestion if the determination of silver (Ag) is requested or if the turbidity is greater than or equal to 1.0 NTU.

This SOP is based on the following methods: EPA 200.7, EPA 6010B, and EPA 6010C.

3.0 **Definitions**

Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 **Interferences**

4.1 **Procedural Interferences**

- 4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

- 4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.
- 4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.
- 4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.
- 4.1.5 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample digestate, using a peristaltic pump, using the method of standard additions (MSA), or using an internal standard.

4.2 Matrix Interferences

- 4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences.
- 4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.
- 4.2.3 Spectral interferences are caused by the overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous phenomena, and stray light from the line emissions of highly concentrated elements.
 - 4.2.3.1 Spectral overlap may be compensated for by the use of inter-element correction factors.
 - 4.2.3.2 Background contribution and stray light can be compensated for by a background correction adjacent to the analyte line.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, 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 to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable latex or nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

The plasma generates high temperatures. Analysts must ensure that all equipment is shut down and cooled off before performing maintenance and troubleshooting in the plasma area.

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

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. Electronic copies of MSDS can be found using the "MSDS Online" button on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit ¹	Signs and symptoms of exposure
Hydrochloric Acid ²	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.
Nitric Acid ²	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.
¹ Exposure limit refers to the OSHA regulatory exposure limit.			
² Always add acid to water to prevent violent reactions.			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Thermo Jarrell Ash TJA ICAP61E-trace, Varian 730 ES, or other suitable inductively coupled plasma emission spectrometer with data system

Top-loading Balance – Verify in accordance with SOP SA-AN-10: *Balance Calibration and Use*

6.2 Lab Supplies

Argon gas supply and appropriate fittings

Cooling water supply

Peristaltic pump

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Pump-style Pipettes – various sizes. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step. pH paper should be checked upon receipt, as follows, to make sure that it is functioning properly.

- Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
- Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper.
- Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

Detergent – used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers provided by the laboratory are as follows:

Waters: 250mL Plastic – purchased with Certificate of Analysis attesting to purity.

Solids: 8oz Plastic or Glass Jar – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard must not exceed the expiration date of the standard that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

- 7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.
- 7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

- 7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date.
- 7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.
- 7.1.5 The expiration date for prepared standards is 6 months from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*.

Hydrochloric acid and nitric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

- 7.2.1 Laboratory Reagent Water – ASTM Type I. The conductivity must be monitored in accordance with SOP AN35: *Conductivity Checks for DI Water*.
- 7.2.2 Nitric acid (HNO₃) – reagent grade. Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.
- 7.2.3 Hydrochloric acid (HCl) – reagent grade. Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials. Stable under ordinary conditions of use and storage.

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*. Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Refer to Attachments 5 and 6 for standard preparation information.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples are routinely collected in 250mL plastic containers containing 1.5mL 1:1 nitric acid preservative or 500mL plastic containers containing 3.0mL 1:1 nitric acid preservative. The preservative should be sufficient to achieve a sample pH of less than 2.

If dissolved metals are requested the sample must be filtered prior to the addition of the preservative. If the sample is to be filtered by the laboratory, the sample must be collected in a 250mL plastic container without preservative. The samples must be acidified with 1.25mL concentrated nitric acid to a pH<2 after filtration.

Samples are stored at room temperature until the time of digestion. Samples must be

digested within 6 months of collection. Digestates are stored at room temperature until the time of analysis and must be analyzed within 6 months of collection.

8.2 Soil Samples

Soil samples are routinely collected in 8oz plastic or glass containers.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of digestion. Samples must be digested within 6 months of collection. Digestates are stored at room temperature until the time of analysis and analyzed within 6 months of collection.

9.0 Quality Control

SOP SA-QA-17: *Analytical Batching and Evaluation of QC Data* and the SOP Summary in Attachment 4 provide requirements for evaluating QC data.

9.1 Batch QC

9.1.1 EPA 200.7 – Drinking Water

A digestion batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The minimum QC items required for each digestion batch are: a method blank and a laboratory control sample (LCS), and a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, and 1 matrix spike.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), and another matrix spike (from sample 11-20).

The routine container supplied for this method is a 250mL container. 50mL is required for digestion. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL.

Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method. For clients who require precision to be reported, the matrix spike must be prepared in duplicate (i.e., MS/MSD). If precision is required for the project and insufficient sample

volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples by EPA 200.7, an LCS at the RL must also be included in the required batch QC.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.2 EPA 200.7 – Clean Water Act

An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The minimum QC items required for each extraction batch are: a method blank and a laboratory control sample (LCS), a matrix spike (MS) to be performed on a minimum of 10% of samples or one per batch – whichever is greater, and a matrix spike duplicate.

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and a matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20), and a matrix spike duplicate.

The routine container supplied for this method is a 250mL container. 50mL is required for extraction. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL.

Note: There is no method-defined batch precision requirement for this method; however, the EPA does require precision for all samples analyzed under the Clean Water Act. If insufficient sample volume is provided to perform the MS/MSD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of the associated analytical SOP.

9.1.3 EPA 6010B and EPA 6010C

A digestion batch consists of up to 20 environmental samples and the associated QC items. The minimum QC items required for each digestion batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) or a sample duplicate. If there is insufficient sample to perform the MS/MSD or sample

duplicate, this situation must be noted in the Batch Information section of the extraction log.

The routine container supplied for this method is a 250mL (water) or 8oz (soil) container. 50mL or 1g are required for digestion. Reduced sample initial volumes may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 25mL or 0.5g.

Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 100mL or 2g.

Note: If insufficient sample volume is provided to perform the MS/MSD or MS/SD, the LCS must be prepared in duplicate (LCS/LCSD). An NCM must be initiated on all samples within the batch to denote this situation

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.1.3 Preparation SOPs

Refer to the following SOPs for specifics on the preparation process:

Matrix	SOP
Water Samples	SA-ME-50
Soil Samples	SA-ME-51

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve must consist of at least one standard (the high standard) and a blank. If a multi-point curve is requested, the calibration curve must consist of a minimum of 3 standards and a blank. The initial calibration standard concentrations currently in use in the laboratory for a multi-point curve included in Attachment 5.

Note: Refer to Attachment 5 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

Tabulate the concentrations and corresponding responses for each analyte. Establish a calibration curve by plotting the concentration along the x-axis and the corresponding response along the y-axis.

The correlation coefficient (r) of the regression curve must be greater than or equal to 0.998 for the initial calibration curve to be acceptable.

If a multi-point calibration curve is used, the upper limit of the linear range is the concentration of the High Standard.

9.2.2 High Standard Read Back

The highest concentration calibration standard must be reanalyzed as an "unknown" after the instrument is calibrated. The results for the re-analysis of the highest concentration calibration standard must be within $\pm 5\%$ of the true value for each target analyte. If the result for any target analyte is outside of this range, the ICP may need to be "profiled" and the standardization/calibration repeated.

9.2.3 Second Source Initial Calibration Verification (ICV)

The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV must be within 10% of the true value to be acceptable for EPA 6010B and EPA 6010C. The ICV must be within 5% of the true value with a %RSD $\leq 3\%$ to be acceptable for EPA Method 200.7.

Note: For the Thermo Trace instrument, 2 replicates are analyzed. For the Varian 730 ES instrument, 3 replicates are analyzed.

The initial calibration verification standard concentration currently in use in the laboratory is given in Attachment 5. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed immediately following the initial calibration. Continuing calibration blanks must be analyzed immediately following each continuing calibration verification (CCV).

The absolute value of the initial and continuing calibration blanks must be $< \frac{1}{2}RL$ to be acceptable for EPA 6010C and EPA Method 200.7. The absolute value of the initial and continuing calibration blanks must be less than 3x the IDL or less than the RL, whichever is smaller, for EPA 6010B.

9.2.5 Continuing Calibration Verification

The initial calibration curve must be verified every 10 samples with a mid-level standard.

The CCV must be within 10% of the true value to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to half the concentration of the High Standard. Refer to Attachment 5 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.6 Internal Standard (ISTD)

This procedure is an internal standard (ISTD) procedure. Yttrium is used as the internal standard for the Thermo Trace ICP (ICP-D) and the Varian 730ES ICP (ICP-E). Scandium may be used as an alternate ISTD for the Varian 730ES ICP.

The internal standard must be added to all standards, samples, and QC items prior to analysis. This is accomplished by means of an additional channel on the peristaltic pump and connected to the sample line with a 'T' or 'Y' connector fitting. This ensures constant concentration of the internal standard and eliminates the possibility of human spiking error. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. A concentration of 7mg/L is used for Yttrium and Scandium.

Any sample containing ISTD recoveries greater than 120% must be diluted and re-analyzed. Although ISTD recoveries less than 50% are extremely rare, the analyst should consider further dilution if this situation occurs.

9.2.6.1 Ionization Effects

High concentrations of some elements, such as Na, K, Ca, and Mg, can produce interferences from their ionization effects. The introduction of additional ions in abundance, such as Lithium, will minimize this interference. Therefore, Lithium is added to the internal standard solution, and is continually pumped at a constant rate.

See Attachment 5 for details on the preparation of the internal standard solution.

9.2.7 Reporting Limit Check Standard

A reporting limit (RL) check standard is used to demonstrate that the ICP is capable of detecting the target compounds at or below the reporting limit. EPA 200.7 requires this check only when utilizing a single point calibration. EPA 6010C requires this check for both single point and multi-point calibrations.

The concentrations in the RL check standard must be at levels that are less than or equal to the reporting limit for the samples being analyzed. The determined concentration must be detected within $\pm 50\%$ (for EPA 200.7) or $\pm 30\%$ (for EPA 6010C) of the true concentration. The RL check standard must be analyzed at the beginning and end of an analysis run (i.e., all samples must be bracketed by this check standard).

EPA 6010B does not require a RL check standard; however, it is the laboratory's standard practice to analyze and evaluate this check standard for EPA 6010B using the criteria outlined in EPA 200.7.

Note: This RL Check Standard is referred to as the LLICV and LLCCV in EPA 6010C.

9.2.8 Interference Check Standards

The purpose of the Interference Check Standard is to prove that the instrument software is adequately correcting for common interferences through the use of interelement correction factors. The concentrations of the target analytes must be within 20% of the true concentrations to be acceptable. The analyst must pay particular attention to false positives and false negatives for elements not present in the interference check solutions.

9.2.9 Serial Dilution

A dilution must be prepared and analyzed on one sample per batch to determine if matrix interferences are present. Compare the results of the diluted and un-diluted aliquots of sample digestate for analytes that are present in the native sample at a concentration $\geq 50 \times$ IDL.

If the results of the dilution are within $\pm 10\%$ of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than $\pm 10\%$, a matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike.

9.2.10 Post-Digestion Spike

A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. The sample selected as the post-digestion spike should be the same sample selected for serial dilution.

The post-digestion spike must be within 20% of the true value to be acceptable. The following table lists corrective action to be taken if these criteria are not met.

Result of Post-Digestion Spikes	Action
Within 80-120% limits	None
>120% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample
<80% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA 4) Qualify all associated samples
<50% recovery	Dilute digestate and repeat spike. <i>Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples)</i> If recoveries are not 80-120%, all associated samples may be re-analyzed by single point MSA. Note: High levels of target analytes may inhibit spike recovery. Consult the Department Manager in events where high levels of targets appear to be interfering

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

9.2.11 Single Point Method of Standard Additions

Two identical aliquots of the sample digestate are taken. One aliquot is spiked with a solution of known concentration. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentrations of both aliquots are measured and the sample concentration is calculated.

Note: The post-digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgment when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

9.2.12 % RSD of Multiple Exposures

The Thermo Trace instrument performs 2 replicates of each sample. The Varian 730 ES instrument performs 3 replicates of each sample. To be acceptable, the %RSD should be <30% for samples with concentrations above the RL.

Note: For ICV evaluation, the %RSD must be <3% for EPA 200.7.

9.2.13 Interelement Correction Factors (IEC)

Interelement correction factors (IEC) for all elements must be determined annually using the manufacturer's guidance.

The lab may combine the linearity study with the IEC study, thereby eliminating redundancy. (Single element linearity check solutions for each analyte should be closely evaluated for all non-spiked elements, and applicable correction factors should be applied according to the instrument's software. The analyst must be careful not to correct for any contamination which may be present in the actual solution.)

The IECs must be verified at the beginning and end of each analytical sequence through the analysis of interferent check solutions ICSA and ICSAB.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 4. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

The sample preparation procedures are given in the following SOPs:

Matrix	SOP #
Water Samples	SA-ME-050
Soil Samples	SA-ME-051

10.2 QC Sample Preparation

Batch QC sample preparation procedures are given in the SOPs listed above. Additional QC items are listed below.

10.2.1 Serial Dilution

Dilute the digestate by a factor of 5 and analyze the dilution using the same procedures used for the un-diluted aliquot.

10.2.2 Post-Digestion Spike

Transfer 10mL of a digestate to a suitable vial. Spike the sample with 0.10mL of CLP Spike I and 0.10mL of Spike II. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

10.3 Analysis

10.3.1 Instrument Operating Conditions

Turn the ICP on and allow it to become thermally stable before beginning to analyze the calibration standards. It will take about an hour for the instrument to warm up. If the optics were turned off, allow 2 hours warm up time.

Run the "Automatic Profile" program. The "Automatic Profile" of the instrument should be checked twice a day to compensate for changes in air pressure, humidity, and temperature. If the environment of the instrument is such that daily changes in the instrument profile are extreme, the instrument should be "profiled" every few hours.

Instrument maintenance must be performed in accordance with Attachment 2 of this SOP.

10.3.2 Internal Standard (ISTD)

Prior to analysis, internal standard must be added to all standards, samples, and QC items. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples.

10.3.3 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described in Section 9.2.1. Once the calibration has been established and verified with a high level standard and an ICV in accordance with Sections 9.2.2 and 9.2.3, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.5.

10.3.4 Sample Analysis

Remove the digestates from the refrigerator and allow them to come to room temperature.

The sample digestate must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.5 Example Analytical Sequence

An example analytical sequence is listed below.

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Instrument Warm-up	
Profile	
Initial Calibration	
High Calibration Standard	Re-analyzed as a sample
ICV	Second Source
ICB	
Reporting Limit Check Standard	
ICP Interference Check Solution A (ICSA)	
ICP Interference Check Solution AB (ICSAB)	
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	

Note: The analytical sequence continues as outlined above and must end with the analysis of the reporting limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

11.0 **Calculations / Data Reduction**

11.1 **Data Reduction**

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

11.1.1 Dilutions

If the concentration of a sample is above the linear range of the ICP, as determined in Attachment 7, the sample digestate must be diluted and reanalyzed.

Dilutions must be prepared in reagent water containing 5% hydrochloric acid and 1% nitric acid by volume.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, the analyst must verify LIMS Worksheet Notes to determine if historical data is available for review.

11.1.3 Chemical Relationships

The analyst must be aware of the following chemical relationships:

- Total Results should be \geq Dissolved results

11.1.4 MARRS Data Reduction and Reporting

Savannah uses the Environmental Information Systems Corporation MARRS program for data reduction and reporting. The following is the procedure used:

An archive file is sent via the laboratory network to a second PC. The MARRS software uploads the archive file and compares the data to the quality control parameters that are built into the software. These parameters may be customized to meet specific project requirements.

11.1.4.1 When the data file is uploaded, the analyst reviews the data to ensure that the QC types are correct. The QC types are: samples, calibration standards, ICV, ICB, CRI, ICSA, ICSAB, CCV, CCB, prep blanks (liquid, solid), LCS (liquid, solid), serial dilutions, post-digestion spikes, MS/MSD, DUP, etc. If any typographical errors are noted by the instrument analyst on the instrument's summary report, then these errors need to be corrected in the MARRS system.

11.1.4.2 The sample data are then compared to the tightest limits for the samples on the run. There are tables set up with the tightest criteria required. These tables are used for the initial data evaluation.

11.1.4.3 After the results are processed, a data review report is printed that shows the samples and QC that exceed the acceptable limits. When the report shows that acceptable limits are exceeded, the analyst will determine if the element is required for the project. If the element is not required, this is noted on the data review report. If the element is required, a reanalysis is initiated for that sample and element.

11.1.4.4 A report is printed that shows that the correct number of CCV/CCBs were analyzed with the samples. If more than 10 samples are analyzed between CCV/CCBs, then all affected samples are reanalyzed.

11.1.4.5 When the data reduction is complete, all compliant data are reported to the LIMS system.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

11.2.4 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

CONC_{Sample} = Concentration of the sample

F = Final volume/weight

I = Initial volume/weight

D = Dilution factor

dw = % Solids decimal equivalent

Note: All dry weight corrections are performed automatically in LIMS.

Note: This calculation assumes all applicable unit correction factors are applied.

11.2.5 Method of Standard Additions

The concentrations of both sample aliquots, Section 9.2.11, are measured and the sample concentration is calculated as follows:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

Where:

S₁ = Absorbance or concentration of the spiked aliquot

S₂ = Absorbance or concentration of the un-spiked aliquot

V_s = Volume of spike solution

V_x = Volume of sample aliquots

C_s = Spike solution concentration

Note: This calculation assumes all applicable unit correction factors are applied.

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. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix and may not be achievable in all environmental matrices. The current MDL associated with this procedure is given in the Method Limit Group (MLG) in LIMS.

At a minimum, the MDL must be determined initially upon method set-up and annually thereafter, and verified annually in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

12.2 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (LCS, MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to

the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.3 Lower Limit of Quantitation Check Sample (LLQC)

EPA 6010C requires a lower limit of quantitation check sample (LLQC) analysis to demonstrate the required reporting limit capability. The laboratory shall prepare and analyze this solution on a yearly basis, in accordance with all applicable preparatory SOPs (i.e. the solution must be digested.) It is recommended that the laboratory utilize the RL check solution (Section 9.2.7) by simply carrying it through the entire preparatory procedure for each of the prep methods associated with EPA 6010C. Digesting this solution on the same prep batch as the yearly MDL studies is preferred. The LLQC must recover within 70-130% to be acceptable, or a new (higher) reporting limit must be established.

12.4 Determination of the Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the concentration of analyte that can be statistically distinguished from the background noise of the instrument. The IDL limit must be determined annually, at a minimum, for each analyte in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

The IDL is defined as three times the average of the standard deviation of seven replicate analyses of the IDL solution performed over three non-consecutive days. The IDL may be elevated above the background noise (blank levels). The current IDL associated with this procedure is given in the Equipment Limit Group (ELG) in LIMS.

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the

QA Department for filing. Note: LCS CDOCs from the *same* source as the calibration standards are permitted.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual (EHSM) and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

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

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.
- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.
- Acidic sample digestions – Neutralize before disposal into drain/sewer system.

15.0 References / Cross-References

- SOP SA-AN-10: *Balance Calibration and Use*

- SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.
 - EPA 200.7, Revision 4.4, EMMC Version: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry; 1994
- *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.
- *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986 (SW-846 Updates III and IV).
 - Method 6010B, Revision 2: Inductively Coupled Plasma-Atomic Emission Spectrometry; December 1996.
 - Method 6010C, Revision 3: Inductively Coupled Plasma-Atomic Emission Spectrometry; February 2007.

16.0 Method Modifications/Clarifications

16.1 Incorporation of Non-Routine Matrices

This procedure may be modified to analyze other matrices (e.g., wipe, waste, tissue, filter, and TCLP/SPLP leachate samples) upon client request. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, filter, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate wipe, waste, filter, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.) and soil QC limits to evaluate TCLP/SPLP leachate samples. Water DOCs can be used to satisfy analyst demonstrations of capability for TCLP/SPLP matrices. Teflon chips, Ottawa sand, or equivalent is used as the blank matrix for wipes, wastes, filters, and tissues unless specifically requested otherwise by the project.

16.1.1 Collection and Handling Procedures for Non-Routine Matrices

Waste (oil) samples are collected in 500mL plastic containers. Waste (oil) samples are stored at room temperature until the time of digestion. Wipe samples are collected in

20mL scintillation vials. Wipe and filter samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until time of digestion. Waste (oil), wipe, and filter samples must be digested within 6 months of collection.

Tissue samples are collected in plastic containers with the size dependent upon the type of tissue being collected. Plastic jars or plastic baggies can be used. Upon receipt, tissue samples must be placed in the freezer at -10° to -20°C for up to 6 months if digestion cannot be completed that day. Tissue samples must be digested within 6 months of thawing.

Digestates for waste (oil), wipe, tissue, and filter samples are stored at room temperature until the time of analysis and must be analyzed within 6 months of collection.

Once the TCLP/SPLP extraction procedure has been performed, the TCLP/SPLP leachate must be transferred to a 500mL plastic container and preserved with 1.0mL nitric acid to a pH <2. Preserved TCLP/SPLP leachates are stored at room temperature until the time of digestion. The leachate sample must be digested within 6 months of completion of the TCLP/SPLP extraction. Digestates are stored at room temperature until the time of analysis and must be analyzed within 6 months of completion of the TCLP/SPLP extraction.

16.1.2 Preparation and Analytical Procedures for Non-Routine Matrices

Wipe, waste, filter, and tissue samples are prepared in the same manner as routine soil samples as outlined in SOP SA-ME-051. TCLP/SPLP matrices are prepared in the same manner as routine water samples as outlined in SOP SA-ME-050. Refer to the applicable preparation SOPs for more information.

Wipe, waste, filter, tissue, and TCLP/SPLP matrices are analyzed in the same manner as routine samples as outlined in this SOP.

16.2 Other Considerations

16.2.1 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 200.7 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory requires this standard to be qualitatively identified to be acceptable.

16.2.2 The stock standards utilized for the Silica procedure are routinely purchased as Silicon (Si). Both Silica (SiO₂) and Silicon (Si) can be reported using this procedure. The following equation is used to convert between Silicon (Si) and Silica (SiO₂):

$$Si = \frac{SiO_2}{2.14}$$

16.2.3 EPA 6010B does not require an RL check standard; however, it is the laboratory's standard practice to analyze and evaluate this check standard for EPA 6010B using the criteria outlined in EPA 200.7.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

- Attachment 1: SOP Summary
- Attachment 2: Sample Collection, Preservation, and Holding Time Table
- Attachment 3: QC Summary
- Attachment 4: Instrument Maintenance and Troubleshooting
- Attachment 5: Standard Preparation Tables
- Attachment 6: Silica/Silicon Standard Preparation
- Attachment 7: Linear Range Determination
- Attachment 8: Element Wavelengths

Attachment 1: SOP Summary

Sample Preparation Summary

Prior to analysis by ICP, the sample must be digested using the sample preparation method appropriate to the matrix. Samples should be prepared according to the appropriate matrix-specific SOP.

Matrix	SOP #
Aqueous Samples	SA-ME-050
Soil Samples	SA-ME-051

Sample Analysis Summary

Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and excited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT) or on to a charge-coupled device (CCD). The PMTs and CCDs located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

Analytical Sequence

Analytical Sequence for samples immediately following an initial calibration:

Description	Comments
Instrument Warm-up	
Profile	
Initial Calibration	
High Calibration Standard	Re-analyzed as a sample
ICV	Second Source
ICB	
Reporting Limit Check Standard	
ICP Interference Check Solution A (ICSA)	
ICP Interference Check Solution AB (ICSAB)	
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	
Samples & Batch QC Items	Up to 10 injections, including QC.
CCV	10-injection clock begins after injection of the CCB
CCB	

Note: The analytical sequence continues as outlined above and must end with the

analysis of the reporting limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Listed below are the holding times and preservation requirements:

Matrix	Routine Sample Container	Minimum Sample Size	Preservation¹	Holding Time²
Water	250mL or 500mL plastic	50mL	1:1 Nitric Acid to pH<2	6 months
Water - Silica	250mL or 500mL plastic	10mL	<6°C but not frozen	6 months
Soil	8oz plastic or glass	1g	<6°C but not frozen	6 months
Soil - Silica	8oz plastic or glass	5g	<6°C but not frozen	6 months

¹Samples requiring dissolved metals must be filtered prior to preservation.

²Inclusive of digestion and analysis.

**Attachment 3:
QC Summary**

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	Single Point: 1 standard and 1 blank Multi-point: Minimum 3 standards and 1 blank Correlation coefficient ≥ 0.998	Recalibrate
Highest Standard	Immediately after every calibration	Recoveries within $\pm 5\%$ of expected values	New initial calibration
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	EPA 6010B and EPA 6010C: within $\pm 10\%$ EPA 200.7: within $\pm 5\%$, $\leq 3\%$ RSD	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within $\pm 10\%$ of the true value	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	EPA 6010C: Absolute value $< \frac{1}{2}$ RL EPA 6010B: Absolute value $< 3 \times$ IDL or $< \text{RL}$ whichever is smaller. EPA 200.7: Absolute value $< \frac{1}{2}$ RL	Terminate the analysis, correct problem and reanalyze the previous 10 samples
Interference check standards (ICSA/ICSAB)	At the beginning and end of an analysis run	$\pm 20\%$ of the true values Pay attention to false positives and false negatives for elements not present in the solutions.	Terminate the analysis, correct the problem, recalibrate, and reanalyze all samples since the last ICS that was in control.

QC Item	Frequency	Criteria	Corrective Action
Low-Level Laboratory Control Sample (LL_LCS) – at the RL	EPA 200.7 DW: One per batch of twenty samples or less for drinking water	Qualitatively detected	If the “regular” LCS meets criteria, initiate NCM and report data If the “regular” LCS does not meet criteria, redigest and reanalyze batch
Laboratory Control Sample (LCS)	One per batch of twenty samples or less	LIMS MLG	Refer to SOP SA-QA-17
Method Blank	One per batch of twenty samples or less	result <½RL or result <10% of the analyte level in the sample	Refer to SOP SA-QA-17
Matrix Spike (MS)	EPA 200.7: 10% of samples prepared; i.e., 2 separate matrix spikes per batch of twenty samples EPA 6010B & EPA 6010C: 5% of samples prepared; i.e., 1 matrix spike per batch of twenty samples	LIMS MLG	Refer to SOP SA-QA-17
Matrix Spike Duplicate (MSD) or Sample Duplicate	EPA 200.7 (Clean Water Act), EPA 6010B, & EPA 6010C: One MSD or sample duplicate per batch of twenty samples or less	LIMS MLG	Refer to SOP SA-QA-17
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	Refer to Section 9.2.9	Refer to Section 9.2.9
Post Digestion Spike	One per batch of twenty samples or less	Refer to Section 9.2.10	Refer to Section 9.2.10
Reporting Limit Check Solution (also known as LLICV)	At the beginning and end of an analysis run (Required for EPA 200.7 when	EPA 200.7: +/-50% of the true concentration EPA 6010C:	Stop the analysis, fix the problem, and reanalyze the affected samples.

QC Item	Frequency	Criteria	Corrective Action
and LLCCV for EPA 6010C)	using a single point calibration. Required for EPA 6010C when using both single point and multi-point calibrations.)	+/-30% of the true concentration EPA 6010B (Internal Criteria): +/-50% of the true concentration	
%RSD (CV) of Multiple Exposures	Evaluate for all Calibration, QC, and samples	Conc. >= RL - Warning: <=20% - Acceptance: <=30%	-if CV>20 but <=30, review data for possible interferences; -if interference present, reanalyze digest -if no interference present, report average -if CV>=30%, reanalyze digest, report the result that has the lower precision value or dilute the digestion and reanalyze
		Conc. < RL -use professional judgment	-use professional judgment
Linear Range of ICP	Determined at least every 6 months in accordance with Attachment 7	% difference <=10%	-reanalyze at a lower concentration
Interelement correction factors (IEC)	Determined at least annually Verified at the beginning and end of an analysis run	Refer to ICSA, ICSAB criteria	See ICSA, ICSAB corrective action
Lower Limit of Quantitation Check Sample	Annually	6010C: 70-130%	- reanalyze at a higher concentration - elevate RL accordingly
Demonstration of Capability (IDOC/CDOC)	Initially, per analyst, and then annually thereafter	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06
Method Detection Limit (MDL)	Upon method/instrument set-up, and then annually thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Instrument Detection Limit (IDL)	Upon method/instrument set-up, and then quarterly thereafter	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

Attachment 4: Preventative Maintenance and Troubleshooting

Preventive Maintenance

Refer to the instrument manufacturer's guides for trouble-shooting items.

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE									
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL	
	D	W	M	Q	SA	A	AN		
ICAP Service Schedule									
Pump Tubing							X	Inspect and replace as needed (Recommend daily)	
Nebulizer							X	Clean as needed	
Filters			X					Inspect monthly, clean or replace as needed	
Chiller Water Filter							X	Clean or replace as needed (Recommend every six months)	
Injector Tip / Torch		X						Inspect weekly, clean or replace as needed	
Tubing Connectors							X	Replace as needed	

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually;
AN = as needed

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory.

All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

**Attachment 5:
Standard Preparation**

Note: All standards must be stored at room temperature and have an expiration date of 6 months from date prepared.

Continuing Calibration Verification (CCV)

Final Volume (mL): 2000

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Ag	1000	CPI	1.0	0.5
Al	10000	SPEX	1.0	5.0
B	1000	CPI	10.0	5.0
Fe	10000	CPI	1.0	5.0
Sr	1000	ABSOLUTE	5.0	2.5
Ti	1000	CPI	1.0	0.5
Na	10000	CPI	0.5	2.5

Multi Element Mixes

CAL STD 2

As	50	CPI	20	0.5
Mo	50			0.5
Pb	50			0.5
Sb	50			0.5
Se	500			5.0
TI	500			5.0

CAL STD 3

Ba	500	CPI	20	5.00
Be	50			0.50
Cd	50			0.50
Co	50			0.50
Cr	500			5.00
Cu	500			5.00
Mn	500			5.00
Ni	250			2.50
Zn	250			2.50

CAL STD 5

Ca	500	CPI	20	5.00
K	1000			10.00
Mg	500			5.00
Na	500			5.00
Sn	500			5.00
V	500			5.00

Internal Standard (ISTD)

Final Volume (mL): 10000

Solvent: 30% HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Amount Used	Final Concentration (mg/L)
Y	10000	CPI	7.0mL	7.0
Lithium Carbonate (powder)	18.78% Li	Mallinckrodt	20g	375.6
Sc	10000	CPI	7.0mL	7.0

MDL & IDL Intermediate

Final Volume:

(mL) 100

Solvent: 5% HCL / 1 % HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks)

Ag	1000	CPI	0.040	0.40
Al	10000	SPEX	0.10	10
As	1000	CPI	0.20	2.0
B	1000	CPI	0.40	4.0
Ba	1000	CPI	0.020	0.20
Be	1000	CPI	0.0050	0.10
Ca	10000	SPEX	0.10	10
Cd	1000	CPI	0.040	0.40
Co	1000	CPI	0.10	1.0
Cr	1000	CPI	0.10	1.0
Cu	1000	CPI	0.10	1.0
Fe	10000	CPI	0.10	10
K	10000	CPI	0.20	20
Mg	10000	SPEX	0.10	10
Mn	1000	CPI	0.020	0.20
Mo	1000	CPI	0.10	1.0
Na	10000	CPI	2.04	204
Ni	1000	CPI	0.10	1.0
Pb	1000	CPI	0.10	1.0
Sb	1000	CPI	0.20	2.0
Se	1000	CPI	0.20	2.0
Sn	1000	CPI	0.20	2.0
Sr	1000	CPI	0.040	0.40
Ti	1000	CPI	0.050	0.50
Tl	1000	CPI	0.20	2.0
V	1000	CPI	0.060	0.60
Zn	1000	CPI	0.10	1.0

CLP SPIKE 1 - Post Spike, LCS/MS Spike

Final Volume:

(mL) 100

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Multi-Element Mixes

CRDL STD				
Ag	20	SPEX	10	2.0
As	20			2.0
Be	10			1.0
Cd	10			1.0
Co	100			10
Cr	20			2.0
Cu	50			5.0
Mn	30			3.0
Ni	80			8.0
Pb	6.0			0.60
Sb	120			12
Se	10			1.0
Tl	20			2.0
V	100			10
Zn	40			4.0

SPIKE II - Post Spike, LCS/MS Spike

Final Volume

(mL): 100

Solvent: 5% HCL / 1 % HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

B	1000	CPI	10	100
Ca	10000	SPEX	5.0	500
K	10000	CPI	5.0	500
Mg	10000	SPEX	5.0	500
Mo	1000	CPI	5.0	50
Na	10000	CPI	5.0	500
Sn	1000	CPI	10	100
Sr	1000	CPI	5.0	50
Ti	1000	CPI	10	100

RL ICP INTERMEDIATE

Final Volume (mL): 100

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Ag	1000	CPI	0.10	1.0
Al	10000	SPEX	0.20	20
As	1000	CPI	0.10	1.0
B	1000	CPI	0.50	5.0
Ba	1000	CPI	0.10	1.0
Be	1000	CPI	0.040	0.4
Ca	10000	SPEX	0.50	50
Cd	1000	CPI	0.050	0.5
Co	1000	CPI	0.10	1.0
Cr	1000	CPI	0.10	1.0
Cu	1000	CPI	0.20	2.0
Fe	10000	CPI	0.050	5.0
K	10000	CPI	1.0	100
Mg	10000	SPEX	0.50	50
Mn	1000	CPI	0.10	1.0
Mo	1000	CPI	0.10	1.0
Na	10000	CPI	0.50	50
Ni	1000	CPI	0.40	4.0
Pb	1000	CPI	0.050	0.50
Sb	1000	CPI	0.20	2.0
Se	1000	CPI	0.10	1.0
Sn	1000	CPI	0.50	5.0
Sr	1000	CPI	0.10	1.0
Ti	1000	CPI	0.10	1.0
Tl	1000	CPI	0.25	2.5
V	1000	CPI	0.10	1.0
Zn	1000	CPI	0.20	2.0

RL ICP Working

Final Volume (mL): 100

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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From RL ICP Intermediate

Ag	1.0	CPI	1.0	0.010
Al	20	SPEX		0.20
As	1.0	CPI		0.010
B	5.0	CPI		0.050
Ba	1.0	CPI		0.010
Be	0.4	CPI		0.0040
Ca	50	SPEX		0.50
Cd	0.5	CPI		0.0050
Co	1.0	CPI		0.010
Cr	1.0	CPI		0.010
Cu	2.0	CPI		0.020
Fe	5.0	CPI		0.050
K	100	CPI		1.0
Mg	50	SPEX		0.50
Mn	1.0	CPI		0.010
Mo	1.0	CPI		0.010
Na	50	CPI		0.50
Ni	4.0	CPI		0.040
Pb	0.50	CPI		0.0050
Sb	2.0	CPI		0.020
Se	1.0	CPI		0.010
Sn	5.0	CPI		0.050
Sr	1.0	CPI		0.010
Ti	1.0	CPI		0.010
Tl	2.5	CPI		0.025
V	1.0	CPI		0.010
Zn	2.0	CPI		0.020

RL LOW INTERMEDIATE

Final Volume (mL) 100

Solvent 5% HCL / 1 % HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Ag	1000	CPI	0.1	1.0
Al	10000	SPEX	0.2	20.0
As	1000	CPI	0.1	1.0
Ba	1000	CPI	0.1	1.0
Be	1000	CPI	0.02	0.2
Ca	10000	SPEX	0.2	20.0
Cd	1000	CPI	0.02	0.2
Co	1000	CPI	0.1	1.0
Cr	1000	CPI	0.06	0.6
Cu	1000	CPI	0.1	1.0
K	10000	CPI	0.2	20.0
Mg	10000	SPEX	0.2	20.0
Mn	1000	CPI	0.1	1.0
Mo	1000	CPI	0.1	1.0
Ni	1000	CPI	0.1	1.0
Pb	1000	CPI	0.06	0.6
Sb	1000	CPI	0.12	1.2
Se	1000	CPI	0.1	1.0
Zn	1000	CPI	0.2	2.0

RL LOW INTERMEDIATE

Final Volume (mL): 100

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Ag	1	CPI	0.50	0.0050
Al	20	SPEX		0.10
As	1	CPI		0.0050
Ba	1	CPI		0.0050
Be	0.2	CPI		0.0010
Ca	20	SPEX		0.10
Cd	0.2	CPI		0.0010
Co	1	CPI		0.0050
Cr	0.6	CPI		0.0030
Cu	1	CPI		0.0050
K	20	CPI		0.10
Mg	20	SPEX		0.10
Mn	1	CPI		0.0050
Mo	1	CPI		0.0050
Ni	1	CPI		0.0050
Pb	0.6	CPI		0.0030
Sb	1.2	CPI		0.0060
Se	1	CPI		0.0050
Zn	2.0	CPI		0.010

ICV

Final Volume (mL): 500

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

K	1000	Element	5.0	10.0
Na	1000	Element	4.5	9.0
Sn	1000	Element	0.5	1.0
Sr	1000	Element	0.5	1.0

Multi Element Stocks

QC19				
As	100	Element	5.0	1.0
Be	100			1.0
Ca	100			1.0
Cd	100			1.0
Co	100			1.0
Cr	100			1.0
Cu	100			1.0
Fe	100			1.0
Mg	100			1.0
Mn	100			1.0
Mo	100			1.0
Ni	100			1.0
Pb	100			1.0
Sb	100			1.0
Se	100			1.0
Tl	100			1.0
V	100			1.0
Zn	100			1.0

QC7				
Ag	100	Element	5.0	1.0
Al	100			1.0
B	100			1.0
Ba	100			1.0
K	1000			10.0
Na	100			1.0
Si	50			0.5

ICSA

Final Volume (mL): 1000

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Multi Element Mixes

<u>Interferents A</u>				
Al	5000	SPEX	100	500.0
Ca	5000			500.0
Mg	5000			500.0
Fe	2000			200.0

ICSAB

Final Volume (mL): 1000

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Multi Element Mixes

Interferents A				
Al	5000	SPEX	100	500.0
Ca	5000			500.0
Mg	5000			500.0
Fe	2000			200.0

Altany C				
Ag	20	Spectro Pure	10	0.20
As	10			0.10
Ba	50			0.50
Be	50			0.50
Cd	100			1.00
Co	50			0.50
Cr	50			0.50
Cu	50			0.50
Mn	50			0.50
Ni	100			1.00
Pb	5			0.05
Sb	60			0.60
Se	5			0.05
Tl	10			0.10
V	50			0.50
Zn	100			1.00

Trace AB				
Mo	100	CPI	10	1.0
Sn	100			1.0

Trace AB

Final Volume (mL): 100

Solvent: 5% HCL / 1 % HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Mo	1000	CPI	10	100.00
Sn	1000	CPI	10	100.00

High Std

Final Volume (mL): 1000

Solvent: 5% HCL / 1 % HNO₃

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Single Element Stocks

Ag	1000	CPI	1.0	1.0
Al	10000	SPEX	1.0	10.0
B	1000	CPI	10.0	10.0
Fe	10000	CPI	1.0	10.0
Sr	1000	ABSOLUTE	5.0	5.0
Ti	1000	CPI	1.0	1.0

Multi Element Mixes

CAL STD 2				
As	50	CPI	20	1.0
Mo	50			1.0
Pb	50			1.0
Sb	50			1.0
Se	500			10.0
Tl	500			10.0

CAL STD 3				
Ba	500	CPI	20	10.00
Be	50			1.00
Cd	50			1.00
Co	50			1.00
Cr	500			10.00
Cu	500			10.00
Mn	500			10.00
Ni	250			5.00
Zn	250			5.00

CAL STD 5				
Ca	500	CPI	20	10.00
K	1000			20.00
Mg	500			10.00
Na	500			10.00
Sn	500			10.00
V	500			10.00

CRI

Final Volume (mL): 500

Solvent: 5% HCL / 1 % HNO3

Purchased Standards	Concentration (mg/L)	Vendor *	Volume Used (mL)	Final Concentration (mg/L)
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Multi Element Mixes

CRDL STD				
Ag	20	SPEX	0.50	0.0200
As	20			0.0200
Be	10			0.0100
Cd	10			0.0100
Co	100			0.1000
Cr	20			0.0200
Cu	50			0.0500
Mn	30			0.0300
Ni	80			0.0800
Pb	6			0.0060
Sb	120			0.1200
Se	10			0.0100
Tl	20			0.0200
V	100			0.1000
Zn	40			0.0400

Attachment 6: Silica/Silicon Standard Preparation

Silicon (Si) stock solutions are usually purchased for this procedure. The following conversion is used to adjust any volumes or concentrations appropriately:

$$Si = \frac{SiO_2}{2.14}$$

- Stock SiO₂ Standard, 10000mg/L Si / 21400mg/L SiO₂ – purchased from CPI. Store at room temperature. This standard must be used by the manufacturer's expiration date.
- Stock Second Source SiO₂ Initial Calibration Verification (ICV), 50mg/L Si / 107mg/L SiO₂ – QC4 Standard, purchased from Absolute. Store at room temperature. This standard must be used by the manufacturer's expiration date.

Note: The ICV must be prepared from a stock standard that is obtained from a different source than the stock standard used to prepare the calibration standard. The second source must be from a separate vendor, unless a second vendor is unavailable, in which case a separate lot from the same vendor may be used.

- Intermediate SiO₂ Standard, 467mg/L Si / 1000mg/L SiO₂ – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the Stock SiO₂ Standard given in the table below to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. Stock SiO ₂ Std (mg/L)	Volume Stock SiO ₂ Std (mL)	Final Volume (mL)	Final Conc. (mg/L)
Silica (SiO ₂) [Silicon (Si)]	21400 [10000]	4.67	100	1000 [467]

- Initial Calibration Standards
 - Preparation of the Calibration Blank (ICB, CCB) – The calibration blank is reagent water. The calibration blank is used as the initial calibration blank (ICB) and the continuing calibration blank (CCB).
 - High Level SiO₂ Calibration Standard, 10mg/L SiO₂ – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the Intermediate SiO₂ Standard given in the table, below, to the volumetric flask. Dilute to a final volume of 100mL with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. SiO ₂ Intermediate Std (mg/L)	Volume SiO ₂ Intermediate Std (mL)	Final Volume (mL)	Final Conc. (mg/L)
Silica (SiO ₂)	1000	1.0	100	10

- Mid Level SiO₂ Calibration Standard (also used as CCV solution), 5.0mg/L SiO₂ – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the stock standard given in the table, below, to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. SiO ₂ Intermediate Std (mg/L)	Volume SiO ₂ Intermediate Std (mL)	Final Volume (mL)	Final Conc. (mg/L)
Silica (SiO ₂)	1000	0.50	100	5

- Low Level SiO₂ Calibration Standard (also used as RL solution), 0.50mg/L – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the stock standard given in the table, below, to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. SiO ₂ Intermediate Std (mg/L)	Volume SiO ₂ Intermediate Std (mL)	Final Volume (mL)	Final Conc. (mg/L)
Silica (SiO ₂)	1000	0.050	100	0.50

- Second Source SiO₂ ICV Standard, 0.50mg/L SiO₂ / 1.07mg/L Si – Add 20mL to 30mL of reagent water to a clean, plastic 100-mL volumetric flask. Add the volume of the stock standard given in the table to the volumetric flask. Dilute to volume with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Element	Conc. of Stock Std (currently from Absolute) (mg/L)	Volume Stock Std (mL)	Final Volume of Cal Std mL)	Final Conc. (mg/L)
Silica (SiO ₂) [Silicon (Si)]	107 [50]	1.0	100	1.07 [0.50]

- Stock ICP Interference A Check Standard – purchased Interference A Stock Standard, from SPEX. Store the standard at room temperature. This standard must be used by its manufacturer's expiration date.

Note: This solution does not contain any SiO_2 . Concentrations are as follows:

Aluminum (Al)	5000mg/L
Calcium (Ca)	5000mg/L
Magnesium (Mg)	5000mg/L
Iron (Fe)	2000mg/L

- ICP Interference A Check Standard, Working – Add 20mL to 30mL of reagent water to a clean 100-mL plastic volumetric flask. Add 10mL of the Stock ICP Interference A Check Standard to the volumetric flask. Dilute to a final volume of 100mL with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Note: This solution does not contain any SiO_2 . Final concentrations are as follows:

Aluminum (Al)	500mg/L
Calcium (Ca)	500mg/L
Magnesium (Mg)	500mg/L
Iron (Fe)	200mg/L

- ICP Interference Check Solution AB – Add 20mL to 30mL of reagent water to a clean 100-mL plastic volumetric flask. Add 10mL of Stock ICP Interference A Check Standard and 0.50mL of the Intermediate SiO_2 Standard to the volumetric flask. Dilute to a final volume of 100mL with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

The final concentrations of this solution should be as follows:

Aluminum (Al)	500mg/L
Calcium (Ca)	500mg/L
Magnesium (Mg)	500mg/L
Iron (Fe)	200mg/L
Silica (SiO_2)	5.0mg/L

- Linearity Check Solution, 100mg/L – P Add 20mL to 30mL of reagent water to a clean 100-mL plastic volumetric flask. Add 10mL of Intermediate SiO_2 Standard to the volumetric flask. Dilute to a final volume of 100mL with reagent water. Store the standard at room temperature. This standard must be used by its parent standard's expiration date or within 6 months of preparation, whichever comes first.

Note: Historically, the Linear Dynamic Range for silica has been 100mg/L; however, the instrument is dynamic. The concentration of this standard may need to be adjusted based how the instrument is performing. Prepare other volumes and/or concentrations according to the following equation:

$$V_s = \frac{V_{lc} \otimes C_{lc}}{C_s}$$

where

V_s = volume of stock standard (mL)

C_s = concentration of stock standard (mg/L)

V_{lc} = volume of linearity check standard to prepare (mL)

C_{lc} = concentration of linearity check standard to prepare (mg/L)

Attachment 7: Linear Range Determination

The linear range must be determined at a minimum of once every 6 months for routine work. The linear range must be determined at a minimum of quarterly for the CLP and DOD QSM programs.

Profile and calibrate the ICP as described in Section 9.2.1.

Prepare individual standards at concentrations (a minimum of three are recommended) that are expected to define the linear range of the instrument. The calibration standards and the linear range standards must be matrix matched; that is, they must have the same percentage of hydrochloric and nitric acids.

Analyze the standards following the analytical sequence described in Section 10.3.5. Verify the calibration after every 10 analyses.

Compare the concentration of the linear range standard with its true concentration as follows:

$$PercentDifference = \left| \frac{C_{cal} - C_{true}}{C_{true}} \right| \otimes 100$$

Where:

C_{cal} = concentration determined from analysis

C_{true} = true concentration of the standard

If the percent difference is less than or equal to 10%, the linear range is confirmed at that concentration. If the percent difference is greater than 10%, repeat the analysis with a lower concentration.

The linear range may be extended by analyzing higher standards and evaluating the results against the 10% difference criterion. The linear range of the ICP for an analyte is the highest standard of that analyte that meets this criterion.

If any calibration regression fit, other than linear, is utilized for the calibration of the ICP (i.e., curvilinear or full fit), the upper limit of the linear range is the concentration of the High Standard.

Attachment 8:
Element Wavelengths

Element	Wavelength ICP-D (nm)	Wavelength ICP-E (nm)
Aluminum (Al)	308.215	308.215
Antimony (Sb)	206.838	206.834
Arsenic (As)	189.042	189.042
Barium (Ba)	493.409	389.178
Beryllium (Be)	313.042	313.042
Boron (B)	249.678	249.678
Cadmium (Cd)	226.502	226.502
Calcium (Ca)	317.933	315.887
Chromium (Cr)	267.716	267.716
Cobalt (Co)	228.616	228.615
Copper (Cu)	324.753	324.753
Iron (Fe)	271.441	271.441
Lead (Pb)	220.353	220.353
Magnesium (Mg)	279.078	279.078
Manganese (Mn)	257.610	257.610
Molybdenum (Mo)	202.030	202.032
Nickel (Ni)	231.604	231.604
Potassium (K)	766.491	766.491
Selenium (Se)	196.026	196.026
Silver (Ag)	328.068	328.068
Sodium (Na)	330.231	330.237
Strontium (Sr)	421.542	216.596
Thallium (Tl)	190.864	190.794
Tin (Sn)	189.989	189.925
Titanium (W)	334.941	334.941
Vanadium (V)	292.402	292.401
Zinc (Zn)	206.200	206.200

Note: Other wavelengths may be used with DM and TM approval.

18.0 Revision History

Summary of Changes from Previous Revision:

- Included the requirement to analyze an MSD with each batch of Clean Water Act samples. Section 9.1.2 and Attachment 3
- Revised ICAL acceptance criteria to greater than or equal to 0.998. The acceptance criteria was previously greater than 0.998. Section 9.2.1 and Attachment 3
- The routine maintenance was revised to match the current form. Attachment 4
- Revised expiration date for silicon standards to equal manufacturers' expiration date. Attachment 6