Test America
INCORPORATED

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20 July 2000

Ms. Gwen Massenburg
USEPA
Mail Stop SR-6J
77 W. Jackson Blvd.
Chicago IL 60604

Ms. Massenburg,

In response to a request by Pat Dunne of Entact, enclosed please find the SOP for ICP Metals. Since this is proprietary information, please handle it accordingly.

If you have any further questions, don't hesitate to call. Thank you.

Sincerely,

TestAmerica, Inc.

Diane Billings
Project Coordinator

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TestAmerica Inc.

Bartlett Division

850 West Bartlett Rd.

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Standard Operating Procedure

Analyte or Suite: Metals

Methodology: Inductively Coupled Plasma Atomic Emission

Reference: SW-846 Method 6010B, revision 2, December 1996
EPA Method 200.7 for Waste Water, 40 CFR Part 136
EPA Method 200.7 r4.4 for Drinking Water, May 1994

SOP Revision # 6 Date revised: February 10, 2000

Magnetic storage: /usr3/sops/BT04-01.6

Approvals:

Division Manager

Operations Manager

Bonnie Stadtmann
Quality Assurance Coordinator

Technical Director

Table of Contents

1. INTRODUCTION AND SCOPE

This SOP describes the simultaneous multielemental determination of elements by ICP. The method is applicable to drinking water, groundwater, waste water, TCLP extracts, soils, sludges, sediments and other solid wastes. Table 1 lists the elements amenable to this method, and the nominal reporting limit for each element.

Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

1.1. Definitions

Analytical Run: A set of runs (including samples and QCIs) done consecutively (one after the other) on the same instrument.

Prep Batch - A set of up to 20 samples of the same matrix prepped by the same analyst(s) using the same techniques. A prep batch consists only of samples and QCI that were prepped on the same calendar day using the same technique. Blanks, MS/MSDs, and standards are not included in the 20 count. All other QC samples, including those originating internally (MDLs, MVSs, and PEs), must be included in the 20 count. Reagent lot number(s) cannot be changed in the middle of a prep batch.

Instrument Detection Limit (IDL): The concentration equivalent to an analyte signal which is equal to three times the standard deviation of a series of seven replicate measurements of a reagent blank's signal at the same wavelength.

Method Detection Limit: The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL standards must be taken through the entire analytical process, including digestion.

Dissolved Metals: Those constituents (metals) which will pass through a 0.45 u membrane filter.

Total Metals: The concentration of metals in an unfiltered sample following vigorous digestion.

Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid. This is a less vigorous digestion that the Total Metals digestion.

Quality Control Indicator (QCI): A general term used to refer to blanks, standards, MS/MSDs, etc...

NIST: The United States Department of Commerce, Technology Administration, National Institute of Standards and Technology (formerly National Bureau of Standards).

2. SUMMARY OF METHOD

Prior to analysis using this method, samples must undergo digestion (except samples for dissolved metals). See the appropriate metals digestion SOP for specific instructions.

Atomic emission spectroscopy is a process in which the light emitted by excited atoms or ions is measured. This phenomenon occurs when sufficient thermal or electrical energy is available to excite a free atom or ion to an unstable energy state. Light is emitted when the atom or ion returns to the fixed or ground state. These wavelengths of light are specific for the elements present in a given sample.

The instrument operates by using a plasma stream to excite the atoms and ions to an unstable energy state. As the atoms and ions return to their ground state, a photomultiplier tube is used to measure the element-emitted light in order to determine the concentration of the various elements.

Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in section 5 is also recognized and appropriate corrections are made.

In order to determine the best sensitivity for elements with wavelengths below 190 nm, the photomultiplier tubes need to be in a vacuum or purged system. UV light below 190nm tends to be absorbed by oxygen, carbon dioxide, and water vapors, thereby reducing the amount of light passing from the entrance slit to the detector. Although argon is preferred, argon or nitrogen can be used to purge the system.

3. SAFETY

This method may involve hazardous materials, operations and equipment. This method 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. For a detailed description of the hazards associated with a specific chemical consult the Material Safety Data Sheets available through the laboratory safety officer.

The ICP spectrometer uses high power levels of radio frequency

energy in the power supply and torch unit. This energy is potentially hazardous if allowed to escape. Safety devices and screening interlocks should not be bypassed or disconnected. The power supply of the instrument is capable of generating lethal voltages.

Never directly view the ICP torch without protective eyeware. Potentially hazardous ultraviolet radiation may be emitted from the torch. Ordinary safety glasses will, in general, provide sufficient protection. Additional side shields will ensure a further margin of safety.

Gases commonly used with ICP instruments include argon and nitrogen. High pressure gas cylinders can be dangerous if mishandled. Move gas cylinders with an approved handcart after insuring that the valve cap is secured. Store gas cylinders in a vertical position only. Fasten securely to an immovable bulkhead or a permanent wall.

When gas cylinders are stored in confined areas, such as a small storage room, ventilation should be adequate to prevent toxic or explosive accumulations of gas. Locate gas cylinders away from heat or ignition sources. Cylinders have a pressure-relief device which will release the contents of the cylinder if the temperature exceeds 52°C.

When the equipment is turned off at the end of the work day, close all gas cylinder valves tightly at the tank. Bleed the remainder of the line to the atmosphere before the exhaust fan is turned off. This is the preferred procedure. In some cases, it may not be possible to do this due to overnight runs and/or configuration of gas lines.

Perform periodic gas leak tests by applying a soap solution or Snoop Leak Detector to all joints and seals. Recommended frequency is once per week and/or whenever a tank is changed. See manufacturer's instruction for proper installation of drain vessel.

4. REAGENTS AND MATERIALS

4.1. Apparatus.

The following apparatus is recommended for performing this procedure. Equivalent items can be used so long as the analytical and QA/QC requirements in this SOP can be met.

4.1.1. Inductively coupled argon plasma emission spectrometer. Computer-controlled emission spectrometers equipped with background correction.

Perkin-Elmer Optima P3000 , Simultaneous ICP
Perkin-Elmer Optima P3000DV, Simultaneous ICP

4.1.2. Compatible printer.

4.1.3. Radio frequency generator.

4.1.4. Peristaltic pumps.

4.1.5 Autosamplers.

4.1.6. Argon gas supply: Welding grade or better.

4.1.7. Pipets: Macro (Oxford) and micro (Eppendorf) pipets with disposable tips.

Oxford pipet 1-5 mL/pipet tip
Oxford pipet 5-20 mL/pipet tip
Eppendorf pipets 1 - 250 ml and tips

4.1.8. Repipettor: used for making dilutions

4.1.9. Assorted Glassware including graduated cylinders and volumetric flasks. Refer to the Glassware Washing SOP for instructions on cleaning glassware.

4.2. Reagents.

The following reagents are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviation from the reagents listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented in the SOP.

4.2.1. Traceability. See the Reagent and Standards Tracking SOP for instructions on ensuring traceablility.

4.2.2. Reagent Grade Chemicals. All reagents must be reagent grade or better.

4.2.3. Deionized water. Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, calibration standards, and dilution water. If the in house de-ionized water is found to be of unacceptable quality, purchased bottled water may be used so long as it is found to be of acceptable quality.

4.2.4. Nitric acid (concentrated). If metal impurities are found to be present, use a spectrograde acid.

4.2.5. Nitric Acid (1:1). prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

4.2.6. Hydrochloric acid (concentrated). If metal impurities are found to be present, use a spectrograde acid.

4.2.7. Hydrochloric Acid (1:1). prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

4.2.8. Gases. Gases should be of high purity. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Air must be cleaned and dried through a suitable filter to remove oil, water, and other foreign substances.

4.2.9. Snoop Leak Detector. Supelco Catalogue no. 2-0434

4.3. Standards

The following standards are recommended for performing this procedure. The use of alternative standards will be allowed as long as the analytical and quality objectives of the SOP can be met. When instructions are given on how to prepare a specific volume of standard, larger or smaller volumes can be prepared as needed. At least one of the standards must be NIST traceable where available.

4.3.1. Standard Logbooks. See the Reagent and Standards Tracking SOP for instructions on ensuring traceablility.

4.3.2. Stock standard metal solutions. Commercially available stock standard solution are to be used. The stock solutions are purchased at concentrations of 100, 1,000 or 10,000 mg/L. Silver stock standard should be limited to a maximum concentration of 2.0mg/L. Silver standards at that concentration are stable for 30 days.

CAUTION: Many metals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling stock solutions.

4.3.3. Mixed Calibration Standard Solutions

Either purchase mixed calibration standards or prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in a volumetric flask. The standards are prepared in a matrix of 5% hydrochloric acid and 6% nitric. This approximates the matrix of sample digestates but is not an exact matrix match to all the different types of digestates analyzed by this method (see section 11 for details). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. The higher the concentration of the elements in the mixed standard, the longer the shelf life.

Shelf Life of Standards:

≥1,000 mg/L = 1 year, or manufacturer's expiration date

<1,000 mg/L = 6 months, or manufacturer's expiration date

<10 mg/L = 6 months

<0.1 mg/L = 1 month

Silver standards = 1 month

See Table 3 for typical standard combinations used in this analysis. Other standard mixes may be used provided the analyst has demonstrated that spectral interferences are not present and that the combined elements are stable together and the analyst has obtained approval from the management team.

4.3.4. General Formula for Preparing Standards. Refer to Table 2 for calibration standard concentrations for each element. The calibration standards are made from the concentrated stock solutions. Prior to creating each standard the analyst should calculate the amount of solution needed to get the desired final concentration. Do not assume that the volumes recorded in the standard logbook for the previous standard are correct. To calculate the volume of stock solution needed to get to a desired concentration use the equation:

$$V_s = \frac{C_f\ V_f}{C_s}$$

Where:

V_s = The volume of stock solution needed in mL
C_f = The final concentration desired in mg/L
V_f = The final volume desired in mL
C_s = Initial concentration (of stock solution) in mg/L

4.3.5. Initial Calibration Verification Standards (ICVS). For each metal analyzed, it is necessary to obtain and analyze an ICVS following each calibration. The ICVS is a second source standard different than that used for preparing the curve. Prepare the ICVS at a concentration that is 10% to 50% of the maximum of the calibration curve. Refer to Table 2 for calibration standard concentrations. Prepare the ICVS in the same acid matrix as the calibration standards. Care should be taken to ensure that the elements are compatible and stable together.

4.3.6. Continuing Calibration Verification Standard (CCVS). Prepare the CCVS from the same source as the calibration curve and at a concentration that is 25% to 50% of the maximum from the calibration curve. Refer to Table 2 for calibration standard concentrations. Prepare the CCVS in the same acid matrix as the calibration standards. Care should be taken that the elements are compatible and stable together.

4.3.7. Interference Check Standards. Interference check standards are prepared standard mixes containing known concentrations of interfering elements that will provide an adequate test of the correction factors.

4.3.7.1. Initial Set Up and Ongoing Verification of IECs. The following solutions are used to initially set up the interelement correction factors and for ongoing verification every 6 months:

200 mg/L - Al;

100 mg/L - Ca, Fe, Mg, and Na;

50 mg/L - Ba, Be, Cd, Ce, Cr, Co, Cu, Mn, Mo, Ni, Sn, Si, Ti, Tl and V.

4.3.7.2. Daily Verification of IECs. After evaluating the interferences found on each instrument and establishing the necessary correction factors, the following ICS solutions are required on a daily basis to verify the adequacy of the correction routine:

ICS_Solution_1: A blank solution spiked with 250ppm of Aluminum, Calcium, Magnesium and 100ppm of Iron

ICS_Solution_2: ICS Solution 1 spiked with 500ppb of all other elements.

ICS_Solution_3: A blank solution spiked with 50ppm of Nickel, Chromium, Manganese, plus Molybdenum at 20ppm and Copper at 40ppm.

5. INTERFERENCES

5.1. Spectral Interferences.

Spectral interferences are caused by: (1) overlap of a spectral line from another element: (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements.

5.1.1. Spectral Overlap And Interelement Correction Factors. Direct spectral overlap is compensated for using Interelement Correction Factors (IECs). Use of the IEC technique requires that the sample be analyzed for each interfering element suspected to be in the sample. IEC's are most useful for interferents likely to be found in high concentration in actual samples. Al, Ca, Fe, and Mg are common interferents. Elements typically found at low concentrations produce negligible interference.

5.1.2. Unresolved Overlap. Unresolved overlap requires selection of an alternate wavelength.

5.1.3. Background Contribution. Background contribution and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. On a simultaneous instrument, the photomultiplier tubes are directly behind and in line with each element exit slit. A spectrum shifter is used to shift the light path to the right or left. Each correction point increases the analytical time 100%. Therefore, it is necessary to determine the common correction points for the elements of interest. Usually three or four common correction points can be determined for all the elements combined. The study should be performed on a variety of matrices and background correction points applicable to the various matrices should be chosen for routine analyses. The number of background correction points should be limited to three or four points.

5.2. Physical Interferences.

Physical Interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.3. Chemical Interferences.

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

5.4. Memory Interference

Memory Interferences occur when analytes in a previous sample contribute to signals measured in the following sample(s). These effects can occur from sample deposition any where in the sample uptake system and in the nebulizer. Sample material may also build up in the plasma torch and spray chamber assembly. Memory effects can be minimized by adequate flushing the system with adequate amounts of reagent blank between sample aspirations. The required rinse time should be established prior to analyzing customer samples.

5.5. High Salt Concentrations

High salt concentrations in the sample can cause analyte signal suppressions and confuse the results of interference tests. Both ICP instruments display negative values. If the instrument displays a negative value, dilute the sample and re-analyze. Post digestion spikes are useful in determining if the sample matrix is diluted sufficiently to minimize the effects of the sample matrix.

5.6. Contamination and Loss.

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention.

6. PROCEDURE

6.1. Preservation and Handling.

6.1.1. Collection. The minimum sample volume required is 100mL for aqueous samples and 2g for non-aqueous samples (100g are needed if TCLP metals need to be done). It is recommended that aqueous samples be collected in 1 liter plastic or 32 oz glass containers, and that non-aqeous samples be collected in 4 - 16 oz jars.

6.1.2. Preservation. Aqueous samples (except Cr VI) must be preserved to pH <2 using approximately 2.5mL of 1 part nitric acid to 2.5 parts water. When samples are received pre-preserved, it is the responsibility of the analyst to verify adequacy of preservation at the time the actual analysis is initiated. Non-aqueous samples do not require preservation.

6.1.3. Holding Time. Metals analyses must be conducted within six months.

6.2. Sample Preparation and Pretreatment.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, total, or total recoverable.

6.2.1. Dissolved Metals.

6.2.1.1. For the determination of dissolved constituents, the unpreserved sample must be filtered through a 0.45 micron membrane filter as soon as practical after collection. A glass fiber pre-filter may be used in combination with the 0.45 micron membrane filter. Glass or

plastic filtering apparatus using membrane filters are recommended to avoid possible contamination. The filtering apparatus should be acid washed prior to use and in between samples. Use the first 50-100 mL of filtered sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate.

6.2.1.2. Acidify the filtrate with 1:1 nitric acid to a pH of <2. Approximately 2-3 mL nitric acid per liter will be needed. Analyses performed on a sample so treated shall be reported as "dissolved" concentration.

6.2.1.3. Dissolved metals samples do not require digestion prior to analysis if the sample has been properly filtered and preserved.

6.2.2. Total Metals. All samples to be analyzed for total metals must be digested prior to analysis. Refer to the appropriate metals preparation SOP for specific instructions.

6.2.3. Total Recoverable Metals. All samples to be analyzed for total recoverable metals must be digested prior to analysis, but the digestion is not as vigorous as a Total Metals digestion. Refer to the appropriate metals preparation SOP for specific instructions.

6.2.4. Turbidity Check for Drinking Water Samples. For drinking water samples, verify that the pH is <2 and then check the turbidity of the sample. Drinking water samples with a turbidity of <1.0 NTU (after acidification) may be analyzed by direct injection as long as no precipitate forms. If precipitate forms in the acidified sample or if the turbidity is not <1.0 NTU, digest the sample according to the drinking water prep SOP prior to analysis.

6.3. Instrument Preparations.

6.3.1. Specific wavelengths are listed in Table 2 for each instrument. Sample matrix may require the analysis to be performed at an alternate wavelength. However, acceptable IECs, MDLs, MVSs, and LDRs must be performed prior to analyzing and reporting customer samples at alternate wavelengths.

6.3.2. The plasma operating conditions must be optimized prior to performing MDLs, MVSs, LDRs, and establishing IECs. Refer to instrument operations manual for specific instruction on optimizing the plasma operating conditions and viewing height.

6.3.3. If the instrument operating conditions (such as nebulizer gas flow rates or incident power) are changed or a new torch injector tube with a different orifice internal diameter installed, the plasma and viewing heights should be re-optimized.

6.4. Interelement Correction Factors (IECs).

After background correction points have been determined, interference correction factors must be added. The IECs will automatically correct the analytical result for interelement interferences. Determine interelement correction factors (IEC)

by analyzing single-element high purity stock solutions at concentrations within the linear range of the instrument. The instrument conditions must match those used for sample analysis. Standards used for flame atomic absorption work may contain some contamination and are not acceptable for determining IEC's. If a significant signal is seen for any element other than the one present in the stock solutions, a factor must be calculated and entered to correct for this.

$$\text{correction factor (k1)} = \frac{\text{apparent concentration of analyte}}{\text{known concentration of interferent}}$$

The IEC factor k1 is used to calculate the corrected analyte concentration as follows:

$$A = B - (C \times D)$$

Where:
A = corrected analyte concentration
B = measured analyte concentration
C = Interferent Concentration in the ICS sample
D = k1

Refer to the instrument manufacturer's manual for more specific instructions on setting up the IEC's.

6.5. Making Measurements in Duplicate.

For the purposes of this test, all analyses are performed in duplicate and the results are averaged. For all standards (calibration standards, ICVSs, CCVSs, ICS-C, LDRs, etc.) the two duplicate runs must agree within 5% RSD. No %RSD criteria is used for blanks because of the high variability in results when no analyte is present. For all other runs including samples, prepped QCIs (LCSs, MS/MSDs, MVSs, MDLs, etc.), ICS-AB and the RLVS the two duplicate runs must agree within 20% RSD.

If the above criteria is not met for the duplicate %RSD, re-analysis is required. Some sample matrices may require dilution in order to bring the duplicate %RSD into control.

In all cases the average result from the duplicate measurements should be used for reporting and evaluating QC.

6.6. Rinse Time (Rinse Blank).

Rinse the system with a dilute nitric acid solution prior to the analysis of each sample. The rinse time will be one minute. This is sometimes referred to as a rinse blank. Shorter rinse times may be validated using the following procedure.

Aspire a standard containing each element at a concentration 10 times over the established LDR. The aspiration time for this standard should be the same as the normal sample analysis period, followed by analysis of a reagent blank at designated intervals. The length of time required to reduce the analyte signals to within a factor of 2 times the established MDL is noted. This

time is then used as the minimum required rinse period.

Document the rinse time study and file in a location that it can be easily retrieved for future reference.

6.7. Instrument Calibration.

6.7.1. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the established linear dynamic range to be valid.

6.7.2. Background Equivalent Concentration (BEC): Determining the BEC provides a measure of plasma and instrument performance. It can be used to check the torch alignment and to optimize the nebulizer gas flow. It is the concentration of analyte required to produce the same intensity as the plasma background at a given wavelength. Affecting the BEC are the accuracy of analyte concentration, spectrometer viewing height, nebulizer gas flow rate, and RF power. The BECs can be useful when setting up IECs.

Calculation of BEC: $\frac{Ib}{Ip - Ib}$ x concentration of standard *

where: Ip = intensity of standard
Ib = intensity of blank
*suggested concentration of standard is 1 ppm manganese

Note: Use of the BEC to determine instrument performance is recommended, but it is optional.

6.7.3. The instrument must be allowed to become thermally stable before beginning (usually 60 min prior to calibration). Follow the manufacturer's instructions to establish the instrument calibration. A minimum of a reagent blank and one standard are required for calibration.

6.8. Blanks

Two types of blanks are required for the analysis. The calibration blank or reagent blank is used in establishing the analytical curve. The preparation blank is used to monitor the entire analytical process for sources of contamination.

6.8.1. Calibration Blank. Prepare by acidifying DI water to the same concentrations of the acids used in the standards. This blank is used for initial and continuing calibration blank determinations.

6.8.2. Preparation Blank. Prepared with each sample digestion batch, see the appropriate metals digestion SOP for specific instructions. The preparation blank contains the same acids and concentrations as the samples.

6.9. Laboratory Control Standard

The LCS is a second source standard used to assess laboratory performance. The LCS must be carried through the entire sample preparation process, including digestion. See the appropriate digestion SOP for specific instructions on preparing the LCS. A LCS is not required for dissolved metals that do not undergo the digestion process. The recommended spiking level for the LCS is 0.5 mg/L. Other spiking levels may be used to satisfy project specific needs.

6.10. Sample Analysis

Set up and analyze all required QCI and samples at the frequencies stated in section 7 of this SOP.

6.11. Calculation And Reporting

6.11.1. Direct determination of liquid samples: Read the analyte value in mg/L from the readout provided by the instrument (the average of two duplicate measurements) and multiply by any dilution factor if a dilution was performed:

mg/L metal in sample = A x dilution factor

where:

A = mg/L of metal in diluted aliquot

$$\text{dilution factor} = \frac{\text{final volume}}{\text{sample aliquot}}$$

6.11.2. For solid samples:

$$\text{ug/g or mg/Kg metal in sample} = A \times \frac{\text{final volume in mL}}{\text{wt. of sample in g}}$$

where:

A = mg/L of metal in processed sample

6.11.3. Soils and sediments should be expressed on a dry weight basis, while waste materials are expressed on a wet weight basis.

conversion of wet weight result to dry weight basis:

$$\frac{\text{wet weight sample result}}{\text{the decimal equivalent of the \% Total Solids}}$$

6.11.4 All samples over the linear range of the analyte must be diluted and re-analyzed. Dilution water must be matrix matched to the acid concentrations in the calibration standards (5% hydrochloric and 6% nitric acid). Include the dilution factor in the final concentration reported.

6.11.5. The interelement correction factors for the following elements are not valid above the ranges indicated. Refer to Table 5 to determine the potential interferences created by the

presence of these elements in the sample matrix. If the compounds listed below exceed the given ranges and thus interfere with the analytes of interest (Table 5), dilute sample accordingly. Choose a dilution which reduces the concentration of the interfering element to below the range.

Molybdenum > 20 mg/L
Calcium > 250 mg/L
Magnesium > 250 mg/L

6.11.6. Evaluate analytical run batch and preparation batch QC according to the criteria in section 7 prior to loading data into LABSYS.

6.11.7. Issue any required LNF forms and place in the job folder prior to loading results into LABSYS.

6.11.8. Use the following equation to calculate RPD:

$$RPD = \left| \frac{(A - B)}{C} \right| \times 100$$

Where: A = MS result in mg/L (NOT percent recovery)
B = MSD result in mg/L
C = Average of the MS and MSD results

7. QUALITY CONTROL

The following details the QC requirements which apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either instrument performance or individual sample performance. Our goal is to produce defensible data of known and documented quality.

7.1. Method Detection Limit (MDL) Studies

A MDL study must be done during initial method validation and then verified annually. If the analytical method is changed, a new MDL study must be performed. Separate MDLs are required for each different metals prep method, for each different wavelength used, and on each instrument used. Follow the "Procedure for Detection Limit Studies" SOP for performing and evaluating the MDL study.

7.2. Linear Dynamic Range (LDR)

7.2.1. Definition and Use of the LDR

The linear dynamic range is defined as the concentration range over which the analyte calibration remains linear. The LDR must be determined for each analyte and for each wavelength. The linear range is determined by analyzing succeedingly higher standard concentrations (at least five) until the observed signal exceeds the criteria given below.

7.2.2. Frequency of LDR

A linear dynamic range analysis must be performed during instrument validation prior to running client samples. For those analytes that periodically approach the upper limit of the range, the range should be verified every six months. LDRs shall also be verified whenever a significant change is made to the method, the instrument, or the operating conditions.

7.2.3. Criteria for LDR

Determine the upper limit of the linear dynamic range by analyzing succeedingly higher standard concentrations until the observed value of the standard exceeds 90 - 110% of the true value. The standard level just below the one that fails is the upper limit of the linear dynamic range.

The LDR can be subsequently verified by analyzing a high standard at the determined LDR. The observed value should be 90 - 110% recovery of the expected value.

7.2.5. Documentation for the LDR

The LDRs (and any subsequent verifications done on the LDR) should be filed in a manner that will ensure that they can be easily found and retrieved by the analyst. The ID number of the LDR standard must be recorded in the raw data.

7.3. Interelement Correction Factors (IECs).

7.3.1. Definition and Use of IECs

After background correction points have been determined, interference correction factors must be calculated as described in section 6.4. The IECs are used to automatically correct the analytical result for interferences caused by other elements. Table 5 lists potential interferences using the wavelengths and operating conditions specified in this SOP.

7.3.2. Frequency of IEC Determination

When an instrument is initially brought online, IECs must be established after optimizing the plasma but before analyzing any samples. The IECs are then verified daily through the analysis of Interference Check Standards (ICSs) at the beginning and end of the analytical run (section 4.3.7.2). The entire correction routine must be verified at a minimum of every six months using the more comprehensive Interference Check Standards in section 4.3.7.1.

7.3.3. Criteria for Verification of IECs

Spiked ICSs: 80% - 120%

Unspiked ICSs: < Reporting Limit

7.3.4. Corrective Action for IECs

If the ICS results indicate that the IECs have changed (section 7.3.3), new IECs will need to be determined. Follow the instrument manual for specific instructions on updating the IEC factors.

The software is capable of reprocessing the analytical run to apply the corrected IEC to the analytical run. This is an acceptable practice so long as all run QCI are in control after re-processing the data.

If no interfering elements are found in the samples the data can be reported without correcting the IECs factors.

7.3.5. Documentation of IEC Verification

File the ICSs in a manner that will allow them to be easily retrieved and referenced to the associated analytical run. Record the ID numbers of the ICSs on the raw data. Keep a record of IECs and changes made to the IECs on file (an electronic record is acceptable).

7.4. Method Validation Sample (MVS)

7.4.1. Definition & Use Of MVS

The purpose of the MVS is to verify that the method can generate precise and accurate analytical data. Method validation samples consist of four replicates of spiked reagent water prepared and analyzed in a manner identical to samples. The solution used to spike MVSs must be from a different source than the calibration standards. Each replicate must be spiked at a concentration of approximately 10 times the most recently determined MDL (the calculated MDL, not the concentration that the MDL study was spiked at). MVSs are used to validate new analyst and new instruments, and to validate changes in analytical equipment or techniques.

7.4.2. Frequency Of MVS

Separate MVSs must be done for each metals prep method used and for each different instrument method performed (wastewater, RCRA, and drinking water methods) and for each element analyzed. Each analyst performing this method is required to perform these method validation studies. Each instrument is required to have method validation studies for all elements and methods it is used for. However, each analyst does not have to analyze a set of method validation samples on every instrument. Method validation must be repeated whenever a significant change in the method or instrumentation is made which could cause the previous MVS to become invalidated.

7.4.3. Criteria For MVS

Method 6010B (Groundwater & Soils) and 200.7 (Waste Water)

The average percent recovery must of the MVSs must fall within 80-120%, and the percent relative standard deviation must be within +/-20%.

Method 200.7 r4.4 (Drinking Water)

The average percent recovery must of the MVSs must fall within 85-115%, and the percent relative standard deviation must be within +/-20%.

7.4.4. Corrective Action For MVS

If the MVS criteria cannot be met, the problem must be identified and corrected. If the problem has been identified as an instrument problem only, the MVS may be re-analyzed after correcting the problem. If the problem includes a preparation problem, then the MVS must be re-prepped and re-analyzed. An acceptable MVS must be obtained prior to analyzing client samples.

7.4.5. Documentation For MVS

One method validation study may serve several purposes including analyst training, method validation, and instrument validation. The MVSs should be filed in a manner that will ensure that they can be easily retrieved for all intended purposes. The standards ID number of the standards used to spike the MVSs must be documented in the metals prep logbook and on the ICP report.

7.5. Analyst Certification

This method is restricted to use by, or under the supervision of analysts trained in the use of ICP and skilled in the interpretation of ICP data (see Analyst Certification SOP).

7.6. Initial Calibration

7.6.1. Definition & Use Of Initial Calibration

The purpose of initial calibration is to relate detector response to sample concentration. For the purposes of this SOP, initial calibration consists of a reagent blank and one standard. Refer to Table 2 for the recommended calibration levels for each element. The initial calibration is used to quantitate samples and QCIs.

7.6.2. Frequency Of Initial Calibration

Initial calibration must be performed daily at the beginning of each analytical run, and must be redone during the corrective action process when a problem is indicated by QCIs that fail (such as ICVS, CCVS, or reagent blank).

7.6.3. Criteria For Initial Calibration

Because a two point calibration is used (a reagent blank and one standard), calibration criteria is not applicable to this method. The calibration standard must be within in the linear range of the analytes of interest.

7.6.4. Corrective Action for Initial Calibration

Not applicable.

7.6.5. Documentation For Initial Calibration Curve

The initial calibration should be filed in a manner that will ensure that it can be easily retrieved and referenced to all associated samples. Record the ID number of ICAL standards in the raw data (e.g., in the injection logbook and on the quant report).

7.7. Initial Calibration Verification Standard (ICVS)

7.7.1. Definition & Use Of ICVS

The purpose of the ICVS is to verify that the calibration standards were chemically pure, prepared properly, and that they have not degraded significantly since the time they were made. The ICVS must be obtained from a second source than the calibration standards. The ICVS must be prepared at a concentration of 10% to 50% of the concentration of the calibration standard. This standard does not go through sample preparation stages.

7.7.2. Frequency Of ICVS

The ICVS must be analyzed three times in sequence each time the calibration standards are remade. The ICVS must also be analyzed daily, after every initial calibration.

7.7.3. Criteria For ICVS

6010B Criteria: ICVS must be +/-10% of the true value.

200.7 (WW) Criteria: ICVS must be +/-5% of the true value.

200.7 (DW) Criteria: The 3 ICVSs analyzed to verify new calibration standards must be averaged and the average needs to be +/-5% of the true value. The daily ICVS must also be +/-5% of the true value.

7.7.4. Corrective Action For ICVS

If the criteria for the ICVS cannot be met, a problem is indicated either with the initial calibration or with the ICVS. Re-evaluate the initial calibration to verify that it was done correctly. Verify the acceptability of the source used for preparing the standards. Verify that both the initial calibration and the ICVS standards were prepared correctly. Correct any deficiencies found. If problems were found with the initial calibration, re-calibrate the instrument and then

re-analyze the ICVS. If the problem was with the ICVS, re-analyze the ICVS. Analysis cannot proceed until the ICVS is in control (if desired, the analyst may allow the run to proceed just for the elements that are in control, and then correct the problem and re-analyze any samples requiring the out of control elements).

7.7.5. Documentation For ICVS

Record the percent recovery of the ICVS on the raw data. The ICVS should be filed in a manner that will insure that it can be easily retrieved and referenced to the associated calibration. Record the ID number of the ICVS in the raw data.

7.8. Continuing Calibration Verification Standard (CCVS)

7.8.1. Definition & Use Of CCVS

The purpose of the CCVS is to establish that the response of the instrument has not changed significantly since the time that the initial calibration was performed. CCVSs must contain the full list of elements being analyzed, and are prepared at a concentration of 25% to 50% of the concentration of the calibration standard.

7.8.2. Frequency Of CCVS

Analyze a minimum of one CCVS at beginning and end of each analytical run. Also, analyze a CCVS after every tenth sample.

7.8.3. Criteria For CCVS

6010B Criteria: CCVS must be +/-10% of the true value.

200.7 (WW) Criteria: CCVS must be +/-5% of the true value.

200.7 (DW) Criteria: Initial CCVS must be +/-5% of the true value, all CCVSs after that must be +/-10%.

7.8.4. Corrective Action For CCVS

If the CCVS acceptance criteria cannot be met, perform any necessary corrective actions and re-calibrate the instrument. Any samples and QCIs analyzed since the last in control CCVS must be re-analyzed.

If desired, the analyst may allow the run to proceed just for the elements that are in control, and then correct the problem and re-analyze any samples requiring the out of control elements.

7.8.5. Documentation For CCVS

The percent difference of each compound should be summarized in a table or report. The CCVS should be filed in a manner that will ensure that it can be easily retrieved and referenced to all associated samples. Record the ID number of the CCVS in the raw data.

7.9. Reagent Blank

7.9.1. Definition & Use Of The Reagent Blank

The reagent blank is a deionized water blank that is subjected to the same conditions that a non-prepared sample undergoes. The reagent blank will determine if any contamination or any memory effects are occurring.

7.9.2. Frequency Of The Reagent Blank

Analyze a minimum of one reagent blank at the beginning and one at the end of each analytical batch. Also, analyze a reagent blank after a minimum of every tenth sample.

7.9.3. Criteria For The Reagent Blank

Results for the reagent blanks must be less than the reporting limit for each target analyte.

7.9.4. Corrective Action For The Reagent Blank

Since the instrument/calculation is zeroed to a reagent blank, a subsequent reagent blank outside the acceptance limit indicates a contamination problem or possibly instrument drift. Perform any necessary corrective actions and re-calibrate the instrument. Any samples and QCIs analyzed since the last in control reagent blank must be re-analyzed.

7.9.5. Documentation For The Reagent Blank

Record the concentration of the reagent blank on the raw data. All blanks should be filed in a manner that will ensure that they can be easily retrieved and referenced to all associated runs.

7.10. Preparation Blanks

7.10.1. Definition & Use Of Preparation Blanks

The purpose of the preparation blank is to ensure that samples are not being contaminated by glassware, reagents, or the analytical system. To accomplish this it is necessary that the blank be carried through all stages of the sample preparation and analysis steps. See the appropriate metals prep SOP for specific instructions on digestion of the preparation blank.

7.10.2. Frequency Of Preparation Blanks

Preparation blanks will be provided by metals prep personnel, with every prep batch. See section 1.1 for a definition of prep batch. Preparation blanks will also be provided with extraction sets done for quality control purposes such as method validation studies and MDL studies.

7.10.3. Criteria For Preparation Blanks

Acceptance criteria requires the procedure blank to be less than the reporting limit. Procedure blanks are not subtracted from the analytical results.

7.10.4. Corrective Action For Preparation Blanks

If a preparation blank does not meet criteria, then the concentration of the blank versus the samples in the prep batch will need to be compared.

If the concentration of the sample is greater than 10x the level of the blank, the sample can be reported with a "B" flag indicating blank contamination.

If the concentration of the sample is less than 10x the level of the blank, the sample should be re-prepped and re-analyzed. If this is not possible (i.e., lack of sample or holding time has expired) the sample must be reported with a "B" flag indicating blank contamination.

Clean samples without hits can be reported without flagging.

If positive values below the reporting limit are observed, they should be evaluated in relation to the sample(s) and extra care should be taken to avoid reporting false positives.

In all cases the amount detected in the blank should be indicated on the report and the source of contamination should be eliminated to prevent the problem from continuing.

7.10.5. Documentation For Preparation Blanks

All hits above the reporting limits should be clearly indicated on the raw data. All preparation blanks should be filed in a manner that will insure that they can be easily retrieved and referenced to all associated samples.

7.11. Laboratory Control Sample (LCS)

7.11.1. Definition & Use Of LCS

The purpose of the LCS is to establish that the techniques being used provide adequate recovery of metals. The LCS consists of an aliquot of reagent water that is spiked and carried through all the stages of sample preparation and analysis. LCSs must be from a different source than the calibration standards. See the appropriate metals prep SOP for specific instructions on preparing the LCS.

7.11.2. Frequency Of LCS

A LCS will be provided by metals prep personnel with every prep batch. See section 1.1 for a definition of prep batch.

7.11.3. Criteria For LCS

LCSs must pass the criteria in Attachment A.

7.11.4. Corrective Action For LCS

If the LCS does not meet criteria, the prep batch is out of control. All associated samples and QCIs must be re-prepped and re-analyzed. If this is not possible (holding time or limited sample) the data must be flagged for each analyte that failed LCS criteria.

7.11.5. Documentation For LCS

The percent recovery of each compound should be summarized in a table or report. The LCS should be filed in a manner that will insure that it can be easily retrieved and referenced to all associated samples. The ID number of the LCS standard must be documented in the metals prep logbook and on the ICP report.

7.12. Matrix Spikes/Matrix Spike Duplicate (MS/MSD)

7.12.1. Definition & Use Of MS/MSD

The purpose of the MS/MSD is to confirm that the matrix being analyzed is not interfering with the recovery of the analytes. MS/MSDs also serve as a measure of the long term precision and accuracy of the method. MS/MSDs are defined as spiked client samples. Select samples to be spiked on a rotating basis from among various client samples, waste streams, and other applicable locations. MS/MSDs are spiked at the same concentration as the LCS. MS/MSDs are carried through all of the preparation and analysis steps that the unspiked native sample is carried through. See the appropriate metals prep SOP for specific instructions on preparing MS/MSDs.

7.12.2. Frequency Of MS/MSD

MS/MSDs will be provided by metals prep personnel with every prep batch. See section 1.1 for a definition of prep batch.

7.12.3. Criteria For MS/MSD

Both the percent recovery and the RPD for the MS/MSD must meet the limits given in Attachment B.

7.12.4. Corrective Action For MS/MSD

If the MS or MSD fails, check percent recovery on the LCS. If the LCS is in control, the procedure is in control and the extraction batch is in control. However, a potential problem exists with the sample that was spiked.

Perform a post digestion spike on the sample that failed MS or MSD criteria. Spike at a concentration of approximately 10 times to 100 times the IDL. If recovery of the post digestion spike is within the control limits given below, report the sample along with the original recovery data from the MS and MSD. If the post digestion spike fails, proceed to analyze the sample according to the method of standard additions.

Post Spike Control Limits

6010B Post Spike Limits: 75% - 125%

200.7 (WW) Post Spike Limits: 90% - 110%

If the native sample is high in metals, the corresponding MS/MSD set may require dilution to the point that the spike amount becomes insignificant. If the MS/MSD requires dilution to the point that the expected amount in the diluted aliquot would be less than the reporting limit, report the result as "diluted out" and flag with the "D" flag. For example, consider a MS/MSD that is spiked at 25ppm for an element with a reporting limit of 1ppm. A 1/25 dilution of the MS/MSD would then result in an expected concentration in the diluted aliquot of 1ppm (plus the level in the sample), and therefore would be reported. While a 1/50 dilution would be reported as "diluted out".

7.12.5. Documentation For MS/MSD

The percent difference of each element should be summarized in a table or report. The MS/MSD should be filed in a manner that will ensure that it can be easily retrieved and referenced to the associated sample. The ID number of the MS/MSD standard must be documented in the metals prep logbook and on the ICP report.

7.13. Method of Standard Additions (MSA).

7.13.1. The method of standard additions technique involves adding known amounts of standard to several aliquots of digested sample. This technique compensates for the matrix interferences that enhance or depress the analyte signal. It does not compensate for additive interferences such as contamination, baseline shift or interelement interferences. MSA is used when interferences are suspected in the samples (e.g., such as when both matrix spike and post digestion spiking attempts fail).

7.13.2. Measure 4 equal volumes of well mixed, digested sample. To one portion add acidified reagent blank. Add an equal volume of three known standards differing in concentration to each of the three remaining aliquots. For example: add 1mL of blank to portion one, 1mL of 25 ppm standard to portion two, 1mL of 50 ppm standard to portion three, and 1mL of 100 ppm standard to portion four.

7.13.3. Analyze the 4 aliquots as unknown samples. Obtain the result of the MSA analysis by plotting a linear regression analysis of the absorbance values versus the spiking concentrations. The intercept value is the concentration of the analyte in the sample. MSA calculations can be done using either an EXCEL spreadsheet designed for that purpose, or through the MSA program in LabSys. The data obtained from this analysis may be reported if the following statements hold true:

1. The analyte curve must be linear over the concentration range of concern. For best results, the slope of the MSA plot should be similar to the standard curve.

2. The effect of the interference should be constant as

the ratio of analyte added to the sample matrix changes. The standard addition should respond in a similar manner as the analyte.

3. The determination must be free from spectral interference and background corrected for nonspecific background interference.

Refer to method SW-846 Method 7000A for Section 8.7.1 for details.

7.13.4. All samples analyzed and reported by MSA must be flagged with the "MSA" flag. An LNF is required to be placed in the job folder. If the MSA analysis fails, report the failure to the Project Manager. The sample will have to be analyzed by an alternate method or Project Management must generate a case narrative on the data.

7.14. Reporting Limit Verification Standard

7.14.1. Definition and Use of RLVS

The Reporting Limit Verification Standard (RLVS) provides information regarding instrument performance at or near the reporting limit. The concentration of the RLVS should equal the reporting limit. If the reporting limit is close to the method detection limit, it may be necessary to raise the RLVS by a factor of 2-5.

7.14.2. Frequency of RLVS

Analyze this standard after performing instrument calibration. In some cases, it may be possible to incorporate the RLVS standard into the calibration curve.

7.14.3. Criteria for RLVS

Acceptance criteria requires the percent recovery to be within ± 25% of the true value.

7.14.4. Corrective Action for RLVS

An out of control RLVS indicates an improperly prepared standard or potential problems with the calibration curve. Re-analyze the RLVS to confirm the out of control result. If the RLVS is too high but samples are less than the client reporting limit data is deemed acceptable and can be reported. If the RLVS is still out of control, identify and correct the source of problem. Re-calibrate and re-analyze the affected samples.

7.14.4. Documentation

Record the percent recovery on the raw data. Record the ID number of the RLVS in the raw data and on the ICP report.

7.15. Serial Dilution.

7.15.1. Definition and Use of Serial Dilution Test.

The serial dilution test is used to test for physical and chemical interferences in the sample matrix. A serial dilution test involves performing at least a 5x dilution on an unspiked client sample.

7.15.2. Frequency of Serial Dilution Test.

Perform a serial dilution test on a minimum of one sample from each prep batch. Any sample requiring dilution in the prep batch can be used for the serial dilution test. If no samples in the batch require dilution, select a sample that is at least 5 times the reporting limit to perform the serial dilution test. If all of the samples in the prep batch are less than 5 times the reporting limit, a serial dilution test is not required.

7.15.3. Criteria for Serial Dilution Test.

6010B: Dilution results must agree within +/-10%.

200.7 (WW): Dilution results must agree within +/-5%

200.7 (DW): Dilution results must agree within +/-10%

7.15.4. Corrective Action for Serial Dilution Test.

If a sample fails the serial dilution test, proceed to analyze the sample using the method of standard additions.

7.15.5. Documentation of Serial Dilution Test.

File the serial dilution test in a manner that will allow it to be easily retreived and referenced to the associated prep batch. Record the calculated percent difference on the raw data or in a report.

8. POLLUTION CONTROL

It is TestAmerica Incorporated'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 upon anticipated usage and reagent stability).

9. WASTE MANAGEMENT

Laboratory 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 the Waste Disposal SOP.

10. REFERENCES

10.1. "Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Atomic Emission Spectrometry", Perkin Elmer.

10.2. "Inductively Coupled Plasma-Atomic Emission Spectroscopy", SW-846 Method 6010B, revision 2 December 1996.

10.3. Users Manuals for the PE Optima 3000DV.

10.4. "Standard Operating Procedure for ICP Metals", revision 3, August 20, 1999 TestAmerica Inc.

10.5. "Inductively Coupled Plasma - Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes", EPA Method 200.7, 40 CFR Part 136 Appendix C.

10.6. "Inductively Coupled Plasma - Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes", EPA Method 200.7 r4.4, May 1994.

11. METHOD DEVIATIONS

Deviations from Method 6010B are listed below:

11.1. Section 3.1.8 of Method 6010B states to calculate recovery criteria for the ICS solution by multiplying the concentration of the interfering element by the value of the correction factor and dividing by 10. This is contradictory to sections 3.1.9 and 8.6.2 of the method which both state that the criteria for ICSs is +/-20%. This SOP uses a criteria of +/-20% for ICSs which are spiked with non-interfering elements and a criteria of <RL for ICSs which are spiked only with the interferences. The criteria based upon the RL is consistent with the criteria for a blank.

11.2. Section 7.5 of Method 6010B requires that the instrument be rinsed for 1 minute between each sample with the calibration blank. This laboratory rinses between each sample using a dilute nitric acid solution instead of the calibration blank.

11.3. Sections 5.4, 5.5, 5.7, and 7.1 of Method 6010B require that standards be matrix matched to the samples. This laboratory utilizes an acid matrix of 5% hydrochloric acid and 6% nitric acid for standards which matches the matrix used for groundwaters and wastewaters, but does not match the matrix used for soils and other samples as defined in the table below.

Sample or QC	Laboratory Acid Conc. In Samples & QC
Dissolved Metals Samples	0.1% nitric acid
Drinking Water Samples	1% nitric acid
Digested Drinking Water Samples	1% hydrochloric acid 1% nitric acid
Aqueous (WW/GW) Samples	5% hydrochloric acid 6% nitric acid
All standards	5% hydrochloric acid 6% nitric acid
Non-aqueous Samples	10% hydrochloric acid 10% nitric acid

11.4. Method 6010B provides the following shelf life for standards. This SOP allows for a longer standard shelf life in some cases as shown below.

Shelf Life of Standards:

Standard Conc.	Method 6010B shelf life	Shelf life used in this SOP
≥1,000 mg/L	1 year	manufacturer's exp. date sometimes to exceed 1 year
<1,000 mg/L	6 months	manufacturer's exp. date sometimes to exceed 6 months
<10 mg/L	1 month	6 months
<0.1 mg/L	daily	1 month
All silver standards	1 month	1 month

Deviations from Method 200.7 (WW) are listed below:

11.5. Sections 5.2 - 5.2.2 of Method 200.7 (WW) recommend that a serial dilution test and a post spike be done whenever a new or unusual sample matrix is encountered. This SOP requires that a serial dilution test be done with each prep batch of 20 samples or less. This SOP requires a post spike be performed whenever the MS or MSD is out of control.

11.6. Section 7.4 of Method 200.7 (WW) states that standard acid concentrations are 1% nitric acid and 5% hydrochloric acid. Section 11.3 of this SOP defines the acid concentrations utilized in this laboratory.

11.7. Section 7.6.2 of Method 200.7 (WW) requires that ICSs be spiked with the elements of interest at 100ug/L or 5 times the estimated detection limit. Section 4.3.7 defines the ICS spiking levels used by this laboratory.

11.8. Section 11.1 of Method 200.7 (WW) states that the reagent blank should be subtracted from all samples. In this SOP a reagent blank is included as a point in the calibration and is therefore not subtracted since this would create a redundancy.

11.9. Section 12.1.2 of Method 200.7 (WW) requires that ICSs be analyzed at the beginning, end, and at period intervals throughout the analytical run. This SOP only requires that the ICSs be analyzed at the beginning and end of the analytical run.

11.10. Section 12.1.3 of Method 200.7 (WW) requires that a second source standard (ICVS) be analyzed whenever new calibration standards are prepared and then again weekly. This

SOP requires that the ICVS be analyzed daily, after each calibration.

Deviations from Method 200.7 r4.4 (DW) are listed below:

11.11. Method 200.7 r4.4 contains the same contradictions discussed in section 11.1 regarding ICS criteria. This SOP uses a criteria of +/-20% for ICSs which are spiked with non-interfering elements and a criteria of <RL for ICSs which are spiked only with the interferences.

11.12. See deviation about matrix matching in section 11.3 of this SOP.

Table 1. Routine Reporting limits for Aqueous Samples

Element	Reporting limit
Aluminum	0.100
Antimony	0.500
Arsenic	0.200
Barium	0.020
Beryllium	0.005
Boron	0.050
Cadmium	0.010
Chromium	0.040
Cobalt	0.100
Copper	0.020
Iron	0.050
Lead	0.200
Manganese	0.010
Molybdenum	0.100
Nickel	0.050
Phosphorus	0.020
Selenium	0.200
Silicon	1.00
Silver	0.040
Strontium	0.010
Tin	1.00
Titanium	0.020
Thallium	0.200
Vanadium	0.050
Zinc	0.020

* Reporting limits in mg/L.
** Actual reporting limits may vary depending on variables such as sample matrix, interferences, dilutions etc.

Table 2. Recommended Wavelengths and Calibration Levels.

Element	P3000DV Wavelength* (nm)	Calibrate to (mg/L)
Aluminum	396.152	10
Antimony	206.833	10
Arsenic	188.979	10
Barium	233.527	10
Beryllium	313.107	5
Boron	208.959	5
Calcium	317.933	10
Cadmium	228.802	5
Chromium	267.716	10
Cobalt	228.802	5
Copper	324.754	5
Iron	238.204	10
Lead	220.353	10
Magnesium	279.079	10
Manganese	257.610	5
Molybdenum	202.030	5

Table 2. Recommended Wavelengths and Calibration Levels (cont.)

Element	P3000DV Wavelength* (nm)	Calibrate to (mg/L)
Nickel	231.604	5
Phosphorus	213.618	
Selenium	196.026	10
Silicon	251.---	100
Silver	328.068	2
Strontium	407.771	5
Tin	224.---	10
Titanium	334.941	5
Thallium	190.800	10
Vanadium	292.402	5
Zinc	213.856	10

* The wavelengths listed are used because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Table 3. Mixed Standard Solutions

Calibration Standard	Elements
I	Al, As, B, Ba, Be, Cd, Cr, Co, Cu Fe, Mn, Mo, No, Pb, Sb, Se, Sr, Tl, Ti, V and Zn
II	Ca, Ce, Mg
III	Sn and Si
IV	Ag
V	P

Table 4. ICP Instrument Operating Conditions

	Simultaneous Optima 3000DV
Incident rf power	1400 watts
Viewing Height above work coil	14 mm
Injector Tube I.D.	2.0 mm
Argon Pressure	76 psi
Aerosol Carrier Argon Flow Rate	0.80 L/min
Auxiliary Argon	0.5 L/min
Plasma Argon Flow Rate	15 L/min
Sample Uptake Rate	2.0 ml/min
Argon supply	Liquid

Table 5. Potential Interferences

Element	Wavelength	Interfering Elements
Aluminum	396.152	Mo, Ce
Antimony	206.833	Cr
Arsenic	188.979	Cr, Mo
Barium	233.527	Ca, Mg, V
Beryllium	313.107	Ce, Ti, V
Boron	208.959	Fe, Mo
Calcium	317.933	Al, Ce, Co, Cr, Cu, Mg, Ti, V
Cadmium	228.802	Ni, V
Cerium	413.765	V
Chromium	267.716	Ca, Co, Mn
Cobalt	228.616	Mo, Ni, Ti
Copper	324.754	Mo
Iron	238.204	V
Lead	220.353	Co, Mo, Ni
Magnesium	279.079	Al, Ce, Co, Mo, Ti, V
Manganese	257.610	Ce
Molybdenum	202.030	None
Nickel	231.604	Mn
Phosphorus	213.618	Mg
Selenium	196.026	None
Silver	328.068	Ca
Strontium	407.771	Ca, Ce
Titanium	334.941	Cr, V
Thallium	190.800	Co, Mn, Mo, Ti, V
Vanadium	292.402	Mo, Ni, Ti
Zinc	213.856	Ca, Ce, Co, Cu, Ni, V

* These interferences and may not be present on all instruments.

Attachment A - ICP LCS Criteria

	Drinking Water [1]	Aqueous (GW & WW) [4]	Non-aqueous [1]
Aluminum	85.0% - 115.0% [2]	81.5% - 120.0% [3]	80.0% - 120.0% [2]
Antimony	Not Analyzed	82.8% - 120.0%	80.0% - 120.0% [2]
Arsenic	85.0% - 115.0% [2]	85.2% - 119.1%	80.0% - 120.0% [2]
Barium	85.0% - 115.0% [2]	81.2% - 120.0% [3]	80.0% - 120.0% [2]
Beryllium	85.0% - 115.0% [2]	83.8% - 117.8%	80.0% - 120.0% [2]
Boron	Not Analyzed	80.2% - 120.0% [3]	80.0% - 120.0% [2]
Cadmium	85.0% - 115.0% [2]	83.7% - 117.9%	80.0% - 120.0% [2]
Calcium	85.0% - 115.0% [2]	86.6% - 120.0% [3]	80.0% - 120.0% [2]
Chromium	85.0% - 115.0% [2]	84.9% - 118.6%	80.0% - 120.0% [2]
Cobalt	Not Analyzed	83.3% - 118.4%	80.0% - 120.0% [2]
Copper	85.0% - 115.0% [2]	85.8% - 120.0% [3]	80.0% - 120.0% [2]
Iron	85.0% - 115.0% [2]	83.6% - 117.9%	80.0% - 120.0% [2]
Lead	85.0% - 115.0% [2]	83.4% - 118.8%	80.0% - 120.0% [2]
Magnesium	Not Analyzed	82.0% - 120.0% [3]	80.0% - 120.0% [2]
Manganese	85.0% - 115.0% [2]	85.1% - 118.9%	80.0% - 120.0% [2]
Molybdenum	Not Analyzed	84.9% - 118.8%	80.0% - 120.0% [2]
Nickel	85.0% - 115.0% [2]	84.8% - 118.7%	80.0% - 120.0% [2]
Potassium	Not Analyzed	80.0% - 120.0% [2]	80.0% - 120.0% [2]
Selenium	85.0% - 115.0% [2]	83.5% - 117.6%	80.0% - 120.0% [2]
Silicon	Not Analyzed	80.0% - 120.0% [2]	80.0% - 120.0% [2]
Silver	85.0% - 115.0% [2]	82.1% - 120.0% [3]	80.0% - 120.0% [2]
Sodium	85.0% - 115.0% [2]	80.0% - 120.0% [2]	80.0% - 120.0% [2]
Strontium	Not Analyzed	84.5% - 119.5%	80.0% - 120.0% [2]
Thallium	Not Analyzed	80.0% - 120.0%	80.0% - 120.0% [2]
Tin	Not Analyzed	86.7% - 108.9%	80.0% - 120.0% [2]
Titanium	Not Analyzed	85.4% - 120.0% [3]	80.0% - 120.0% [2]
Vanadium	Not Analyzed	84.8% - 119.5%	80.0% - 120.0% [2]
Zinc	85.0% - 115.0% [2]	86.2% - 120.0% [3]	80.0% - 120.0% [2]

Attachment A - ICP LCS Criteria

1. Statistical limits developed 1/31/00 through 2/3/00.
2. Not enough data was available to develop limits, therefore the method limits are used.
3. Statistical limits did not meet or exceed method requirements, therefore the tighter limits from the method are used
4. Statistical limits developed 2/24/00.

QA Approval/Date:

[signature] / 2/24/00

Analyst Signature/Date:

[signature] / 2/24/00		_____ / _____	
Kevin D Wang / 2/24/00		_____ / _____	
_____ / _____		_____ / _____	
_____ / _____		_____ / _____	
_____ / _____		_____ / _____	

Attachment B

ICP MS/MSD Criteria

	Drinking Water [1]		Aqueous (GW & WW) [1]		Non-aqueous [1]	
	Percent Recovery	RPD	Percent Recovery	RPD	Percent Recovery	RPD
Aluminum	70.0% - 130.0% [3]	<20.0 [3]	75.0% - 125.0% [3]	<17.5	75.0% - 125.0% [2]	<20.0 [2]
Antimony	Not Analyzed		75.0% - 125.0% [3]	<20.0 [3]	75.0% - 125.0% [2]	<20.0 [2]
Arsenic	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 125.0% [3]	<9.1	75.0% - 125.0% [2]	<20.0 [2]
Barium	70.0% - 130.0% [3]	<9.6	75.0% - 124.4% [3]	<11.8	75.0% - 125.0% [2]	<20.0 [2]
Beryllium	91.2% - 116.2%	<7.2	76.6% - 117.0%	<14.2	75.0% - 125.0% [2]	<20.0 [2]
Boron	Not Analyzed		75.0% - 125.0% [3]	<20.0 [3]	75.0% - 125.0% [2]	<20.0 [2]
Cadmium	89.6% - 115.9%	<7.0	75.0% - 115.4% [3]	<12.9	75.0% - 125.0% [2]	<20.0 [2]
Calcium	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 125.0% [2]	<20.0 [2]	75.0% - 125.0% [2]	<20.0 [2]
Chromium	90.7% - 114.2%	<7.5	75.0% - 117.3% [3]	<12.3	75.0% - 125.0% [2]	<20.0 [2]
Cobalt	Not Analyzed		75.0% - 118.2% [3]	<11.9	75.0% - 125.0% [2]	<20.0 [2]
Copper	84.3% - 117.2%	<11.1	75.0% - 125.0% [3]	<16.6	75.0% - 125.0% [2]	<20.0 [2]
Iron	75.2% - 125.3%	<17.4	75.0% - 125.0% [3]	<20.0 [3]	75.0% - 125.0% [2]	<20.0 [2]
Lead	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 121.5% [3]	<18.0	75.0% - 125.0% [2]	<20.0 [2]
Magnesium	Not Analyzed		75.0% - 125.0% [2]	<20.0 [2]	75.0% - 125.0% [2]	<20.0 [2]
Manganese	89.5% - 115.8%	<10.5	75.4% - 115.4%	<17.5	75.0% - 125.0% [2]	<20.0 [2]
Molybdenum	Not Analyzed		78.4% - 115.2%	<14.3	75.0% - 125.0% [2]	<20.0 [2]
Nickel	89.1% - 114.0%	<11.1	75.0% - 121.9% [3]	<19.9	75.0% - 125.0% [2]	<20.0 [2]
Potassium	Not Analyzed		75.0% - 125.0% [2]	<20.0 [2]	75.0% - 125.0% [2]	<20.0 [2]
Selenium	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 122.3% [3]	<19 0	75.0% - 125.0% [2]	<20.0 [2]
Silicon	Not Analyzed		75.0% - 125.0% [2]	<20 0 [2]	75.0% - 125.0% [2]	<20.0 [2]
Silver	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 125.0% [3]	<11.7	75 0% - 125.0% [2]	<20.0 [2]
Sodium	70.0% - 130.0% [2]	<20.0 [2]	75.0% - 125.0% [2]	<20.0 [2]	75 0% - 125.0% [2]	<20.0 [2]
Strontium	Not Analyzed		75.0% - 125.0% [3]	<12 7	75.0% - 125.0% [2]	<20.0 [2]
Thallium	Not Analyzed		79.1% - 112.2%	<19.0	75.0% - 125.0% [2]	<20.0 [2]
Tin	Not Analyzed		77.2% - 120.6%	<17.5	75.0% - 125.0% [2]	<20.0 [2]
Titanium	Not Analyzed		81.8% - 111 6%	<17 9	75.0% - 125.0% [2]	<20.0 [2]
Vanadium	Not Analyzed		77.9% - 119.9%	<13 1	75.0% - 125.0% [2]	<20.0 [2]
Zinc	89.1% - 120.4%	<11.1	75.0% - 125.0% [3]	<13.7	75 0% - 125.0% [2]	<20.0 [2]

Attachment B

ICP MS/MSD Criteria

1. Statistical limits developed 1/31/00 through 2/3/00.
2. Not enough data was available to develop limits, therefore the method limits are used.
3. Statistical limits did not meet or exceed method requirements, therefore the tighter limits from the method are used.

QA Approval/Date:

Bonnie Stadelman 2/24/00

Analyst Signature/Date:

[signature] / 2/24/00		_____ / _____	
Kevin D. Wang / 2/24/00		_____ / _____	
_____ / _____		_____ / _____	
_____ / _____		_____ / _____	
_____ / _____		_____ / _____	