

STANDARD OPERATING PROCEDURE

For USEPA METHOD 200.7, Rev. 4.4

Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry

SOP #: EPA 200.7

SOP REVISION #: 4.2

DATE: December 2012

Page 1 of 38

This and all other DEAWES SOP and QA documents are available (read/print only) to all WES employees on the WES server (w:\dea-qap\SOPs & QA Docs). It should be noted that the controlled SOP & QA documents are only those viewed on-line on the WES server. If this is a printed copy, it is an uncontrolled version and may not be the latest version currently in use.



MassDEP

Massachusetts Department of Environmental Protection

Division of Environmental Analysis

Senator William X. Wall Experiment Station

37 Shattuck Street, Lawrence, MA 01843

Originally

Prepared by:

Barbara A. Eddy

Barbara A. Eddy, Chemist

Date: March 1999

Revised by:

Carol A. Batdorf

Carol A. Batdorf, Chemist

Date: December 6, 2012

Approved by:

James H. Sullivan

James Sullivan, Laboratory Supervisor

Date: December 7, 2012

Approved by:

John J. Bardzik

John Bardzik, Laboratory Certification/Quality Assurance Officer

Date: December 7, 2012

Approved by:

Ann Marie Allen

Ann Marie Allen, Deputy Director and QA Manager

Date: December 10, 2012

Approved by:

Oscar E. Pancorbo

Oscar Pancorbo, Director

Date: December 10, 2012



TABLE OF CONTENTS

	Page
LIST OF REVISIONS	3
LIST OF TABLES AND FORMS	6
1.0 SCOPE AND APPLICATION	7
2.0 SUMMARY OF METHOD	8
3.0 DEFINITIONS	9
4.0 INTERFERENCES	11
5.0 SAFETY	12
6.0 EQUIPMENT AND SUPPLIES	12
7.0 REAGENTS AND STANDARDS	14
8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE	16
9.0 QUALITY CONTROL	17
10.0 CALIBRATION AND STANDARDIZATION	20
12.0 DATA ANALYSIS AND CALCULATIONS	29
13.0 METHOD PERFORMANCE	30
14.0 POLLUTION PREVENTION	30
15.0 WASTE MANAGEMENT	30
16.0 REFERENCES	30
17.0 TABLES AND VALIDATION DATA	31



LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	March 1999	None	
1.0	October 2000	New ICP software Iron accuracy, precision, and MDL data updated (9/15/2000 data)	11 30-33
1.1	November 2000	Accuracy, precision and MDL data updated (Tables 6,7, & 8)	30-33
1.2	December 2001	Table 2 – Table 8 renumbered to Table 3 – Table 9 New Table 2	26 – 33 26
2.0	March 2003	Addition of new matrix – fish biota Table 6 deleted, Table 7-9 renumbered to Table 6-8 Table 8 values updated Table 9 added Table 10 added	Throughout document 31 – 33 33 34 34
2.1	January 2004	Section 1.1 – Identified the elements that are analyzed by this method in drinking water samples	5
2.2	April 2004	Section 6.2 – ICP general maintenance procedures added Section 7.7 – Standards preparation revised Section 7.8.4 – Added MRL (RDL) check standard prep Section 9.3.2 – LFB preparation and calculation Section 9.4.3 – MRL check std and LFM preparation Section 10.2 – Instrument calibration procedure updated Section 11.0 – Instrument daily and monthly maintenance added Section 11.5.8 – Analytical sequence added Table 2 – QC elements and acceptance criteria updated Table 8 – Updated MDL data (3/16/2004)	11 12 13 15 17 18 18-19 20 28-29
3.0	December 2006	Replaced old DEP Logo with state seal + MassDEP	Title page & header
		Numerous minor revisions throughout New ICP instrument and operating software (Section 6.1) New instrument and software operating procedures (Section 11.0) 2006 MDL data (Table 8) 2006 SDWA interelement correction factors (Table 11)	11 19 38 40



Rev. #	Date	Description of Revision	Page #
3.1	January 2008	Section 7.7.1 – Standards preparation revised.	14
		Section 7.13 – Revised plasma solutions to include 10 mg/L Mn for axial and radial optimization.	16
		Section 8.1 – Included pH log sheet as part of sample collection, preservation, and storage.	16
		Section 9.2.4 – MDL preparation and calculations.	17
		Section 11.1.3 – Took out WinLab offline; step may cause data management problems.	21
		Section 11.4.7 – Added time needed for machine to stabilize before starting calibration sequence.	23
		Section 11.5.1– Added axial and radial alignment instructions	23
		New Section 11.5.2 – Added mercury alignment instructions	23
		Old Sections 11.5.2 and 11.5.3 – Renumbered to 11.5.3 and 11.5.4, respectively	23
		Section 11.6.7 – Changed analytical sequence	23
3.2	March 2010	Table 2 – Updated	32
		Section 6.9.3 changed from Conical Phillips beakers to Environmental Express	12
		Section 7.7.1.7 – Change in standard preparation	13
		Section 11.5.2 – Mercury alignment deleted	22
		Renumbered sections 11.5.3 and 11.5.4 to 11.5.2 and 11.5.3	22
		Table 5 – Updated MDL data	35



Rev. #	Date	Description of Revision	Page #
4.0	September 2010	Added definitions of IEC, MRL, MRL check standard, and QCS-SRM in Sections 3.7, 3.14, 3.15, and 3.17, respectively	9 & 10
		Deleted definition of solid sample in Section 3.19 – Method no longer used in our laboratory to test solid samples	10
		Section 6.9 – Revised lab-ware cleaning procedure	13
		Section 7.1 & Forms Section – Added links to Standard-Reagent Preparation Bench Sheets	14 & 38
		Section 9.2.4 – Added procedure for use of QCS-SRM	17
		Section 9.2.5 – Updated MDL procedure	17
		Section 11.1.1.3 – Removed old air compressor from service; now using new building-wide compressed air system	21
		Section 11.4.3 – Updated location and temperature set point of water re-circulator	22
		Section 13.0 – Deleted reference to MDLs for fish/biological tissue; method no longer used to test fish/biological tissue	29
		Section 16.0 – Added Reference # 5	30
		Table 2 – Updated	32
		Deleted Tables 3 (IDLs), 6 (old accuracy data), 7 (old precision data), 9 (MDL 2.0 g fish/biological tissue), and 10 (MDL 5.0 g fish/biological tissue) – renumbered remaining tables	34-38
4.1	April 2011	Table 2 – Internal Standard acceptance criteria – added number range for Y	32
		Table 2 – LRB acceptance criteria – changed acceptance wording	33
		Table 5 – Updated MDL data	36
		Table 6 – Updated ICF data	37
		Section 11.1 – New gas delivery system in new laboratory wing	21
		Section 11.3 – New exhaust system in new laboratory wing	22
4.2	December 2012	Section 7.7 – Specify Bench Form for recording Calibration Std information/preparation Section 10.2 – Specify Bench Form for recording Calibration Std information/preparation Section 11.4.6 – Specify Form for recording QC Std information/preparation Section 11.5.2 – Describe data backup procedure Section 16.0 – Added references 6 - 9 Table 5 – Updated MDL Table and added MDLs for Boron and Lead Table 6 – Updated Interement Correction Table	



LIST OF TABLES AND FORMS

	Page
TABLE 1. QUALITY CONTROL TESTS AND ACCEPTANCE LIMITS FOR THE ANALYSIS OF METALS BY EPA METHOD 200.7	31
TABLE 2. QUALITY CONTROL ELEMENTS AND ACCEPTANCE LIMITS FOR EPA METHOD 200.7 DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY	32
TABLE 3. ON-LINE METHOD INTER-ELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 100-MG/L LEVEL	34
TABLE 4. INSTRUMENT CALIBRATION STANDARD FOR INTERELEMENT CORRECTION TEST	35
TABLE 5. METHOD DETECTION LIMITS (MDLS) FOR TRACE METAL ANALYSIS IN REAGENT WATER BY EPA METHOD 200.7 (06/28/2012 – 08/08/2012)	36
TABLE 6. 2012 INTERELEMENT CORRECTION FACTORS FOR CERTIFIED SDWA BY EPA 200.7	37
FORM 1. ICP STANDARDS PREPARATION FOR EPA 200.7	38
FORM 2. YTTRIUM AND CERIUM STANDARDS PREPARATION FOR EPA 200.7	38
FORM 3. NITRIC ACID STANDARDS PREPARATION FOR EPA 200.7	38
FORM 4. IEC STANDARDS PREPARATION FOR EPA 200.7	38



1.0 SCOPE AND APPLICATION

- 1.1 Dual View inductively coupled plasma-atomic emission spectrometry (ICP-AES) or optical emission spectrometry (ICP-OES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, fish/biological tissue, and solid wastes. This method is applicable to the following analytes:

<u>Analyte</u>		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium*	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium*	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper*	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel*	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

*In our laboratory, this method is used to test drinking water samples only for the elements designated with an asterisk in the above table (i.e., barium, chromium, copper, and nickel). Annual proficiency tests and U.S. EPA certification for the analysis of drinking water by this method is limited to these elements.

- 1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)], consult both the appropriate



sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

- 1.3 ICP-AES is used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, a determination is made to ensure that the dissolved solids are < 0.2% (w/v) (Sect. 4.2).
- 1.4 With the exception of silver, all metals determined with this method are analyzed directly by pneumatic nebulization without acid digestion only if the sample has been properly preserved with acid and has a turbidity of < 1 NTU at the time of analysis; this total recoverable determination procedure is referred to as "direct analysis."
- 1.5 For the determination of total recoverable analytes in aqueous and solid samples, a digestion/extraction is performed prior to analysis when the elements are not in solution (e.g., fish/biological tissues, soils, sludges, sediments, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material $\geq 1\%$ (w/v) are extracted as a solid type sample.
- 1.6 When determining boron in aqueous samples, only plastic, PTFE is used from the time of sample collection to completion of analysis. For the accurate determination of boron in solid samples, only PTFE beakers are used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. Borosilicate glass is avoided to prevent contamination of boron.
- 1.7 Low silver recoveries for samples with high chloride concentrations are avoided by digesting these samples prior to analysis. The total recoverable sample digestion procedure given in this method is performed for the determination of silver in aqueous samples containing concentrations up to 0.1mg/L Ag. Wastewater samples that contain higher concentrations of silver (> 50 mg/Kg) are treated in the same manner. Also, the extraction of tin from solid samples is performed using aliquots < 1 g when determined sample concentrations exceed 1%.
- 1.8 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis is completed as soon as possible after sample preparation.
- 1.9 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrix.
- 1.10 Initial demonstration performance data described in Section 9.2 was performed and is documented and kept on file.

2.0 SUMMARY OF METHOD

- 2.1 An aliquot of a well-mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing un-dissolved material, analytes are first digested in a microwave digestion system. After cooling, the sample is made up to volume and filtered. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid to pH ≤ 2 .



- 2.2 The analysis described in this method involves multi-elemental determinations by inductively coupled plasma optical emission spectrometry (ICP-OES) using a simultaneous instrument. The instrument measures characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the dual view configured plasma torch. Element-specific emission spectra are produced by radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is used to compensate for variable background contribution to the determination of the analytes. Background is measured adjacent to the analyte wavelength during analysis. Interferences are considered and addressed in Sections 4, 7, 9, 10, and 11.

3.0 DEFINITIONS

- 3.1 Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.
- 3.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.3 Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45- μ m membrane filter assembly prior to sample acidification.
- 3.4 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sample site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.5 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.
- 3.6 Instrument Performance Check (IPC) Solution - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
- 3.7 Interelement Correction (IEC) - A method of correcting for spectral interferences. It uses mathematical correction factors to reallocate emission intensities.
- 3.8 Internal Standard - Pure analyte (s) added to a sample, extract, or standard solution in known amount (s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.
- 3.9 Laboratory Duplicates (Sample and Sample Duplicate) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of the sample and the sample duplicate indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.10 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose



is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

- 3.11 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.
- 3.12 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.
- 3.13 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.
- 3.14 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
- 3.15 Minimum Reporting Limit (MRL) - The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the MRL check standard for that analyte and can only be used if acceptable quality control criteria for the analyte at this concentration are met.
- 3.16 MRL Check Standard - Low-level standard with concentration 3 to 5 times the MDL value. The standard is analyzed at the beginning of each analytical run before the samples are run.
- 3.17 Plasma Solution - A solution that is used to determine the optimum orientation of the quartz torch for viewing the plasma.
- 3.18 Quality Control Sample (QCS) - A solution of method analytes of known concentrations, which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
- 3.19 Quality Control Sample - Standard Reference Material (QCS-SRM) - A Sample of a matrix similar to the sample being analyzed, which contains analytes of a known or accepted concentration. The QCS-SRM is obtained from a source external to the laboratory and contains the analytes of interest at certified concentrations for the method of interest. The QCS-SRM is processed in the same manner as the sample, unlike the QCS in 3.17, and is used to check method performance.
- 3.20 Spectral Interference Check (SIC) Solution - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.
- 3.21 Standard Addition - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.



- 3.22 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.23 Total Recoverable Analyte - The concentration of analyte determined either by "direct analysis" of an unfiltered acid-preserved drinking water sample with turbidity of < 1 NTU or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.
- 3.24 Water Sample - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm water runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

- 4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.
- 4.1.1 Background emission and stray light are compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity is determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement is free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.
- 4.1.2 Spectral overlaps are avoided by using an alternate wavelength; potential on-line spectral interferences observed for the recommended wavelengths are given in Table 3. Alternate wavelengths are used for all metals analyzed by this method. Wavelengths other than the recommended wavelengths are used in this method and on-line and off-line spectral interference effects from all method analytes have been determined and documented and are kept on file. Tests are done to determine the spectral interference using analyte concentrations that adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient.
- 4.1.3 Inter-element corrections are dependent on the selection of background correction points. Background correction points avoid all interfering emission lines that may appear at the location of the selected background correction point. To determine the appropriate location for off-line background correction, the user scans the area on either side adjacent to the wavelength and records the apparent emission intensity from all other analytes. This spectral information is documented and kept on file electronically.
- 4.1.4 Interference effects are evaluated for the instrument used in this method. Instrument operating conditions (such as power, torch x-y viewing position, and argon flow rate) may change emission intensities. Interference correction tables available in the instrument computer software are inadequate as a stand-alone technique for interference correction and are not relied upon by the user. The wavelengths used by the analyst (Table 3) have interferences that are documented and kept on file.



- 4.1.5 Interelement correction tables are not used; SIC solutions are routinely analyzed to verify the absence of interelement spectral interference.
- 4.2 Physical interferences associated with samples containing high dissolved solids or changing viscosity are reduced by the nebulizer and cyclonic spray chamber. An internal standard is mixed with all samples entering the plasma and the emission intensity of that standard is continuously monitored. Corrected emission intensities are used to calculate the concentration of the analyte being measured.
- 4.3 Chemical interferences from molecular compound formation or ionization effects are reduced by the axial configuration of the plasma and the use of a shear gas that eliminates the cooler region of the plasma where emission from easily ionized elements like potassium and sodium take place.
- 4.4 A continuous calibration blank (CCB) is analyzed after calibration, after every 10 samples, and at the end of the analytical run; the analyst monitors the concentration of the CCB.

5.0 SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. All laboratory personnel are trained on the laboratory safety procedures applicable to and the OSHA and other regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Specifically, concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. These reagents are used in a fume hood and if skin or eye contact occurs, large volumes of water are applied to flush the area of contact. An emergency shower and eyewash station are located in the laboratory. Safety glasses are used for eye protection, and protective clothing is worn.
- 5.2 Acidification of samples is done in a fume hood to prevent the inhalation of toxic gases, such as cyanide or sulfide.
- 5.3 All personnel handling potentially infectious environmental samples are immunized against known disease causative agents.
- 5.4 Caution is used when viewing the plasma. All instrument interlocks must be engaged for plasma to ignite, which provides the user of the method some protection from exposure to ultraviolet emissions.
- 5.5 All laboratory personnel fully comply with all relevant federal, state, and local waste management and disposal regulations. (Sect 14.0 and 15.0)

6.0 EQUIPMENT AND SUPPLIES

6.1 Dual-view inductively coupled plasma emission spectrometer:

- 6.1.1 Instrumentation: P. E. Optima 3300DV, Serial # 069N9042801
- 6.1.2 Software Winlab 32 for ICP, Version 3.1.0.0107
Plasma Generator Firmware Version 4.05



- 6.1.3 Torch Module: The quick-change torch module is the quartz torch, torch block, spray chamber, and nebulizer/end cap all in one assembly. This module can be quickly removed from the sample compartment for cleaning or replacement of new torch. The torch has an alumina injector with a 2.0-mm I.D. The load coil is water-cooled. Refer to Hardware Guide for the Optima 3300 DV.
- 6.1.4 Spray Chamber: A cyclonic spray chamber and Gemcone Nebulizer are utilized on this instrument. A Scott double-pass spray chamber and Gem Tip cross-flow pneumatic nebulizer are available for other applications.
- 6.1.5 Peristaltic Pump: The peristaltic pump is fully computer-controlled. Pump speeds are programmable in the Method Editor. Coupled with the pump is the mixing block, where standards and samples are mixed with the internal standard.
- 6.1.6 Autosampler: The AS-90 Autosampler is configured for this instrument. It is computer controlled and programmable. This system uses Tray B or Tray C. Tray B has 98 sample locations and 8 standard locations. Tray C has 44 sample and standard locations (50 mL tube size). Standard and sample ID are programmed into the Method Editor Calibration Page and Sample Information File.
- 6.2 General Maintenance Procedure for Dual View Inductively Coupled Plasma Emission Spectrometer: ICP maintenance is performed by the lead analyst on a daily basis (See Section 11.5). Major maintenance operations are performed by a Perkin-Elmer Customer Service Engineer. Service calls are placed to the company only when the lead analyst is not capable of performing the required maintenance. Service call reports are kept on file.
- 6.3 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.
- 6.4 A temperature adjustable hot plate or Hot Block capable of maintaining a temperature of 95°C, or a microwave digestion system with PTFE sample inserts
- 6.5 A gravity-convection drying oven with thermostatic control capable of maintaining a temperature of 180 ± 5°C.
- 6.6 Assortment of air displacement pipetters capable of delivering volumes ranging from 0.1 to 2500 µl with corresponding metals-free disposable pipette tips.
- 6.7 Mortar and pestle, ceramic or nonmetallic material.
- 6.8 Polypropylene sieve, 5-mesh (4-mm opening).
- 6.9 Labware: For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area is designated for trace element sample handling. Field sample containers used in the determination of trace elements are purchased as pre-cleaned glass or HDPE containers. Laboratory containers for sample handling and storage are bought trace metal-free or pre-cleaned. Volumetric flasks and other glassware used to make standards, etc., are cleaned as follows: glassware is washed with a detergent solution made from Citramax, rinsed with tap water, soaked for four or more hours in 20% (v/v) nitric acid or hydrochloric acid, rinsed with reagent water, and stored in a clean cabinet. Microwave digestion vessels are run through the cleaning cycle twice, rinsing with reagent water in between cleaning cycles.



- 6.9.1 Glassware: Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).
- 6.9.2 Assorted glass calibrated Type A volumetric pipettes.
- 6.9.3 Environmental Express: Hot Block, disposable digestion cups, and filters
- 6.9.4 PTFE microwave digestion vessels
- 6.10 Argon Tank: High purity
- 6.11 Nitrogen Tank: Pre-purified
- 6.12 Semi-automatic change panel allows for a continuous argon gas supply from a two-argon tank set up while ICP is running.

7.0 REAGENTS AND STANDARDS

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

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

7.2 Hydrochloric acid, concentrated (sp. gr. 1.19) (HCl)

- 7.2.1 Hydrochloric acid (1+1): Add 500-mL concentrated HCl diluted to 1 L with reagent water.
- 7.2.2 Hydrochloric Acid (1+4): Add 200-mL concentrated HCl diluted to 1 L with reagent water.

7.3 Nitric Acid, concentrated (sp. gr. 1.41) (HNO₃)

- 7.3.1 Nitric Acid (1+1): Add 500-mL concentrated HNO₃ to 400 mL of reagent water and dilute to 1 L.
- 7.3.2 Nitric acid (1+2): Add 100-mL concentrated HNO₃ to 200 mL of reagent water.

7.4 Reagent water: ASTM Type I reagent-grade water

7.5 Hydrogen Peroxide, 30%, stabilized certified reagent grade.

7.6 Standard Stock Solutions: Stock standards are purchased. They are replaced when expiration date is exceeded.

7.7 Preparation of Working Calibration Standard Solutions: Calibration standard solutions are prepared as necessary (usually every 2-3 months or more frequently, if needed). Standards near the reporting limit (< 30 ppb) are usually prepared more frequently when their concentrations are no longer verifiable. See Form 1

- 7.7.1 Standard Stock Solutions: 1,000 mg/L or 100 mg/L single or multi-element certified standard (s) are purchased. From this stock, prepare the following standards using the appropriate acid diluent, 2% HNO₃.

- 7.7.1.1 100 mg/L: 10 mL of 1000 mg/L, Q.S. to 100 mL with 2% HNO₃ used only if 1000 mg/L standard is the first standard.



- 7.7.1.2 10 mg/L: 10 mL of 100 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.3 5.0 mg/L: 5 mL of 100 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.4 1.0 mg/L: 10 mL of 10 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.5 0.5 mg/L: 5 mL of 10 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.6 0.1 mg/L: 10 mL of 1.0 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.7 0.05 mg/L: 5 mL of 1.0 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.8 0.03 mg/L: 3 mL of 1.0 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.9 0.01 mg/L: 10 mL of 0.10 mg/L, Q.S. to 100 mL with 2% HNO₃
- 7.7.1.10 Other standards may be prepared as needed.

7.8 Blanks: Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve; the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure; the laboratory fortified blank is used to assess routine laboratory performance; and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.8.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards.

7.8.2 Laboratory reagent blank (LRB) contains all the reagents in the same volumes as used in the processing of the samples. The LRB is carried through the same entire preparation scheme as the samples including sample digestion.

7.8.3 Rinse blank is prepared by acidifying reagent water to the same concentrations of acid as used in the calibration blank.

7.8.4 Laboratory fortified blank (LFB) is prepared by spiking an aliquot of the laboratory reagent blank with a single element or multi-element standard solution. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion.

7.9 Instrument Performance Check (IPC) Solution: The IPC solution is used to periodically verify instrument performance during analysis. It is prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. The IPC is prepared from the same standard stock solutions used to prepare the calibration standards.

7.10 Quality Control Sample (QCS): Analysis of a QCS (3.18) is performed for initial verification of calibration standards in order to verify instrument performance. The QCS is obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards.

7.11 Spectral Interference Check (SIC) Solutions: When interelement corrections are applied, SIC solutions with adequate concentrations of interfering elements are analyzed to verify any interelement correction factors.



- 7.11.1 Interferences from iron and aluminum are frequently present when soils or solid waste samples are analyzed. In addition to using alternate wavelengths, SIC solutions for iron and aluminum are analyzed when these metals are present in high concentrations to verify that the interelement correction factors used are accurate.
- 7.11.2 Correction routine is considered to be operating properly when the analyte(s) concentration determined from analysis of each interferent solution falls within a specific concentration range. This range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. A change in the correction factor of more than 10% should be reviewed and the correction factor should be updated.
- 7.11.3 If the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements at the 10-mg/L level, daily verification is not determined. However, all interelement spectral correction factors are verified annually and updated when necessary.
- 7.12 Since alternate wavelengths are used, SIC solutions are used to verify the absence of interelement effects at the wavelengths selected. These data are kept on file with the sample analysis. If the SIC solution confirms an operative interference that is $\geq 10\%$ of the analyte concentration, the analyte is determined using a wavelength and background correction location free of the interference or the sample is diluted to reduce the interfering element.
- 7.13 Plasma Solution: Plasma solutions (1.0 mg/L Mn & 10.0 mg/L Mn) are used to determine the optimum viewing position of the plasma torch. An axial and radial optimization is performed routinely and aligns the torch with the detectors.
- 7.14 Internal Standard Solution (Y): The internal standard solution is prepared by acidifying reagent water to 2% HNO₃ and adding yttrium to a concentration of 20 mg/L (e.g., 40 mL of 1000 mg/L Y + 40 mL HNO₃, Q.S. to 2 L with reagent water).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Appropriate preservation and pretreatment steps are performed on all samples analyzed by this method. The pH of all aqueous samples is tested immediately prior to the direct analysis of any sample (pH is recorded on a pH log sheet that is included with the sample reports).
- 8.2 For the determination of the dissolved elements, the sample is filtered through a 0.45- μ m pore diameter membrane filter at the time of collection or as soon thereafter. The sample is acidified with (1+1) nitric acid immediately following filtration to pH < 2.
- 8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH < 2. The sample is held for sixteen hours, and then verified to be pH < 2 just prior to analysis.
- 8.4 Solid samples do not require preservation other than storage at 4°C.
- 8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user.
- 8.6 Fish/biological tissue samples should be stored at -10°C to -20°C.



9.0 QUALITY CONTROL

- 9.1 The quality control program for this method consists of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and quality control standards as a continuous check on laboratory performance. Records of these data are maintained and kept on file.

9.2 Initial Demonstration of Performance

- 9.2.1 Initial demonstration of performance was conducted immediately after instrument installation. LDR, MDL, and IDL were produced prior to any analysis of environmental samples.
- 9.2.2 Linear Dynamic Range (LDR) (also referred to as the Linear Calibration Range – LCR) was established for each wavelength utilized and was determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR was determined by analyzing increasingly higher standard concentrations of the analyte until the observed analyte concentration was no more than 10% below the stated concentration of the standard. The LDRs are documented and kept on file. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit are diluted and reanalyzed. The LDRs are verified annually or whenever a change in analytical or instrument performance occurs, which would then dictate that the LDRs be re-determined.
- 9.2.3 Quality control sample (QCS): The QCS (3.18) is analyzed with every analytical run to verify the calibration standards. To verify the calibration standards, the mean concentrations from the QCS must be within $\pm 5\%$ of the stated values. If the calibration standards are not verified, performance is unacceptable and the determination of analytes is not continued. The source of the problem is identified and corrected before proceeding with any analyses.
- 9.2.4 Quality Control Sample-Standard Reference Material (QCS-SRM) (Sect. 3.18)
QCS-SRM is analyzed with every analytical run to verify the method performance. The QCS-SRM recovery must be within the manufacturer's specifications or the stated specification for the sample matrix recoveries.
- 9.2.5 Method detection limit (MDL): MDLs are established for all wavelengths utilized, (see Table 5), using reagent water (blank) fortified at a concentration of two to five times the MDL (Table 5). To determine MDL values, seven replicate aliquots of the fortified reagent water are processed through the entire analytical method or a set standard will be processed through the entire analytical method during a sample run. Seven results from these set standard samples will constitute the data set for the MDL study. The results may be from at least three different days and no more than three results from any one day will be used. Two data points are determined on each of two days; three data points are determined on a third day. No data points are dropped. Another method for obtaining the MDL values is to take the results from the method reporting level (MRL) standards that are run before each ICP sample run. Collect seven days' worth of runs and use those MRL values for the data points for the MDL study.

Calculation of the MDL is as follows:

$$\text{MDL} = (t) \times (s)$$

Where:



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

s = standard deviation of the replicate analyses

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

9.3 Assessing Laboratory Performance

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

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

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

Where:

R = Percent recovery

LRB = Laboratory reagent blank.

LFB = Laboratory fortified blank.

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

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

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

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

LFB is calculated as follows:

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

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

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



UPPER CONTROL LIMIT = $x + 3S$

LOWER CONTROL LIMIT = $x - 3S$

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

- 9.3.4 Instrument performance check (IPC) solution is analyzed with every analytical run. Immediately after calibration, and at the end of the analytical run, the IPC and calibration blank are analyzed to verify that the instrument is within $\pm 5\%$ of initial calibration. Subsequent analyses of the IPC solution must be within $\pm 10\%$ of calibration. If the calibration cannot be verified within the specified limits, the IPC and the calibration blank are reanalyzed. If the second analysis of the IPC solution or the calibration blank is outside the limits, sample analysis is discontinued, and the cause of the problem is determined, corrected, and/or the instrument recalibrated. All samples following the last acceptable IPC solution are reanalyzed. The analysis data of the calibration blank and IPC solution are kept on file with the sample analysis data.
- 9.3.5 Spectral interference check (SIC) solution: All determinations performed in the laboratory are verified by analyzing SIC solutions. The preparation and periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routines are given in Section 7.11.

9.4 Assessing Analyte Recovery and Data Quality

- 9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Separate aliquots from the sample are taken for replicate and fortified analyses to assess the effect. Laboratory fortified matrix (LFM) samples and duplicate samples are processed to assess matrix effects.
- 9.4.2 The laboratory adds a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot is a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration is the same as that used in the laboratory-fortified blank (Sect. 7.8). For solid samples, however, the concentration added is expressed as mg/kg and is calculated for one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor $100 \text{ (mg/L} \times 0.1\text{L/0.001kg} = 100, \text{ Sect. 12.5)}$.
- 9.4.3 Percent recovery for each analyte is calculated using the following equation:

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

Where:

R = Percent recovery

C_s = Fortified sample concentration.

C = Sample background concentration.



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

9.4.3.1 The analyst will spike a sample with a concentration above the MRL but not above the LDR of calibration. If normal spike concentrations do not meet this criterion, on-line spikes will be prepared and analyzed.

9.4.3.2 LFM is prepared by adding 0.1 milliliters of 10 mg/L standard and QS to 10 mL with reagent water. LFM is acidified in the same manner as samples and standards. Higher or lower LFM's are prepared to correspond with the range of the sample concentrations.

9.4.3.3 The above LFM's spike amount is calculated as follows:

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

9.4.4 If the recovery of the analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. Method of standard additions may be employed. (Sect. 9.5) or the data user will be informed of the matrix effect.

9.4.5 Reference materials are utilized for every analytical run. They are analyzed to provide additional performance data, and demonstrate the ability to perform the method on a particular matrix.

9.5 Method of Standard Additions (MSA)

May be performed on samples that demonstrate matrix interference.

9.5.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is < 20% of the sample analyte concentration, the following dilution is used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions is employed to provide for accurate data.

9.5.2 Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection limit in the original solution but < 90% of the linear limit), an analysis of a 1+4 dilution should agree (after correction for the fivefold dilution) within $\pm 10\%$ of the original determination. If not, a chemical or physical interference effect is suspected and the associated data flagged accordingly. The method of standard additions provides more accurate data for samples failing this test.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Plasma operating conditions are determined by the user and then stored by the instrument. The instrument then automatically adjusts the system conditions to remain within the prescribed operational settings and makes continuous diagnostic adjustments.



10.2 After plasma has been “conditioned”, a calibration blank is aspirated followed by the calibration standards (See Table 4 for Mixed Calibration Standard Solutions). Instrument is calibrated with a mixed calibration standard solution, which is used at full strength (100 mg/L) or diluted as needed. Dilutions are recorded on Standard/QC Preparation bench sheets that are attached to each QC Batch report (See Form 1).

10.3 Method Editor controls how the sample is analyzed

10.3.1 Go to File>... Open>Click on Method - the OPEN METHOD Window appears

10.3.2 Click on a Method that has been developed, or create a New Method.

10.3.3 Once the method is open, check ALL the “pages” in the method, so you can see what is required for analysis to occur. The method editor controls how the sample is analyzed; observe element wavelengths, standard locations and Q.C. settings. Check all settings.

11.0 PROCEDURE - Instrument Operating Procedure & Daily Maintenance – The following actions are performed on days that the instrument is used. All maintenance performed is logged in the ICP maintenance logbook.

11.1 Standard Operating Procedure for ICP

11.1.1 Gas Supply:

11.1.1.1 Nitrogen supply should be on at all times. Check gas supply.

11.1.1.2 Argon supply should be on at all times. Argon pressure must be > 75 psi and argon must be available on a constant basis.

11.1.2 Turn on Computer and Screen

11.1.3 Bring up WinLab 32: The diagnostics screen will come up. Want the three boxes to be checked and green. The computer will do this if everything is correct between the computer and spectrometer. Continue to set up the machine, samples and file list while waiting for the spectrometer to warm up.

11.1.4 Maintenance of Sample Introduction System: Check Autosampler activity, probe location, and draining of waste. F11 will move probe up or down.

11.1.5 Change peristaltic pump tubing on pump head every time the ICP is run. Black/Black (sample) on top, Red/Red (Waste) in the middle, and Green/Orange (internal standard) on the bottom. Align peristaltic pump tubes on the rollers to be in the middle under each magazine arm fitting.

11.2 Setting up Sample Information List

11.2.1 Go to File, New, Sample Information file, LimslinkSIF.sid

11.2.2 Fill in Batch ID month day year,

11.2.3 Fill in File Description box – name of test and/or metals, list samples in batch

Double click on Sample ID – fill in prefix, number, sample number range and set up sample list. Then go back to fill in duplicates, blanks and LFM – go to the line below where you want a line added – go to EDIT – insert row. Fill in auto sample location column. (For tray B samples start at 17.) Save – File – File- Save As – year 1st or 2nd half – enter name month day year.



- a) First Column is for the Auto Sequence this is numbered 1 to 100, etc. This is not the Autosampler location, but simply the analytical sequence number. These numbers are "fixed" in the file.
- b) Second Column is the Auto Sampler Location number. Usually samples start in A/S location 17 and can go as high as 106. Autosampler tray B is used for the ICP, and can contain 106 samples. The Autosampler locations 1 thru 16 are usually dedicated to standards and QCS samples. The first sample to be analyzed is usually located in autosampler location 17. Identifications of Standards and Q.C.S. are NOT typed in the Sample Info File. (They are found in Method Editor)
- c) Third Column is Sample ID. Type up to 25 characters for each sample I.D. Ex. 97-001 Note that filling in the Sample Information File may be done either while the instrument warms up or while the plasma is stabilizing.

11.3 Preparing to Light Plasma

- 11.3.1 Overhead exhaust hood is on at all times.
- 11.3.2 Put in the Method – File – Pick method
- 11.3.3 Put 2% HNO₃ in wash cup
- 11.3.4 Put sample probe in liquid (F11)
- 11.3.5 Clamp down peristaltic tubing on pump head.
- 11.3.6 Put internal standard tubing in cup with reagent grade water.

11.4 Igniting Plasma: In the Plasma Control Window, Click the plasma toggle switch to (ON) to ignite plasma. The ignition of the plasma takes a minute or so. Pump gases and nebulizer are now activated. Analyst should check the mixing block, nebulizer tips and nebulizer spray pattern. Liquid of some sort sample, internal standard, and/or rinse solution should be running through the lines when the plasma is lit. If no liquid is flowing the torch will start to glow red and then melt.

- 11.4.1 If there is a problem with ignition, the plasma will not light and the "switch" will be turned off. Plasma ignition should occur on demand. Occasionally two or three attempts are necessary to light the plasma, especially if room air has entered the gas lines or water is in the compressed air lines. See Sections 11.4.2 and 11.4.3. If these appear to be in order, then open torch assembly compartment and check nebulizer and spray chamber for residue buildup, check for leaks and replace O-rings if showing signs of wear. Clean or replace torch components. Reassemble torch and attempt plasma ignition again.
- 11.4.2 IF PROBLEMS HAPPEN: Go to SYSTEM heading at the top bar on the screen. Go to Diagnostics or look at the message log on the screen. Any problems with the instrument can be seen on these windows. It is usually a lack of Argon, or an ambient temperature problem. Make sure the Argon gas is sufficient and that the ICP room is not too hot.
- 11.4.3 The Water Re-circulator is an important accessory for the ICP. It is located in the WES Ground Floor Lab Equipment Room #0133. Check the operation of this unit; especially if the water flow in the diagnostics window is not acceptable. Clean pump filter every six months. Temperature is currently set at 18°C.



- 11.4.4 The plasma needs to be “conditioned” for approximately 30 minutes before you can analyze any standards or samples.
 - 11.4.5 Test for bubble flow in the tubing coming off of the pump head. Lift the sample probe in and out of the 2% HNO₃ to introduce bubbles to the system. Look for smooth running bubbles in the tubing past the mixing block. Adjust tension on the tube magazine arms if needed. Leave sample probe in 2% HNO₃ once bubble pattern has been checked. Note- waste stream should always have bubbles in the line (Red/Red tubing).
 - 11.4.6 Test bubble pattern for the internal standard tubing. If bubble pattern is not steady adjust clips on pump head. Place internal standard tubing into the internal standard receptacle. Prepare new internal standard solution if necessary and record solution preparation in QC/Standard Preparation Bench Sheet (See Form 2).
 - 11.4.7 Minimize diagnostics and plasma control screens once plasma has stabilized. PE recommends a 30 to 60 minute warm-up instrument stability period before running calibration sequence & sample analyses.
- 11.5 Sample Analysis: Before analysis can be performed, the analyst should perform the following maintenance on an as-needed basis.
- 11.5.1 Spectrophotometer Axial & Radial Alignment – Perform after any change to torch or if misalignment suspected. To perform this, go to the “Tools” heading in the top heading of the ICP software. Click on Spectrophotometer Control and select Axial.. Click on Align View; Select element & wavelength. Aspirate a 1.00-mg/L standard solution of manganese then change to Radial and aspirate 10 mg/L of standard solution of manganese. The software will determine maximum emission intensity. Axial & Radial alignment of optics is automatically adjusted and accepted. Print the results and keep on file.
 - 11.5.2 Winlabs Library Manager – Files for data should be archived electronically. Periodic or monthly maintenance is recommended for proper operation of instrument. The files are backed-up to the network server by saving files to a thumb drive and saving that to the ICP backup program on a computer connected to the network server.
 - 11.5.3 Go to File>...Open>... Click on Sample Info File Open a sample information file that has been developed, or create a New Sample Info File, see 11.2.
- 11.6 Method Editor – Pull up method editor – Modify or at least check all the tabs
- 11.6.1 Go to Calibration- check if all standards in the method will be used – add or delete as needed (highlight row to make the change. Note - when turning off the ICP when the question is asked do you wish to save your changes to the method, say No.
 - 11.6.2 Go to Schedule QC – review all QC
 - 11.6.3 Go to Analysis – pick what analytes are needed for the run. Enable/disable elements – double click in grey enable box – activates a short cut to take all the checks away, then check off elements needed for run plus internal standard e.g.Y.
 - 11.6.4 Go to Automated Analysis Control – enter a name in the results data set name box. Review the Sample Information File.
 - 11.6.5 Go to Analyze tab – check if sequence looks like what you want. If no samples are in the list, either there is no sample information file or the auto sample locations are missing from the sample information file.
 - 11.6.6 Print sequence list



11.6.7 Load samples into tray according to the following sequence list:

Typical Analytical Sequence

Sequence Sample ID

- 1 Calibration Blank
- 2 Calibration Standard Solutions
IEC(s) [Inter Element Correction Solution(s)] (Table 4) or
SIC(s) [Spectral Interference Check Solutions(s)],
- 3 Performance Check Standard(s)
- 4 Reagent Blank (CCB)
- 5 Quality Control Sample(s) [QCS(s) ($\pm 5\%$)], Performance
Check Standard(s).
- 6 MRL(s) Minimum Reporting Level Standard(s), Performance
Check Standard(s)
- 7 IPC A(s) ($\pm 5\%$) Calibration Standard(s), Performance Check
Standard(s)
- 8 Continuous Calibration Blank (CCB)
- 9 Sample 1
- 10 Sample 2
- 11 Sample 3
- 12 Sample 4
- 13 Sample 5
- 14 Sample 6
- 15 Sample 7
- 16 Sample 8
- 17 Sample 8 Duplicate
- 18 Sample 8 Laboratory Fortified Matrix (LFM)
- 19 IPC B ($\pm 10\%$)
- 20 CCB
An additional set of no more than 10 samples, including one
or more Laboratory Fortified Blank (LFB), LFM's, Matrix
QCS(s), and duplicates as required by the method. An IPC B
and CCB must be at the start of a sample set of 10 and at the
end. If there are fewer than 10 samples in the last set of
samples, the following sequence finishes the sample run.
- 21
- 22 QCS(s), Performance Check Standard(s)
- 23 IPC B ($\pm 10\%$), Performance Check Standard(s)
- 24 CCB

11.7 Results Data File - Saving Raw Data in a Text File During analysis, the raw data can be viewed in the Results Data File. If the data in this file are validated and reported, it is important that this file be saved. When your analysis is complete,

11.7.1 Keep the Results Window OPEN,



- 11.7.2 Go to the FILE heading at the top of the screen and then to SAVE AS.
- 11.7.3 Choose TEXT. A Text File Window will open,
- 11.7.4 Type in a file name for this raw data: Example 080497. The Results Data File is now saved as a Text File, and will have the extension 080497.TXT. This file can be viewed through WORDPAD or NOTEPAD.
- 11.8 Retrieving Text Files: Use the EXPLORE command. (At Windows Start, right click mouse and access Explore) The pathway will be C:/ICPUSERS/USER1/REPORT. Notepad (small) or Wordpad (large) will appear
- 11.9 Printing Reports: Validated data is printed on reports through UTILITIES
- 11.9.1 Go to FILE> UTILITIES or double click on Data Manager icon
- 11.9.2 Highlight the file to be reported. Click on the Report icon and a report utility appears which has several pages which allow choices to be made about samples to be reported, analytes and wavelengths, and final report format.
- 11.9.3 Click on Use Existing Design or Create Design to begin. If Use Existing Design is chosen, a report format will appear; otherwise, select the appropriate choices on each page of the utility using Next or Back to toggle between the utility's pages. Preview may be chosen on any page at any time to see the current report format.
- 11.9.4 After selecting samples, analytes, etc., it is recommended to include a descriptive header for the report as well as include the report name and page number by proceeding to the appropriate utility page and filling it in.
- 11.9.5 Once the report is in the desired format, select Preview. Check the report for errors or omissions. Check that the last page is not blank. A bug in the format will occasionally include blank pages in the print out. Click the printer icon and either print all or exclude the last page, if blank.
- 11.9.6 Date and initial the report.
- 11.10 Sample Preparation: The following are the usual sample preparation procedures used. Alternate preparation procedures are acceptable if they meet data requirements and any regulatory requirements of the sample.
- | | |
|-------------------------------------|--------------|
| SDWA Metals | Method 200.2 |
| Rivers/Ponds Total | Method 3015 |
| Total Recoverable | Method 3005 |
| Total Suspended -0.45 μm | Method 3005 |
| Dissolved -0.45 μm | Method 3005 |
| Total High TDS | Method 3010C |
- 11.11 Sample Information Editor - Addition of column headings: It is recommended that you have the sample information editor window open while reading.
- 11.11.1 Matrix Check Samples (Optional): Note that the functions described in this section do not work well. If used, it is the responsibility of the analyst to check that they are calculating results correctly.



%Difference for duplicates

%Recovery for laboratory fortified matrix

Add the "Matrix check samples" column heading to the Sample Information Editor.

NOTE: The least complicated way of accomplishing this is to list your samples in the Sample Information Editor as follows:

Example

Seq #	A/S location	Sample ID
1	10	97-001
2	11	97-001 Dup
3	12	97-001 LFM

- 11.11.2 To add columns to the sample information editor, click on the EDIT heading at the top of the windows menu.
- 11.11.3 Activate "Parameters List". Another window opens.
- 11.11.4 Click on the "Vary by Sample" choice.
- 11.11.5 Scroll down the list until you see "Matrix Check Samples", activate, and then click on the "ADD" icon.
- 11.11.6 EXIT
- 11.11.7 In sample Info File, scroll across columns to locate this addition.

Adding these columns to the sample information editor communicates the location of your duplicates and spikes (LFM) samples to the computer so it can calculate % difference in the case of duplicates and % Recovery in the case of LFM.

Now, your Sample Information Editor should look something like this:

Seq #	A/S location	Sample ID.	Matrix Check Samples
1	10	97-001	<i>Empty Block</i>
2	11	97-001 Dup.	Double click Here (see Dup*) Do not type anything here.
3	12	97-001 LFM	Double click Here (see LFM*) Do not type anything here.

- 11.11.8 Dup* Double click in the empty block where the column and row coincides with the Duplicate Sample location. In this case, it is the Row for Seq.#2, and Column for Matrix Check Samples.



11.11.9 Double click in the empty block in this column. The "Matrix Check Sample Entry" window appears.

11.11.10 In the Select Option area choose "Duplicate" (It may already be so.)

11.11.11 In the Sample Numbers Area, the Sequence #'s appear.

For this example:

97-001 should be Seq #1, Reference (original).

97-001 Dup should be Seq #2, Current (duplicate).

NOTE: Refer to **Sample Info File** to see which Seq # is Orig and Dup. Simply clicking on OK should do it. *These selections tell the computer that you want it to compare the concentrations determined during analysis and compare their results. The computer will do this by calculating % difference, and reporting it to you in the results window. This fulfills the Q.C. requirement for precision and should be done for 10% of all samples analyzed.*

11.11.12 LFM* Double click in the empty block where the column and row coincides with the LFM Sample location. In this case, it is the Row for Seq #3, and Column for Matrix Check Samples.

11.11.13 The "Matrix Check Sample Entry" window appears.

11.11.14 In the Select Option are Choose "Recovery Set Number" 1 or 2 etc.

Note: Type in the Recovery Set Number that coincides with the concentration you used in the Method Editor on the Checks Page.

11.11.15 This is another way that the Method Editor and Sample Information Editor communicate.

11.11.16 The value for your LFM that you prescribe in the Method Editor for the Recovery Set Number column is what the computer will use to calculate % Recovery.

11.11.17 In the Sample Numbers Area, the Sequence #'s appear.

Seq #1 refers to the original, or reference (Decrease the # of sequence if necessary to match)

Seq # 3 refers to the LFM, or current. Make sure these #'s appear in the Sample Reference Area, so the computer will correctly calculate the LFM concentration

The % Recovery value can be observed in the Results Window. (See Results Window Section)

When you are done, your Sample Information Editor should look like this.

Seq #	A/S location	Sample ID.	Matrix Check Samples
1	10	97-001	
2	11	97-001 Dup	Duplicate of 1
3	12	97-001 LFM	Recovery (1) of 1



- 11.12 Analyze QC Before: Optional - Note that the functions described in this section do not work well. If used, it is the responsibility of the analyst to check that they are calculating results correctly.

11.12.1 Choose "Vary by sample", scroll down the list and choose "Analyze Q.C. Before".

11.12.2 Click on "ADD", and the column should appear in your sample information editor. Adding this column to the Sample Information Editor allows you to determine WHICH QCS samples will be used, and WHEN your Quality Control sample(s) will be analyzed during the run.

NOTE: Quality Control Samples are identified in the Method Editor, on the first page of the "QC" Window.

11.12.3 The Method Editor communicates with the Sample Editor about what the QCS is called, e.g., (TMA) and what the true value/acceptable ranges are for the QCS.

The heading on the column is	QC1	QC2	QC3	etc
QC Sample I.D.	TM A	TM B	TM C	
Autosampler Location	7	8	9	
Failure Action	Continue	Continue	Continue	

Concentrations for these references are typed in the next page called QC Sample Concentrations and Limits

11.12.4 In the Sample Information page, under the Analyze QC Before column, simply type in what QC# you want analyzed. Typing the # in this Column in the Seq #1 Row will cause the QCS to be analyzed first, hence the name, Analyze QC Before.

Seq #	A/S location	Sample ID.	Analyze QC Before
1	10	97-001	1
2	11	97-001 Dup	
3	12	97-001 LFM	after 1

This example will produce an analytical sequence that will analyze QC Sample #1 first, then the samples will be analyzed, and after 97-001 LFM is analyzed, QCS #1 will be analyzed again.

11.12.5 When all samples are typed into the Sample Information Editor, including the Quality Control Samples, you must name this as a SIF file.

11.12.6 Go to the File heading at the upper left of the screen. Scroll down to Sample Information Editor and click Name your file, usually by the date,

Example 080497

The file is now 080497.SIF (8/4/97)

- 11.13 Library Manager: It is very important to maintain the Library Manager. Too many Data Files in the library can corrupt the data management system on the instrument. Maintenance of the Library is performed monthly or as needed.

11.13.1 Open the Data Manager either by double clicking its icon on the desk top or choosing File-Utilities-Data Manager in Winlab. Library Manager functions are CHECK, ARCHIVE, DELETE, and Restore icons.



- 11.13.2 Highlight all DATA FILES in the Library that you wish to work with. (To Highlight all, hold CTRL and Click left mouse.)
- 11.13.3 Click on CHECK Icon. All Data Files will be checked for errors.
- 11.13.4 Highlight Files and click on ARCHIVE icon. ARCHIVE window appears, highlight files to archive.
- 11.13.5 Choose selected data sets option and below it, name the file to archive to. Winlab includes a default address and file name but alternate addresses may be used if valid.
- 11.13.6 Select Okay. The archiving process may take several minutes depending upon the size and number of files being archived. Files may be restored from archive at any time. Note that the archived files are included in the back-up to the network server mentioned in 11.5.2.
- 11.14 Message Log
- Errors from instrument are logged in the "Message Log" (Blinking in Lower Right Corner). Go to SYSTEM Heading > **Message Log**. Message Log appears. Note Errors, keep records of Error Codes, if instrument is having problems.

Show records to Perkin Elmer Service Engineer, Peter Cannon

Telephone #: 1-800-762-8288 ICP, Serial #069N6092002

12.0 DATA ANALYSIS AND CALCULATIONS

- 12.1 Sample data are reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.
- 12.2 For dissolved aqueous analytes, report the data generated directly from the instrument with allowance for sample dilution. Concentrations below IDL and MDL are not reported.
- 12.3 For total recoverable aqueous analytes, multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data to the proper significant figure.
- 12.4 For total recoverable analytes in solid samples, round the solution analyte concentrations to the proper significant figure in mg/L.
- 12.5 For total recoverable analytes in solid samples, the (C) concentration in mg/kg is calculated as follows:

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

Where:

C = Concentration in extract (mg/L)

V = Volume of extract (L,)



D = Dilution factor (undiluted = 1)

W = Weight of sample aliquot extracted (kg)

13.0 METHOD PERFORMANCE

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

14.0 POLLUTION PREVENTION

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

15.0 WASTE MANAGEMENT

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

16.0 REFERENCES

- 1. U.S. Environmental Protection Agency. 1984. *Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes-Method 200.7*, May. 1984.
- 2. U.S. Environmental Protection Agency. 1986. *Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010, SW-846 Test Methods for Evaluating Solid Waste, 3rd edition*, 1986.
- 3. U.S. Environmental Protection Agency. 1992. *Inductively Coupled Plasma-Atomic Emission Spectrometry Method for the Analysis of Waters and Solids, EMMC*, July 1992.
- 4. Perkin-Elmer Sciex. 1998. *Software Guide for Winlab 32 for ICP*, version 3.1.
- 5. U.S. Environmental Protection Agency. 1994. *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Rev. 4.4*, 1994.



6. U.S. Environmental Protection Agency. 1994. Method 200.2 – *Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, Revision 2.8* EMMC Version, 1994.
7. U.S. Environmental Protection Agency. 1992. Method 3005A – *Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FIAA or ICP Spectroscopy, Revision 1*, July 1992.
8. U.S. Environmental Protection Agency. 2007. Method 3015A – *Microwave Assisted Acid Digestion of Aqueous Samples and Extracts, Revision 1*, February 2007.
9. U.S. Environmental Protection Agency. 1992. Method 3010A – *Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FIAA or ICP Spectroscopy, Revision 1*, July 1992.

17.0 TABLES AND VALIDATION DATA

TABLE 1. Quality Control Tests and Acceptance Limits for the Analysis of Metals by EPA Method 200.7

Accuracy			Precision		
QC Test	Acceptance Limits (% Recovery)	Frequency	QC Test	Acceptance Limits (RPD ^a)	Frequency
LFB ^b	85 – 115 ^e	≥ 10%	Duplicates	≤ 20 ^f	≥ 10%
LFM ^c	70 – 130 ^e	≥ 10%			
QCS ^d	95 – 105 ^e	≥ 10%			

^a RPD = relative percent difference among duplicates.

^b LFB = laboratory fortified blank sample.

^c LFM = laboratory fortified matrix sample

^d QCS = quality control sample from source outside of the laboratory.

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

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



TABLE 2. Quality Control Elements and Acceptance Limits for EPA Method 200.7 Determination Of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Linear Dynamic Range (LDR)	Every year and according to the judgment of the analyst.	Six standards, two of which are close to the upper limit of the LDR with an observed analyte conc. no more than 10% below the stated conc. of the standard.	Check/service instrument.
Instrument Stability	45-minute warm-up	RSD < 5% of highest calibration standard in curve	Determine and correct the cause, recalibrate before analyzing samples
Spectrometer Control Torch View	Should be done at least annually, or as necessary.	1ppm Manganese standard is aspirated into the plasma, and alignment corrections are made automatically.	Performed during torch cleaning
Initial Calibration	Every run	$r^2 > 0.995$	Recalibrate with new standards
Internal Standard	Every run. Yttrium is added to all standards and sample solutions.	Yttrium emission intensity measured at 371.029 nm is continuously monitored and corrections are made to match the relative response. (Internal Standard Recoveries: 80 – 120%)	Check Yttrium flow rate.
Instrument Performance Check Sol. IPC A Initial Performance Calibration Check(s) and IPC B Continuing Performance Calibration Check(s)	Immediately following each calibration, after every tenth sample and at the end of the run	IPC A ($\pm 5\%$) First IPC(s) run after the calibration curve. IPC B ($\pm 10\%$) Concentration a midpoint standard of the calibration.	Reanalyze IPC, if outside range, recalibrate, and repeat analysis. Re-analyze sample since last successful IPC B, or discontinue & recalibrate instrument if necessary.
Calibration Blank (CCB)	Immediately following each calibration, after every tenth sample and at the end of the run	< MDL, but > a negative signal in concentration units equal to the MDL	Reanalyze. Determine cause, or recalibrate instrument. If it is not possible to reanalyze, qualify the data if sample concentration is < 10 times the CCB. If the sample's concentration is "Not Detect" or greater than or equal to 10 times the CCB, no qualification is needed.



TABLE 2. Quality Control Elements and Acceptance Limits for EPA Method 200.7 Determination Of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry

QC Elements	Frequency	Acceptance Criteria	Corrective Action
Quality Control Sample (QCS)	After calibration and at the end of the run.	$\pm 5\%$ Recovery	Acceptable range must be met before continuing with sample analysis. Recalibrate and repeat.
Laboratory Reagent Blank (LRB)	One with each batch of 20 or fewer samples	$< 1/2$ the analyte MRL or $< 10\%$ of the analyte level measured in the sample	Determine and eliminate the source of contamination & then repeat sample analysis. If reanalysis is not possible, the data may be qualified.
Laboratory Duplicate	Every 10 or fewer samples or less	$RPD \leq 20\%$	Repeat using fresh sample. If failure continues, check sample for non-homogeneity and system for problems. If the sample is not homogeneous, note this with the Duplicate's results.
LFM	Every 10 or fewer samples or less	70 – 130% Note: Recovery calculations are not required if the concentration added is less than 25% of the unfortified sample concentration	If laboratory performance shown to be in control, LRB and LFB or QCS within acceptance criteria, problem is a matrix effect – qualify data.
LFB	One with each batch of 20 or fewer samples	85 – 115%	The source of the problem must be identified and resolved before continuing analysis
MDL determination (USEPA, 1997)	Annually or a new operator, or judgment of the analyst	Target analyte concentration spiked into the blank matrix must not exceed 10 times (approximately) the experimentally determined MDL (7 spiked blanks) if RSD from analysis of 7 aliquots is $< 10\%$, conc. used to determine MDL is too high.	Repeat MDL study spiking the blank matrix with lower concentration of the target analyte
MRL Check Standard	At the beginning of every analytical run	$\pm 20\%$	Acceptable range must be met before reporting data. If not



TABLE 2. Quality Control Elements and Acceptance Limits for EPA Method 200.7 Determination Of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry

QC Elements	Frequency	Acceptance Criteria	Corrective Action
			acceptable, then recalibrate and repeat. If the problem persists, suspect the MDL and MRL are too low for the analysis conditions.
SIC Solution	2 times per analytical run*	The concentration in the SIC of the analyte of interest must be within \pm the MDL	If the interfering analyte is > 10 mg/L in the sample and does not meet acceptance criteria, retest the SIC. If this fails again, prepare fresh SIC and retest. If it fails again, redo IEC table.
*Section 7.13.5 of EPA Method 200.7, Revision 4.4, May 1994: If the analyzed samples (e.g., finished drinking water) do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required but all interelement spectral correction factors must be verified annually and updated if necessary.			

TABLE 3. On-Line Method Inter-element Spectral Interferences Arising from Interferants at the 100-mg/L Level

Analyte	Wavelength	Interferant
Aluminum	396.152	None
Antimony	206.833	None
Arsenic	188.979	None
Barium	233.527	None
Beryllium	313.042	None
Boron	249.773	None
Cadmium	214.438	Fe
Calcium	315.887	None
Chromium	205.552	Ni
Cobalt	228.616	Ba, Ni, Cr
Copper	324.754	None



TABLE 3. On-Line Method Inter-element Spectral Interferences Arising from Interferants at the 100-mg/L Level

Analyte	Wavelength	Interferant
Iron	259.94	None
Lead	220.353	Ni, Fe
Magnesium	279.079	None
Manganese	257.61	None
Molybdenum	203.844	None
Nickel	231.604	None
Potassium	404.721	None
Selenium	196.026	Fe
Silver	328.068	Mn
Sodium	588.995	None
Strontium	460.733	None
Thallium	190.8	Mn
Tin	334.941	Fe, Mn
Titanium	334.941	None
Vanadium	292.402	Fe, Cr
Zinc	206.2	Ni

TABLE 4. Instrument Calibration Standard for Interelement Correction test

Solution	Analytes	
100 mg/L	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn	



TABLE 5. Method Detection Limits (MDLs) for Trace Metal Analysis in Reagent Water by EPA Method 200.7 (06/28/2012 – 08/08/2012)

Analyte	Wavelength	MDL (mg/L) ^a	Spike Concentration (mg/L)
Aluminum	308.215	0.10	0.30
Aluminum	396.153	0.13	0.40
Antimony	206.836	0.05	0.20
Antimony	217.582	0.04	0.20
Arsenic	188.979	0.04	0.10
Arsenic	193.696	0.06	0.20
Barium	233.527	0.02	0.05
Barium	455.403	0.02	0.10
Barium	493.408	0.01	0.20
Beryllium	313.042	0.03	0.10
Beryllium	313.107	0.02	0.02
Boron	249.677	0.04	0.20
Boron	249.772	0.04	0.20
Cadmium	226.502	0.03	0.05
Cadmium	214.440	0.02	0.05
Calcium	315.887	0.12	0.30
Calcium	317.933	0.14	0.30
Chromium	205.560	0.02	0.05
Chromium	267.716	0.02	0.05
Cobalt	228.616	0.02	0.10
Copper	224.700	0.02	0.05
Copper	324.752	0.03	0.05
Iron	259.939	0.02	0.05
Iron	238.204	0.02	0.05
Lead	220.353	0.02	0.05
Lead	217.00	0.04	0.10
Lead	261.418	0.04	0.10
Magnesium	279.077	0.02	0.05
Manganese	257.610	0.01	0.05
Manganese	260.568	0.02	0.05
Molybdenum	203.845	0.03	0.10
Nickel	231.604	0.02	0.05
Nickel	341.476	0.03	0.05
Potassium	766.490	0.73	3.0
Selenium	196.026	0.05	0.20
Silica	251.611	0.03	0.10
Silver	328.068	0.02	0.05
Silver	338.289	0.02	0.10
Sodium	588.995	0.20	0.40
Sodium	330.237	0.08	0.20
Thallium	190.801	0.02	0.10
Thallium	276.787	0.04	0.10
Titanium	334.940	0.02	0.05
Vanadium	292.402	0.02	0.10
Zinc	206.200	0.02	0.05



Analyte	Wavelength	MDL (mg/L) ^a	Spike Concentration (mg/L)
Zinc	213.857	0.02	0.05
^a Based on seven determinations spiked at the concentrations shown and run on 06-28-12, 07-02-12, 07-10-12, 07-11-12, 07-16-12, 08-01-12, 08-08-12			

TABLE 6. 2012 Interelement Correction Factors for certified SDWA by EPA 200.7						
	Ni	Fe	Mo	Co	Cu	Be
Ba 493.409	0	0	0	0	0	0
Cr 205.560	0	-0.387675	0.152363	-0.242915	-0.370814	-3.49328
Cu 324.752	-0.216578	-0.344389	0.328779	-0.810859	NA	-0.316409
Ni 231.604	NA	-0.321515	-1.50276	0.415651	-0.318603	-0.643863

NA: Not Applicable.



- FORM 1. ICP Standards Preparation for EPA 200.7**
[Bench Data Collection Forms\ICP Standards Prep for 200-7.doc](#)
- FORM 2. Yttrium and Cerium Standards Preparation for EPA 200.7**
[Bench Data Collection Forms\Yttrium and Cerium Std Prep for EPA 200-7.doc](#)
- FORM 3. Nitric Acid Standards Preparation for EPA 200.7**
[Bench Data Collection Forms\Nitric Acid Prep for EPA 200-7.doc](#)
- FORM 4. IEC Standards Preparation for EPA 200.7**
[Bench Data Collection Forms\IEC Standards Prep for EPA 200.7.doc](#)