

STANDARD OPERATING PROCEDURE

For

USEPA METHOD 200.7

Determination Of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry

SOP #: EPA 200.7

REVISION #: 3.1

DATE: January 2008

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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 35
3.0	December 2006	Replaced old DEP Logo with state seal + MassDEP	Title page & header



Rev. #	Date	Description of Revision	Page #
		Numerous minor revisions throughout	
		New ICP instrument and operating software (Section 6.1)	11
		New instrument and software operating procedures (Section 11.0)	19
		2006 MDL data (Table 8)	38
		2006 SDWA interelement correction factors (Table 11)	40
3.1	January 2008	Section 7.13 – Revised plasma solutions to include 10 mg/L Mn for axial and radial optimization. Section 7.7.1 – Standards preparation revised. Section 8.1 – Included pH log sheet as part of sample collection, preservation, and storage. Section 9.2.4 – MDL preparation and calculations. Section 11.1.3 – Took out WinLab offline; step may cause data management problems. Section 11.4.7 – Added time needed for machine to stabilize before starting calibration sequence. Section 11.5.1– Added axial and radial alignment instructions Section 11.5.3 – Renumbered to 11.5.4 Section 11.5.2 – Renumbered to 11.5.3 New Section 11.5.2 – Added mercury alignment instructions Section 11.6.7 – Changed analytical sequence Table 2 – Revised	



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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 ($> 50\text{ mg/Kg}$) are treated in the same manner. Also, the extraction of tin from solid samples is performed using aliquots $< 1\text{ g}$ 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. Table 2 provides estimated instrument detection limits for the listed wavelengths. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, and selected operating conditions.
- 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 $\leq \text{pH } 2$.



- 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 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.
- 3.8 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.
- 3.9 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.



- 3.10 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.
- 3.11 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.
- 3.12 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.
- 3.13 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.
- 3.14 Plasma Solution - A solution that is used to determine the optimum orientation of the quartz torch for viewing the plasma.
- 3.15 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.
- 3.16 Quality Control Sample (QCS) - A Sample of a matrix similar to the sample being analyzed, which contains analytes of a known or accepted concentration. The QCS is obtained from a source external to the laboratory and contains the analytes of interest at certified concentrations for the method of interest. This QCS is processed in the same manner as the sample, unlike the QCS in 3.15, and is used to check method performance.
- 3.17 Solid Sample - For the purpose of this method, a sample taken from material classified as either fish/biological tissue, soil, sediment or sludge.
- 3.18 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.
- 3.19 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.
- 3.20 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.
- 3.21 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 (Sect. 11.2.1), 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.



- 3.22 Water Sample - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, stormwater 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 (**response to deviation cited in on-site audit of March 1998**). 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 2) have interferences that are documented and kept on file.
- 4.1.5 Since interelement correction tables, Table 11, are not used, SIC solutions are routinely analyzed to verify the absence of interelement spectral interference. (**Response to deviation cited in U.S. EPA on-site audit of March 1998**).
- 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 11.2). Major maintenance operations are performed by a Perkin-Elmer Customer Service Engineer. Service calls are placed to company only when 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 $180 \pm 5^\circ\text{C}$.
- 6.6 Assortment of air displacement pipetters capable of delivering volumes ranging from 0.1 to 2500 μL with corresponding metals free disposable pipet 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 with the laboratory environment from dust, etc. A clean laboratory work area is designated for trace element sample handling. Sample containers used in the determination of trace elements are sufficiently cleaned. Sample cleaning procedure involves washing with a detergent solution, rinsing with tap water, soaking for 4 h or more in 20% (v/v) nitric acid or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and stored clean. 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 Conical Phillips beakers (Corning), 250-mL with 50-mm ribbed watch glasses
 - 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.

- 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.

- 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 0.04 mg/L: 4 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 (3.15) 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 determined apparent analyte(s) concentration 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% HNO_3 and adding yttrium to a concentration of 20ppm, e.g., 40 mL of 1000 ppm Y + 40 mL HNO_3 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- μm 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 $\text{pH} < 2$.
- 8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to $\text{pH} < 2$. The sample is held for sixteen hours, and then verified to be $\text{pH} < 2$ 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 For fish/biological tissue samples, they 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) was established for each wavelength utilized (See Table 2) 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. Also referred to as the Linear Calibration Range (LCR).

9.2.3 Quality control sample (QCS) - The QCS (3.15) 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 on with any analyses.

9.2.4 Method detection limit (MDL) - MDLs are established for all wavelengths utilized, (see Table 8), using reagent water (blank) fortified at a concentration of two to five times the estimated instrument detection limit (see Table 2). 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.

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 deviations 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 10 samples of the same matrix. LRB data is 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 LFB are prepared to correspond with the range of the sample concentrations.

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

$$\text{UPPER CONTROL LIMIT} = x + 3S$$

$$\text{LOWER CONTROL LIMIT} = x - 3S$$

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 is used to establish an on-going precision statement for the level of concentrations included in the LFB. This data is kept on file and available for review.

- 9.3.4 Instrument performance checks (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 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 is kept on file with the sample analyses data.



- 9.3.5 Spectral interference check (SIC) solution - All determinations performed in the laboratory are verified by analyzing SIC solutions. **(Response to deviation cited in U.S. EPA on-site audit of WES on March 1998).** The preparation and periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routines are given in Section 7.11.3. Special cases of verification are described 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 (mg/L x 0.1L/0.001kg = 100, 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 RDL 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 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 The 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 5 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 in Standard/QC Preparation Logbook.
- 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 Turn on dual argon tank delivery system Argon pressure must be > 75 psi and argon must be available on a constant basis.
- 11.1.1.3 Check the air compressor currently located in the boiler room. Water must be drained from the tank on a regular basis, especially during the humid months, which may be as often as daily. Otherwise, water will be forced through the compressed air line and into the instrument. If this occurs, the plasma will not light or remain lit.
- 11.1.2 Turn on Computer and Screen - Log on (run instrument) - Password (runinstrument#1)
- 11.1.3 Bring up WinLab 32 – argon note will come up – click OK. 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 location 1 thru 16 is 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 Turn on hood
- 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 the compressed air lines. See 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 THIS HAPPENS: 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 Clean Room #2102. Check the operation of this unit; especially if the water flow in the diagnostics window is not acceptable. Clean pump filter every six months.
 - 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 Logbook.
 - 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 or standard solution of manganese. The software will determine maximum emission intensity. Axial & Radial alignment of optics is automatically adjusted; accept the value results from adjustment are printed and kept on file.

- 11.5.2 Mercury Alignment – Perform before each run. Click on Spectrophotometer control and select Hg alignment. Once alignment is completed, go to Results and record values.
- 11.5.3 Winlabs Library Manager – Files for data should be archived electronically. Periodic or monthly maintenance is recommended for proper operation of instrument. The files are automatically backed-up to the network server by leaving the instrument computer logged off but running overnight.
- 11.5.4 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)] or SIC(s) [Spectral Interference Check Solutions(s)], Performance
3	Check Standard(s)
4	Reagent Blank (CCB) Quality Control Sample(s) [QCS(s) ($\pm 5\%$)], Performance
5	Check Standard(s). MRL(s) Minimum Reporting Limit Standard(s), Performance
6	Check Standard(s) IPC A(s) ($\pm 5\%$) Calibration Standard(s), Performance Check
7	Standard(s)



- 8 CCB Continuous Calibration Blank
- 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 less than 10 samples in the last set of samples, the following sequence finishes the sample run.

- 21 QCS(s), Performance Check Standard(s)
- 22 IPC B ($\pm 10\%$), Performance Check Standard(s)
- 23 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 is 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 preparations used. Alternate preparations 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 μ m | Method 3005 |
| Dissolved -0.45 μ m | Method 3005 |
| Total TCLP Extracts | Method 3015 |
| Total High TDS | Method 3010B |
| RCRA | Method 3051 |
| Total for Wastes Liquid/Solid | Method 3051 |
| Total for Soil, Sludge, Sediment | Method 3051 |
| Fish/Biological Tissue | Method 3052 |
- 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, Ex, (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 11.4.2.

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 8 are the MDLs for total recoverable metals determined for the wavelengths used in this method. The MDLs were determined in reagent water blank matrix. The listed MDLs for solids were determined for the wavelengths used in this method. The solids MDLs were



determined by fortifying solid matrix samples (actual samples). The fish/biological tissue MDLs were determined by fortifying solid matrix samples (actual samples).

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. 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. 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. 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.



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. Preference of the analyst.	Six standards, two of which are close to the upper limit of the LDR.	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.	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 an 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.
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



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
			and repeat.
Laboratory Reagent Blank (LRB)	One with each batch of 20 or less samples	< 2.2 times the analyte MDL 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 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 homogenous, note this with the Duplicate's results.
LFM	Every 10 samples or less	70 – 130% Note: Recovery calculation 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 preference of the analyst	Target analyte concentration spiked into the blank matrix must not exceed 10 times (approximately) the experimentally determined MDL (7 spiked blanks)	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 acceptable, then recalibrate and repeat. If the problem persists, suspect the MDL and MRL are too low for the analysis conditions.



TABLE 3. Wavelengths and Instrument Detection Limits

Analyte	Wavelength	IDL µg/L	Calibrated to 1 mg/L
Aluminum	396.152	1.62	1.00
Antimony	206.833	2.31	1.00
Arsenic	188.979	2.66	1.00
Barium	233.527	0.11	1.00
Beryllium	313.042	0.89	1.00
Boron	249.773	3.65	1.00
Cadmium	214.438	0.23	1.00
Calcium	315.887	1.84	1.00
Chromium	205.552	1.01	1.00
Cobalt	228.616	0.47	1.00
Copper	324.754	0.76	1.00
Iron	259.94	0.26	1.00
Lead	220.353	9.82	1.00
Magnesium	279.079	3.68	1.00
Manganese	257.61	0.5	1.00
Molybdenum	203.844	2.5	1.00
Nickel	231.604	1.19	1.00
Potassium	404.721	1.3	1.00
Selenium	196.026	6.1	1.00
Silver	328.068	1.1	1.00
Sodium	588.995	1.23	1.00
Strontium	460.733	0.45	1.00
Thallium	190.8	0.58	1.00
Tin	334.941	4.57	1.00
Titanium	334.941	0.17	1.00
Vanadium	292.402	0.33	1.00
Zinc	206.2	0.41	1.00



TABLE 4. 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
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 5. Instrument Calibration Standard for
Interelement Correction test**

Solution	Analytes
100 ppm	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 6. Accuracy of Trace Metal Analysis in Actual Liquid Samples by EPA Method 200.7

Analyte	Wavelength	Date	Accuracy (% Recovery) ^a					
			Mean	SD ^b	Warning Limits (± 2 SD)		Control Limits (± 3 SD)	
					Upper (UWL)	Lower (LWL)	Upper (UCL)	Lower (LCL)
Aluminum	396.152	08/30/00	94	1.9	98	91	100	89
Antimony	206.833	08/30/00	81	2.4	86	76	88	74
Arsenic	188.979	08/30/00	95	0.71	96	94	97	93
Barium	233.527	01/03/00	101	1.1	103	98	104	97
Barium	455.403	01/03/00	101	1.1	103	98	104	97
Beryllium	313.042	08/30/00	87	1.3	90	85	91	84
Boron	249.773	01/03/00	94	6.1	106	81	112	75
Cadmium	226.502	08/30/00	87	1.6	90	84	92	82
Cadmium	214.438	08/30/00	87	1.6	90	84	92	82
Calcium	315.887	10/19/00	97	4.8	107	88	112	83
Chromium	205.552	09/08/00	103	3.4	110	96	113	93
Chromium	267.716	09/08/00	103	3.4	110	96	113	93
Cobalt	228.616	11/19/98	98	2.5	103	93	105	90
Copper	324.754	09/07/00	106	8.2	122	89	130	81
Iron	259.940	09/15/00	106	3.6	112	90	115	85
Lead	220.353	09/07/00	86	2.1	90	81	92	79
Magnesium	279.079	10/19/00	96	4.3	105	88	109	83
Manganese	257.610	10/06/99	99	0.47	100	98	100	97
Molybdenum	203.884	10/06/99	99	8.9	117	81	126	72
Nickel	231.604	09/07/00	84	3.2	90	77	93	74
Nickel	232.003	09/07/00	86	3.2	92	75	95	72
Selenium	196.026	09/07/00	88	3.2	94	81	97	78
Silver	328.068	10/16/00	95	4.9	105	85	110	80
Sodium	588.995	10/18/00	98	1.5	101	95	102	93
Strontium	460.733	10/06/00	106	3.8	113	98	117	94
Thallium	190.8	08/30/00	84	1.4	87	81	88	80
Titanium	334.941	10/06/99	98	4.8	107	88	112	83
Vanadium	292.402	10/06/99	99	2.2	103	95	106	93
Zinc	206.200	09/07/00	94	3.1	100	88	103	85
Zinc	213.856	09/07/00	90	3.1	96	84	99	81
^a Based on the analysis of 20 samples								
^b SD = Standard deviation								



TABLE 7. Precision of Trace Metals Analysis in Actual Liquid Samples by EPA Method 200.7

Analyte	Wavelength	Date	Precision ^a Relative Percent Difference (RPD) ^a					
			Mean	SD ^b	Warning Limits (± 2 SD)		Control Limits (± 3 SD)	
					Upper (UWL)	Lower (LWL)	Upper (UCL)	Lower (LCL)
Aluminum	396.152	08/30/00	0.67	2.7	6.1	0	8.8	0
Antimony	206.833	08/30/00	0.30	0.64	1.6	0	2.2	0
Arsenic	188.979	09/07/00	0.25	0.61	1.5	0	2.1	0
Barium	233.527	09/07/00	0.25	0.61	1.5	0	2.1	0
Barium	455.403	09/07/00	0.10	0.29	0.68	0	0.97	0
Beryllium	313.042	08/30/00	0.20	0.51	1.3	0	1.8	0
Boron	249.773	09/07/00	0.21	0.65	1.5	0	2.2	0
Cadmium	226.502	09/07/00	0.19	0.52	1.2	0	1.8	0
Cadmium	214.438	09/07/00	0.17	0.55	1.3	0	1.8	0
Calcium	315.887	12/30/98	0.27	0.61	1.5	0	2.0	0
Chromium	205.552	09/07/00	0.25	0.60	1.5	0	2.0	0
Chromium	267.716	09/07/00	0.26	0.62	1.5	0	2.0	0
Cobalt	228.616	10/06/99	0.20	0.60	1.4	0	2.0	0
Copper	324.754	09/07/00	1.8	4.9	12	0	16	0
Iron	259.940	10/03/00	0.26	1.1	2.4	0	3.4	0
Lead	220.353	09/07/00	0.10	0.29	0.68	0	0.97	0
Magnesium	279.079	10/19/00	0.37	0.64	1.7	0	2.3	0
Manganese	257.610	10/06/99	0.02	0.07	0.16	0	0.23	0
Molybdenum	203.884	10/06/99	0.04	0.12	0.29	0	0.41	0
Nickel	231.604	09/07/00	0.15	0.39	0.93	0	1.3	0
Nickel	232.003	09/07/00	0.14	0.36	0.86	0	1.2	0
Potassium	404.721	10/06/99	0.22	0.58	1.4	0	2.0	0
Selenium	196.026	09/07/00	0.25	0.61	1.5	0	2.1	0
Silver	328.068	10/16/00	0.21	0.90	1.9	0	2.8	0
Sodium	588.995	10/06/00	0.20	0.59	1.4	0	2.0	0
Strontium	460.733	10/06/99	0.19	0.58	1.4	0	2.0	0
Thallium	190.8	10/06/99	0.21	0.61	1.5	0	2.0	0
Titanium	334.941	10/06/99	0.02	0.07	0.16	0	0.23	0
Vanadium	292.402	10/06/99	0.20	0.59	1.4	0	2.0	0
Zinc	206.200	08/30/00	1.7	4.6	11	0	15	0
Zinc	213.856	08/30/00	1.7	4.6	11	0	15	0
^a Based on the analysis of 20 samples								
^b SD = Standard deviation								



TABLE 8. Method Detection Limits (MDLs) for Trace Metal Analysis in Reagent Water by EPA Method 200.7 as of 12/6/2006

Analyte	Wavelength	MDL (mg/L)
Aluminum	308.215	0.100 ^e
Aluminum	396.153	0.300 ^e
Antimony	206.836	0.010 ^d
Antimony	217.582	0.010 ^d
Arsenic	188.979	0.010 ^d
Arsenic	193.696	0.020 ^d
Barium	233.527	0.010 ^c
Barium	455.403	0.010 ^d
Barium	493.408	0.010 ^d
Beryllium	313.042	0.010 ^d
Beryllium	313.107	0.010 ^d
Cadmium	226.502	0.010 ^d
Cadmium	214.440	0.010 ^d
Calcium	315.887	0.030 ^d
Calcium	317.933	0.050 ^d
Chromium	205.560	0.010 ^c
Chromium	267.716	0.010 ^d
Cobalt	228.616	0.010 ^d
Copper	224.700	0.010 ^d
Copper	324.752	0.010 ^c
Iron	259.939	0.010 ^d
Iron	238.204	0.010 ^d
Lead	220.353	0.010 ^d
Magnesium	279.077	0.010 ^d
Manganese	257.610	0.010 ^c
Manganese	260.568	0.010 ^d
Molybdenum	203.845	0.010 ^d
Nickel	231.604	0.010 ^c
Nickel	341.476	0.030 ^d
Potassium	766.490	0.020 ^e
Selenium	196.026	0.010 ^d
Silica	251.611	0.070 ^c
Silver	328.068	0.010 ^c
Silver	338.289	0.020 ^d
Sodium	588.995	0.020 ^e
Sodium	330.237	0.100 ^e
Thallium	190.801	0.010 ^d
Thallium	276.787	0.020 ^c
Titanium	334.940	0.010 ^d
Vanadium	292.402	0.010 ^d
Zinc	206.200	0.020 ^d
Zinc	213.857	0.010 ^c



TABLE 8. Method Detection Limits (MDLs) for Trace Metal Analysis in Reagent Water by EPA Method 200.7 as of 12/6/2006

Analyte	Wavelength	MDL (mg/L)
^a Recovery of spiked concentration ^b SD = standard deviation of mean concentration measured ^c Average from seven determinations spiked at 0.1 mg/L done on three different dates ^d Average from seven determinations spiked at 0.05 mg/L done on three different dates ^e From seven determinations spiked at 0.25 mg/L		

TABLE 9. Method Detection Limits (MDLs) for Trace Metal Analysis in Fish/Biological Tissue by EPA Method 200.7 (2.0 g sample size/40 mL volume)

Analyte	Wavelength	Date of Study	Accuracy (Mean % Recovery ^a)	Precision (SD ^b in mg/Kg)	MDL ^c (mg/Kg)
Cadmium	214.440	3/25/03	79	0.040	0.13
Chromium	267.716	3/25/03	77	0.051	0.16
Copper	324.752	3/25/03	78	0.106	0.33
Lead	220.353	3/25/03	93	0.093	0.29
^a Recovery of spiked concentration ^b SD = standard deviation of mean concentration measured ^c From seven determinations spiked at 2.5 mg/Kg					

TABLE 10. Method Detection Limits (MDLs) for Trace Metal Analysis in Fish/Biological Tissue by EPA Method 200.7 (5.0 g sample size/20 mL volume)

Analyte	Wavelength	Date of Study	Accuracy (Mean % Recovery ^a)	Precision (SD ^b in mg/Kg)	MDL ^c (mg/Kg)
Cadmium	214.440	04/08/03	78	0.016	0.051
Chromium	267.716	04/08/03	78	0.026	0.082
Copper	324.752	04/08/03	79	0.010	0.031
Lead	220.353	04/08/03	78	0.020	0.063
^a Recovery of spiked concentration ^b SD = standard deviation of mean concentration measured ^c From seven determinations spiked at 1.0 mg/Kg					



TABLE 11. 2006 SDWA Interelement Correction Factors

	Ni	Ti	Fe	Ce	Be	Mo	Co	Tl
Ba 493.409	0	0	0	0	0	0	0	0
Cd 226.502	-1.65908	- 1.38215	-1.03112	-1.34708	0	0	0	0
Cr 205.552	0.0641086	0	0	0	-4.04299	1.4432	0	0
Cu 324.754	0	0	0	0	0	-0.110007	0	0
Ni 231.604	0	0	0	0	0	0	0.86056	1.29256