METHOD 200.15

DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER BY ULTRASONIC NEBULIZATION INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSIONSPECTROMETRY

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DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER BY ULTRASONIC NEBULIZATION INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Ultrasonic nebulization inductively coupled plasma-atomic emission spectrometry (UNICP-AES) is used to determine metals and some nonmetals in solution. This method provides procedures for the determination of dissolved and total recoverable elements in ground waters and surface waters, and total recoverable elements in drinking water supplies. This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Number (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
Cerium[a]	(Ce)	7440-45-1
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
Lithium	(Li)	7439-93-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO_2)	7631-86-9

(continues on next page)

[a]Cerium has been included as method analyte for correction of potential interelement spectral interference.

Analyte		Chemical Abstract Services Registry Number (CASRN)
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thalllium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

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 Dissolved analytes are determined by UNICP-AES after suitable filtration, acid preservation, and reagent matrix matching to the calibration standards. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 For the determination of total recoverable analytes in aqueous samples that contain particulate or suspended solids a digestion/extraction is required prior to analysis. If the sample contains undissolved solids >1%, the sample should be analyzed using one of the other spectrochemical methods - 200.7, 200.8, or 200.9 given in this manual.

1.5 Where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly without acid digestion if the sample has been properly preserved with acid, has turbidity of <1 NTU at the time of analysis and is presented to the instrument in the same reagent/acid matrix as the calibration standards. This total recoverable determination procedure is referred to as "direct analysis".

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. This method is suitable for the total recoverable determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of water samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver.

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 should be completed as soon as possible after sample preparation.

1.9 This method is not suitable for the determination of organo-mercury compounds.

1.10 Sample matrices can significantly affect the analytical response of selenium. The resulting effect is signal enhancement when compared to a single element calibration standard. The effect can range from 20-60% and is influenced by both the nature and concentration of the other element(s) in solution. The standardization routine utilized in this method partially compensates for this enhancement in the analysis of ambient or drinking waters where the total concentration of the matrix cations (Ca, K, Mg, and Na) range from 10-300 mg/L. However, for critical determinations of selenium, method of standard additions or recognized proven methodology such as graphite furnace atomic absorption should be used.

1.11 Ultrasonic nebulization being more efficient than direct pneumatic nebulization a greater portion of the sample aerosol and analyte reaches the plasma. The increased amount of analyte causes higher signal intensities which decreases the linear concentration range. Also, interelement spectral interferences become more significant at lower concentrations when compared to pneumatic nebulization. Sample analyte concentrations that exceed 90% of the determined upper limit of the linear dynamic range should be diluted and reanalyzed.

1.12 Detection limits and linear ranges for the elements will vary with the wavelength selected, the instrument system, operating conditions, and sample matrices. Listed in Table 4 are typical method detection limits determined in reagent blank matrix for the recommended wavelengths with background correction using the instrument operating conditions given in Table 5. The MDLs listed are for both total recoverable determinations by "direct analysis" and where sample digestion is employed.

1.13 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a well mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered 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 acids and hydrogen peroxide, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multielemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is desolvated before being transported to the plasma torch. Element specific emission spectra are produced by a 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 required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis. Various interferences must be considered and addressed appropriately as discussed 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 (Section 7.11.1).

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 (Section 7.10).

3.3 **Dissolved Analyte** - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 11.1).

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 sampling 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 (Section 8.4).

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 10 replicate measurements of the calibration blank signal at the same wavelength (Table 1).

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 (Sections 7.12 and 9.3.4).

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 (Section 11.4).

3.8 **Laboratory Duplicates (LD1 and LD2)** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates 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 (Sections 7.11.3 and 9.3.2).

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 (Section 9.4).

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 (Sections 7.11.2 and 9.3.1).

3.12 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Section 9.2.2).

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 (Section 9.2.4 and Table 4).

3.14 **Plasma Solution** - A solution that is used to determine the optimum height above the work coil for viewing the plasma (Sections 7.16 and 10.2.2).

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 (Sections. 7.13 and 9.2.3).

3.16 **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 (Sections 7.14, 7.15, and 9.3.5).

3.17 **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 (Sections 9.5.1 and 11.4).

3.18 **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 (Section 7.9).

3.19 **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 (Section 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 (Section 11.2).

3.20 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, ambient surface, or ground water.

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 can usually be 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 may 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 will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be 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 may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables.[3] Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.14. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.[3,4]

4.1.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to utilize a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference, but

not exceed the upper LDR limit of the analyte. Normally, for ultrasonic nebulization 20 mg/L single element solutions are sufficient, however, for the major constituent analytes (calcium, magnesium, potassium and sodium) found in all waters, or other analytes encountered at elevated levels, a more appropriate test would be to use a concentration near the upper LDR limit (Section 9.2.2). See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are not used, either on-going SIC solutions (Section 7.15) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, greater than the analyte IDL, or false negative analyte concentration, less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of this misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, e.g., 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2 Physical interferences are effects associated with the sample nebulization and aerosol transport processes. These effects can cause significant inaccuracies and can occur especially in samples containing high dissolved solids or high acid concentrations. Because ultrasonic nebulization provides more efficient nebulization, these effects may become more predominant at lower concentrations compared to pneumatic nebulization. If physical interferences are present, they must be reduced by diluting the sample or using an appropriate internal standard element. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique using pneumatic nebulization, but when evident, are usually matrix dependent. However, with ultrasonic nebulization the aerosol droplets are desolvated and the water vapor is removed as condensate before the analyte enters the plasma. This desolvation step changes the nature of the aerosol

and affects the emission intensity of certain analytes. A difference in signal intensity has been observed between the stable valence states of arsenic (As (III) and As (V)) and chromium (Cr (III) and Cr (VI)) when analyzed as a desolvated aerosol. For arsenic the higher valance state gives the more intense signal, while for chromium the opposite is true. A similar phenomenon occurs for selenium, however, in this situation signal intensity is affected by varying concentrations of other method analytes in solution. Fortunately, for arsenic and chromium the effect can be controlled by the addition of hydrogen peroxide to the mixed acid solutions of samples and calibration standards alike prior to ultrasonic nebulization. For selenium the effect is somewhat controlled by approximating the matrix of the calibration standard to the sample matrix.[5] Effects observed from the plasma alone can be minimized by careful selection of operating conditions such as incident power, observation height, and nebulizer gas flow.

4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. These effects can be minimized by flushing the system with a rinse blank between samples (Section 7.11.4). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by nebulizing a standard containing elements corresponding to either their LDR or a concentration 10 times those usually encountered. The nebulization time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be re-analyzed after a long rinse period.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have 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. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[6-9] A reference file of material data handling sheets should also be made 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. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma emission spectrometer:

6.1.1 Computer-controlled emission spectrometer with background-correction capability. The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply - High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

6.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.5 Ultrasonic nebulizer - A radio-frequency powered oscillating transducer plate capable of providing a densely populated, extremely fine desolvated aerosol.

6.1.6 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

6.2 Analytical balance, with capability to measure to 0.1 mg, for use in preparing standards, and for determining dissolved solids.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

6.4 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.5 A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

6.6 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1-2500 µL with an assortment of high quality disposable pipet tips.

6.7 Labware - All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include 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 storing clean.[1,2] Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.7.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.7.2 Assorted calibrated pipettes.

6.7.3 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.

6.7.4 (Optional) PTFE and/or quartz Griffin beakers, 250 mL with PTFE covers.

6.7.5 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1 L capacities.

6.7.6 One-piece stem FEP wash bottle with screw closure, 125 mL capacity.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications[10] should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

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

7.2.1 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Hydrochloric acid (1+20) - Add 10 mL concentrated HCl to 200 mL reagent water.

7.3 Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

7.3.1 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2) - Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5) - Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9) - Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 Reagent water. All references to water in this method refer to ASTM Type I grade water.[11]

7.5 Ammonium hydroxide, concentrated (sp. gr. 0.902).

7.6 Tartaric acid, ACS reagent grade.

7.7 Hydrogen peroxide, 30%, not-stabilized certified reagent grade.

7.8 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.9 Standard Stock Solutions - Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99-99.999% pure). All compounds must be dried for one hour at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1 L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg) x gravimetric factor}}{\text{volume (L)}}$$

where:

gravimetric factor = the weight fraction of the analyte in the compound

7.9.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.9.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 1.000 g of antimony powder, weighed accurately to at least four significant figures, in 20.0 mL (1+1) HNO_3 and 10.0 mL concentrated HCl. Add 100 mL reagent water and 1.50 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool solution and add reagent water to volume in a 1 L volumetric flask.

7.9.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.437 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least four significant figures, in 150 mL (1+2) HNO_3 with heating and stirring to degas and dissolve compound. Let solution cool and dilute with reagent water in 1 L volumetric flask.

7.9.5 Beryllium solution, stock, 1 mL = 1000 µg Be: DO NOT DRY. Dissolve 19.66 g $BeSO_4 \bullet 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.6 Boron solution, stock, 1 mL = 1000 µg B: DO NOT DRY. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1 L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric

container. Use of a nonglass volumetric flask is recommended to avoid boron contamination from glassware.

7.9.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.9.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.498 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180°C for one hour before weighing, weighed accurately to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.9 Cerium solution, stock, 1 mL = 1000 µg Ce: Slurry 1.228 g CeO_2 (Ce fraction = 0.8141), weighed accurately to at least four significant figures, in 100 mL concentrated HNO_3 and evaporate to dryness. Slurry the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 dropwise in 1 mL increments allowing periods of stirring between the 1 mL additions. Boil off excess H_2O_2 before diluting to volume in a 1 L volumetric flask with reagent water.

7.9.10 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1 L volumetric flask with reagent water.

7.9.11 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.000 g Co metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.12 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1 L volumetric flask with reagent water.

7.9.13 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.000 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to four significant figures, in 100 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.9.14 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.15 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.324 g Li_2CO_3 (Li fraction = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.16 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.000 g cleanly polished Mg ribbon, accurately weighed to at least four significant figures, in **slowly** added 5.0 mL (1+1) HCl (**CAUTION:** reaction is vigorous). Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.17 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.000 g of manganese metal, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.18 Mercury solution, stock, 1 mL = 1000 µg Hg: DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1 L volumetric flask with reagent water.

7.9.19 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.500 g MoO_3 (Mo fraction = 0.6666), weighed accurately to at least four significant figures, in a mixture of 100 mL reagent water and 10.0 mL concentrated NH_4OH, heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.9.20 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.907 g KCl (K fraction = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in reagent water, add 20 mL (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.22 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: DO NOT DRY. Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1+20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

7.9.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.542 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 1.685 g $SrCO_3$ (Sr fraction = 0.5935), weighed accurately to at least four significant figures, in 200 mL reagent water with dropwise addition of 100 mL (1+1) HCl. Dilute to volume in a 1 L volumetric flask with reagent water.

7.9.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.303 g $TlNO_3$ (Tl fraction = 0.7672), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in 200 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with (1+1) HCl in a 1 L volumetric flask.

7.9.29 Titanium solution, stock, 1 mL = 1000 µg Ti: DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \bullet H_2O$ (Ti fraction = 0.1629), weighed accurately to at least four significant figures, in 100 mL reagent water. Dilute to volume in a 1 L volumetric flask with reagent water.

7.9.30 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.9.31 Yttrium solution, stock 1 mL = 200 µg Y: Dissolve 0.254 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.9.32 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.000 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.10 Mixed Calibration Standard Solutions - Prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions in 500 mL volumetric flasks containing 20 mL (1+1) HNO_3, 10 mL (1+1) HCl, and 2 mL 30% H_2O_2 (not-stabilized) and dilute to volume with reagent water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid-cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution. For the recommended wavelengths listed in Table 1 some typical calibration standard combinations are given in Table 3.

Note: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.1 mg/L.

7.11 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.

7.11.1 The calibration blank is prepared by adding HNO_3, HCl and H_2O_2 to reagent water to the same concentrations as used for the calibration standard solutions. The calibration blank should be stored in a FEP bottle.

7.11.2 The laboratory reagent blank (LRB) must contain all the reagents (HNO_3, HCl, and H_2O_2)in the same volumes as used in the processing of the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.11.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank to a concentration of 0.2 mg/L with all analytes of interest except aluminum, calcium, iron, magnesium, potassium, selenium, silica, silver, and sodium. The elements of calcium, magnesium, and sodium should be added to a concentration of 10.0 mg/L each, while silica (Section 1.6) and potassium should be added to a concentration of 5.0 mg/L, and aluminum, iron, and selenium to a concentration 0.5 mg/L. If silver is included, it should be added to a concentration of 0.05 mg/L. (The analyzed value for Se may indicate a positive bias, Sections 1.10 and 4.3.) The LFB must be carried through the

same entire preparation scheme as the samples including sample digestion, when applicable.

7.11.4 The rinse blank is prepared by acidifying reagent water to the same concentrations of the acids as used for the calibration standard solutions and stored in a convenient manner.

7.12 Instrument Performance Check (IPC) Solution - Two IPC solutions are used to periodically verify instrument performance during analysis. They should be prepared in the same acid/hydrogen peroxide mixture as the calibration standards by combining method analytes at appropriate concentrations. The first IPC solution should contain 10 mg/L each of calcium, magnesium, and sodium and 1.0 mg/L of selenium. All other analytes should be combined in the second IPC solution each to a recommended concentration of 0.5 mg/L, except for potassium which should be 5.0 mg/L and silver, which must be limited to concentration ≤0.1 mg/L. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in FEP bottles. (Following verification and if convenient, the QCS solutions required in Section 7.13 can be substituted for the IPC solutions.) Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.13 Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analyses of QCS solutions are required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid/hydrogen peroxide mixture as the calibration standards. The QCS for calcium, magnesium, sodium, and selenium should be prepared as a separate solution from a single element stock solutions with Ca, Mg, and Na each at a concentration of 10.0 mg/L and Se at a concentration of 1.0 mg/L (Sections 1.10 and 4.3). The other analytes can be combined in a second QCS solution each at concentrations of 0.5 mg/L, except for potassium which should be 5.0 mg/L and silver, which must be limited to a concentration of ≤0.1 mg/L for solution stability. The QCS solutions should be stored in FEP bottles and analyzed as needed to meet data-quality needs. Fresh solutions should be prepared quarterly or more frequently as needed.

7.14 Spectral Interference Check (SIC) Solutions - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors.

7.14.1 SIC solutions containing (a) 30 mg/L Fe; (b) 20 mg/L AL; (c) 10 mg/L Ba; (d) 5 mg/L Be; (e) 5 mg/L Cd; (f) 5 mg/L Ce; (g) 5 mg/L Co; (h) 5 mg/L Cr; (i) 5 mg/L Cu; (j) 5 mg/L Mn; (k) 5 mg/L Mo; (l) 5 mg/L Ni; (m) 5 mg/L Sn; (n) 20 mg/L SiO_2; (o) 5 mg/L Ti; (p) 5 mg/L Tl and (q) 5 mg/L V should be prepared in the same acid/hydrogen peroxide mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the

recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. (Multielement SIC solutions[1] may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution and the concentration of the interferant is not above its upper LDR limit, Section 9.2.2.)

Note: If wavelengths other than those recommended in Table 1 are used, other solutions different from those above (a through q) may be required.

7.14.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.14.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.14.4 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a thru q) should fall within a specific concentration range bracketing the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

Note: The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

7.14.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of the interfering elements at the 1 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

7.14.6 If the instrument does not display negative values, fortify the SIC solution with the elements of interest at 0.1 or 0.2 mg/L and test for analyte

recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

7.15 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., ≥1 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is ≥10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

7.16 Plasma Solution - The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 1 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a 500 mL volumetric flask containing 20 mL (1+1) HNO_3, 10 mL (1+1) HCl, and 2 mL 30% H_2O_2 (not-stabilized) and diluting to volume with reagent water. Store in a FEP bottle.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must**be tested immediately prior to aliquoting for analysis to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate 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 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then

verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.4 A field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR) - The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing succeedingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined LDR limit must be diluted and reanalyzed. The LDRs should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation

and analyses of QCS solutions (Section 7.13). To verify the calibration standards the determined mean concentrations from three analyses of the QCS must be within ±5% of the stated values. If the calibration standard can not be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL) - MDLs must be established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[12] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where:

t = Student's 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

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inapprop-riately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 4.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Section 1.2). MDLs should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Section 7.11.2) with each 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 should be suspected. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB (Section 7.11.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

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

where:

R = percent recovery
LFB = laboratory fortified blank
LRB = laboratory reagent blank
s = concentration equivalent of analyte added to fortify the LRB solution

If the recovery of any 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.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be 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 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be

used to established an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution - For all determinations the laboratory must analyze the IPC solution (Section 7.12) and a calibration blank immediately following daily calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be less than the analyte IDL, but greater than the lower 3-sigma control limit of the calibration blank. Analysis of the IPC solution immediately following calibration must verify that the instrument is within ±10% of calibration with a relative standard deviation <3% from replicate integrations ≥4. Subsequent analyses of the IPC solution also must be within ±10% of calibration. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.3.5 Spectral interference check (SIC) solution - For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions. The preparation and required periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routine are given in Section 7.14. Special cases where on-going verification is required are described in Section 7.15.

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. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required. Also, other tests such as the analyte addition test (Section 9.5.1) and sample dilution test (Section 9.5.2) can indicate if matrix effects are operative.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. The added analyte concentration must be the same as that used in the laboratory fortified

blank (Section 9.3.2). Over time, samples from all routine sample sources should be fortified.

Note: The concentration of calcium, magnesium, sodium and strontium in environmental waters can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the LFB may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis using the criteria given in Section 9.5.2 is recommended. Also, if specified by the data user, laboratory or program, samples can be fortified at different concentrations, but even major constituents should be limited to ≤10 mg/L so as not to alter the sample matrix and affect the analysis.

9.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70-130%. Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery may be 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

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects and analysis by method of standard addition or the use of an internal standard(s) (Section 11.4) should be considered.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.5 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.4.

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 85-115% 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 test should be 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 or the use of an appropriate internal standard element may provide more 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 ±10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions using ultrasonic nebulization usually vary from 1100-1500 watts forward power, 12-16 mm viewing height, 12-19 L/min. argon coolant flow, 0.5-1 L/min. argon aerosol flow, 1.5-2.5 mL/min. sample pumping rate with a one minutes preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). The ultrasonic nebulizer is normally operated at <50 watts incident power with the desolvation temperature set at 140°C and a condenser temperature of 5°C.

10.2 Prior to using this method optimize the plasma operating conditions. The following procedure is recommended for vertically configured plasmas. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

10.2.1 Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Turn on the power to the ultrasonic nebulizer including the heating tube and chiller and allow both instruments to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. Set the peristaltic pump to deliver an uptake rate between 1.8 and 2.0 mL/min. in a steady even flow. While nebulizing the 200 µg/mL solution of yttrium (Section 7.9.31), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5-20 mm above the top of the work coil.[13] Record the nebulizer gas flow rate or pressure setting for future reference.

10.2.2 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 10.2.1 and nebulize the plasma solution (Section 7.16), containing 2.0 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14-18 mm above the top of the work coil. (This region of the plasma is commonly referred to as the analytical zone.)[14] Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity counts for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

10.2.3 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits. Refer to Tables 1 and 4 for comparison of IDLs and MDLs, respectively.

10.2.4 If either the instrument operating conditions, such as incident power and/or nebulizer gas flow rate are changed, or a new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be reoptimized.

10.2.5 Before daily calibration and after the instrument warmup period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be reset to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same from day-to-day (<2% change).

10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Section 11.3) to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.4 After completing the initial demonstration of performance, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction and for correction of interelement spectral interference in particular are given in Section 4.1. To determine the appropriate location for background correction and to establish the interelement interference correction routine, repeated spectral scan about the analyte wavelength and repeated analyses of the single element solutions may be required. Criteria for determining

an interelement spectral interference is an apparent positive or negative concentration on the analyte that is outside the 3-sigma control limits of the calibration blank for the analyte. (The upper-control limit is the analyte IDL.) Once established, the entire routine must be initially and periodically verified annually or whenever there is a change in instrument operating conditions (Section 10.2.5). Only a portion of the correction routine must be verified more frequently or on a daily basis. Test criteria and required solutions are described in Section 7.14. Initial and periodic verification data of the routine should be kept on file. Special cases where on-going verification are required is described in Section 7.15.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground water and surface waters pipet or accurately transfer an aliquot (≥20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add the appropriate volumes of (1+1) nitric acid and (1+1) hydrochloric acid and 30% hydrogen peroxide (not-stabilized) to adjust the reagent concentration of the aliquot to approximate a 2% (v/v) nitric acid, 1% (v/v) hydrochloric acid, and 0.4% (v/v) 30% hydrogen peroxide solution (e.g., add 1.0 mL (1+1) HNO_3, 0.5 mL (1+1) HCl, and 0.1 mL 30% H_2O_2 to a 25 mL aliquot of sample). Cap the tube and mix. The sample is ready for analysis (Section 1.3). Allowance for sample dilution from the addition of acids and hydrogen peroxide should be made in data calculations.

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure in Section 11.2 prior to analysis.

11.2 Aqueous Sample Preparation - Total Recoverable Analytes

11.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation (Section 1.2). For the determination of total recoverable analytes in all other samples follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with <1 NTU turbidity, and aqueous samples containing undissolved solids >1%, Section 1.4), transfer a 100 mL (±1 mL) aliquot from a well mixed, acid preserved sample to a 250 mL Griffin beaker (Sections 1.2, 1.3, 1.6, 1.7, 1.8, and 1.9). (When necessary, smaller sample aliquot volumes may be used.)

11.2.3 Add 2.0 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about one hour for a 50 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the $HCl\text{-}H_2O$ azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask, add 0.2 mL of 30% hydrogen peroxide (Section 7.7), make to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the uptake system to the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Sample Analysis

11.3.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.3.2 Configure the instrument system to the selected power and operating conditions as determined in Sections 10.1 and 10.2.

11.3.3 The instrument and nebulizer system must be allowed to become thermally stable before calibration and analyses. This usually requires at least 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.3.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.10) and the calibration blank (Section 7.11.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, nebulize all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.11.4) for a minimum of 60 seconds (Section 4.4) between each standard. The calibration line should consist of a minimum of a calibration blank and a high standard. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance.[15]

11.3.5 After completion of the initial requirements of this method (Sections 10.3 and 10.4), samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LFBs, LFMs, and check solutions.

11.3.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4.

11.3.7 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed (see Section 11.3.8). Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised and determination by another approved test procedure (Section 1.2) that is either more sensitive and/or interference free is recommended.

11.3.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5 are recommended.

11.3.9 Report data as directed in Section 12.0.

11.4 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique[16] compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc. (mg/L or mg/kg)} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where:

C = Concentration of the standard solution (mg/L)
S_1 = Signal for fortified aliquot
S_2 = Signal for unfortified aliquot
V_1 = Volume of the standard addition (L)
V_2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data should be reported in units of µg/L for all elements except Ca, K, Mg, Na, and SiO_2 which should be reported in mg/L.

12.2 For µg/L data values less than ten, two significant figures should be used for reporting element concentrations. For data values greater than or equal to ten, three significant figures should be used. For the analytes Ca, K, Mg, Na, and SiO_2 with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. When the MDLs for those analytes are ≥0.01 mg/L, round the data values to the 100th place and report analyte concentrations up to three significant figures.

12.3 For dissolved analytes (Section 11.1) and total recoverable analyses of drinking water with turbidity <1NTU (Section 11.2.1), report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the laboratory determined "direct analysis" 1X MDL concentration.

12.4 For total recoverable aqueous analytes (Sections 11.2.2 through 11.2.7) report data as instructed in Section 12.2. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the data accordingly using the appropriate dilution factor. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the laboratory determined analyte 2X MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.5 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 METHOD PERFORMANCE

13.1 Listed in Table 4 are typical single laboratory "direct analysis" 1X MDLs and total recoverable preconcentrated 2X MDLs determined for the recommended wavelengths using simultaneous ICP-AES and the instrument conditions listed in Table 5. The MDLs were determined in reagent blank matrix (best case situation). PTFE beakers were used in the total recoverable determinations to avoid boron and silica contamination from glassware with the final dilution to 50 mL completed in polypropylene centrifuged tubes. Theoretically the preconcentrated 2X MDLs should be lower than the "direct analysis" 1X MDLs, however, for those analytes where the 2X MDLs values are significantly higher (2X MDL greater than two times the 1X MDL) environmental contamination is suspected.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 6 for four different drinking water supplies (two ground waters and two surface waters) and an ambient surface water. The precision and recovery data

were collected by simultaneous ICP-AES utilizing the recommended wavelengths given in Table 1 and the instrument conditions listed in Table 5. The unfiltered drinking waters were prepared using the procedure described in Section 11.1 while the total recoverable procedure (Sections 11.2.2 through 11.2.7) was used to prepare the ambient surface water. For each matrix, five replicate aliquots were prepared, analyzed and the average of the five determinations used to define the sample background concentration of each analyte. In addition, two further pairs of duplicates were fortified at different concentration levels. For each method analyte, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples are listed in Table 6. The variance of the five replicate sample background determinations is included in the calculated standard deviation of the percent recovery when the analyte concentration in the sample was greater than the MDL. Fortified sample data for the matrix analytes Ca, K, Mg, Na, Sr, and SiO_2 are not included. However, the precision and mean sample background concentrations for these six analytes are listed separately in Table 7.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation (e.g., Section 7.9). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Management for Waste Reduction”, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult “The Waste Management Manual for Laboratory Personnel”, available from the American Chemical Society at the address listed in the Section 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1: WAVELENGTHS, ESTIMATED INSTRUMENT DETECTION LIMITS, AND RECOMMENDED CALIBRATION

Analyte	Wavelength[a] (nm)	Detection Limit[b] (µg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	1	2
Antimony	206.833	1	1
Arsenic	193.759	3	2
Barium	493.409	0.2	0.2
Beryllium	313.042	0.05	0.2
Boron	249.678	2	0.5
Cadmium	226.502	0.2	0.5
Calcium	315.887	1	40
Cerium	413.765	20	0.5
Chromium	205.552	0.9	1
Cobalt	228.616	0.4	0.5
Copper	324.754	0.3	0.5
Iron	259.940	0.3	2
Lead	220.353	2	2
Lithium	670.784	0.4	1
Magnesium	279.079	2	10
Manganese	257.610	0.2	0.5
Mercury	194.227	3	0.5
Molybdenum	203.844	1	2
Nickel	231.604	0.8	0.5
Potassium	766.491	40	10
Selenium	196.090	8	2
Silica (SiO_2)	251.611	10 (SiO_2)	2
Silver	328.068	0.3	0.1
Sodium	588.995	3	20
Strontium	421.552	0.1	0.2
Thallium	190.864	5	1
Tin	189.980	4	1
Titanium	334.941	0.1	2
Vanadium	292.402	0.6	0.5
Zinc	213.856	0.4	1

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1).

[b]The listed EMSL-Cincinnati estimated 3-sigma instrumental detection limits are provided only as a guide to instrumental limits.

[c]Suggested concentration for instrument calibration. Other calibration limits in the linear ranges may be used.

TABLE 2. ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 20 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant*
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

*These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

TABLE 3. MIXED STANDARD SOLUTIONS[1]

Solution	Analytes
I	Ag, As, B, Ba, Cd, Cu, Mn, and Sb
II	K, Li, Mo, Sr, and Ti
III	Co, V, and Ce
IV	Al, Cr, Hg, SiO_2, Sn, and Zn
V	Be, Fe, Ni, Pb, and Tl
VI	Se, Ca, Mg, and Na

[1]See Table 1 for recommended calibration concentrations. See Sections 1.10 and 4.3 for discussion on desolvation affects on As, Cr, and Se. See Section 7.10 and 7.11 for preparation of calibration standard and blank solutions.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

Analyte	1X MDL Direct Analysis, µg/L	2X MDL Total Recoverable Digestion, µg/L[2]
Ag	0.6	0.6
Al	4	20
As	3	2
B	2	4
Ba	0.2	0.2
Be	0.05	0.02
Cd	0.4	0.2
Ce	5	5
Co	0.6	0.4
Cr	2	0.4
Cu	2	0.7
Fe	2	10
Hg	3	2
Li	0.7	0.9
Mn	0.09	0.08
Mo	2	1
Ni	0.7	0.8
Pb	4	2
Sb	3	3
Se*	5	3
Sn	5	2
Sr	0.08	0.2
Ti	0.2	0.3
Tl	6	2
V	2	0.5
Zn	0.5	0.7
	1X MDL, mg/L	2X MDL, mg/L[2]
Ca		0.03
K	0.005	0.05
Mg	0.09	0.01
Na	0.005	0.05
SiO_2	0.04	0.03
	0.002	

[1]Method detection limits are sample dependent and may vary as the sample matrix varies.

[2]MDL concentrations are computed for original matrix with allowance for 2x sample preconcentration during preparation. Samples were processed in PTFE and diluted in 50 mL plastic centrifuge tubes.

*Se MDL determined in tap water due to common matrix enhancement (Section 1.10).

TABLE 5. INDUCTIVELY COUPLED PLASMA AND ULTRSONIC NEBULIZER INSTRUMENT OPERATING CONDITIONS

ICP SPECTROMETER	
Incident rf power	1400 watts
Reflected rf power	<5 watts
Viewing height about work coil	15 mm
Injector tube orifice i.d.	1 mm
Argon supply	liquid argon
Argon pressure	40 psi
Coolant argon flow rate	19 L/min.
Auxiliary (plasma) argon flow rate	300 mL/min.
ULTRASONIC NEBULIZER	
Aerosol carrier argon flow rate	570 mL/min.
Sample uptake rate controlled to	1.8 mL/min.
Transducer power 1.4 MHz auto-tuned	35 watts
Desolvation temperature	140°C
Condenser temperature	5°C

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

REGION 2 – TAP WATER

Analyte	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.6	10.0	114	2.0	3.5	100	104	0.3	0.6
Al	10.4	40.0	115	3.8	0.4	400	105	0.8	1.2
As	<3	30.0	118	0.7	1.1	300	112	0.9	1.6
B	5.3	20.0	94	3.8	0.8	200	95	0.6	0.9
Ba	5.8	20.0	100	1.6	2.4	200	101	0.4	0.7
Be	<0.05	4.0	101	0.9	1.8	40	103	0.3	0.6
Cd	<0.4	4.0	110	0.4	0.7	40	105	0.4	0.7
Ce	<5	50.0	107	0.1	0.2	500	103	0.5	0.9
Co	<0.6	20.0	102	1.4	2.6	200	104	0.3	0.7
Cr	<2	20.0	101	1.0	2.0	200	106	0.2	0.3
Cu	152	20.0	*	*	*	200	103	0.7	0.6
Fe	106	20.0	*	*	*	200	105	0.7	0.8
Hg	<3	30.0	106	2.2	4.1	300	107	0.3	0.6
Li	0.72	20.0	100	1.9	2.7	200	102	0.4	0.6
Mn	5.9	10.0	101	1.9	2.3	100	104	0.5	0.9
Mo	<2	20.0	96	3.3	6.8	200	101	0.3	0.5
Ni	<0.7	10.0	111	0.4	0.6	100	105	0.2	0.4
Pb	12.4	15.0	107	8.8	4.9	400	109	0.4	0.6
Sb	<3	30.0	112	0.3	0.6	300	110	0.5	1.0
Se	<5	50.0	94	1.9	4.0	500	107	1.2	2.3
Sn	<5	40.0	106	1.2	2.4	400	107	0.1	0.2
Ti	<0.2	20.0	102	1.3	2.5	200	104	0.4	0.7
Tl	<6	40.0	119	1.6	2.7	400	109	0.1	0.2
V	<2	20.0	103	2.0	3.9	200	102	1.2	2.3
Zn	5.6	20.0	108	1.2	0.5	200	110	0.6	1.0

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <25% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

REGION 5 – TAP WATER

Analyte	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.6	10.0	114	0.7	1.1	100	104	0.3	0.6
Al	98.3	40.0	108	5.1	1.0	400	105	0.8	1.2
As	<3	30.0	110	1.5	2.7	300	112	0.9	1.6
B	26.8	20.0	104	2.6	0.2	200	95	0.6	0.9
Ba	30.2	20.0	105	1.4	1.0	200	101	0.4	0.7
Be	<0.05	4.0	110	0.1	0.3	40	103	0.3	0.6
Cd	<0.4	4.0	106	2.3	4.3	40	105	0.4	0.7
Ce	<5	50.0	108	4.7	8.7	500	103	0.5	0.9
Co	<0.6	20.0	108	0.5	1.0	200	104	0.3	0.7
Cr	<2	20.0	105	0.2	0.5	200	106	0.2	0.3
Cu	3.9	20.0	92	0.8	0.9	200	103	0.7	0.6
Fe	7.3	20.0	98	0.7	0.0	200	105	0.7	0.8
Hg	<3	30.0	103	4.3	8.4	300	107	0.3	0.6
Li	4.4	20.0	108	1.5	0.3	200	102	0.4	0.6
Mn	0.26	10.0	108	0.3	0.1	100	104	0.5	0.9
Mo	<2	20.0	107	0.8	1.4	200	101	0.3	0.5
Ni	1.0	10.0	108	4.6	5.6	100	105	0.2	0.4
Pb	<4	15.0	98	5.7	11.6	400	109	0.4	0.6
Sb	<3	30.0	117	1.7	2.8	300	110	0.5	1.0
Se	<5	50.0	101	6.4	12.7	500	107	1.2	2.3
Sn	<5	40.0	119	1.1	1.9	400	107	0.1	0.2
Ti	0.23	20.0	109	0.1	0.0	200	104	0.4	0.7
Tl	<6	40.0	108	2.9	5.3	400	109	0.1	0.2
V	<2	20.0	105	3.0	5.7	200	102	1.2	2.3
Zn	4.5	20.0	111	0.8	0.2	200	110	0.6	1.0

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

REGION 6 – TAP WATER

Analyte	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.6	10.0	102	1.0	2.0	100	103	0.3	0.6
Al	<4	40.0	111	3.8	6.8	400	106	0.3	0.5
As	5.2	30.0	110	8.6	10.7	300	107	1.4	2.3
B	98.7	20.0	*	*	*	200	97	0.5	0.3
Ba	18.0	20.0	102	1.0	0.7	200	99	0.1	0.1
Be	0.07	4.0	102	0.7	1.3	40	99	0.3	0.6
Cd	<0.4	4.0	95	2.9	6.1	40	89	0.6	1.3
Ce	<5	50.0	93	3.0	6.5	500	98	0.4	0.9
Co	<0.6	20.0	95	1.6	3.3	200	92	0.4	0.9
Cr	<2	20.0	97	1.0	2.1	200	94	0.4	0.8
Cu	2.1	20.0	98	1.8	2.3	200	101	0.4	0.7
Fe	<2	20.0	97	2.0	3.3	200	96	0.6	1.3
Hg	<3	30.0	105	1.2	2.2	300	103	0.8	1.6
Li	34.4	20.0	116	2.4	0.7	200	108	0.3	0.3
Mn	1.5	10.0	97	1.1	1.9	100	95	0.3	0.7
Mo	52.7	20.0	102	7.6	2.1	200	95	0.9	0.9
Ni	<0.7	10.0	101	2.0	4.1	100	92	0.8	1.8
Pb	<4	15.0	89	8.7	19.5	400	97	0.1	0.2
Sb	<3	30.0	115	0.3	0.6	300	105	0.7	1.4
Se	<5	50.0	119	0.3	0.5	500	117	1.1	1.9
Sn	6.1	40.0	110	7.9	6.6	400	100	2.3	4.4
Ti	2.5	20.0	104	0.9	1.4	200	102	0.2	0.3
Tl	<6	40.0	106	3.8	7.1	400	101	0.5	0.9
V	<2	20.0	100	3.3	6.5	200	98	0.5	1.1
Zn	3.6	20.0	103	1.2	1.7	200	100	0.2	0.3

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <25% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

REGION 10 – TAP WATER

Analyte	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.6	10.0	115	0.5	0.9	100	109	0.6	1.1
Al	4.8	40.0	101	3.7	4.4	400	108	0.5	0.7
As	<3	30.0	122	5.5	9.0	300	115	0.4	0.6
B	24.4	20.0	90	1.9	1.4	200	86	1.0	2.1
Ba	10.7	20.0	104	0.8	1.0	200	105	0.4	0.8
Be	<0.05	4.0	108	0.7	1.2	40	108	0.2	0.4
Cd	<0.4	4.0	109	1.9	3.4	40	105	0.4	0.7
Ce	<5	50.0	115	1.1	1.9	500	107	0.1	0.2
Co	<0.6	20.0	106	0.6	1.1	200	105	0.3	0.5
Cr	<2	20.0	106	0.2	0.5	200	107	0.3	0.5
Cu	<2	20.0	115	0.5	0.9	200	106	0.4	0.7
Fe	11.0	20.0	130	1.6	1.6	200	106	0.1	0.0
Hg	<3	30.0	111	3.3	6.0	300	107	1.1	2.0
Li	1.2	20.0	107	1.7	1.8	200	107	0.9	1.7
Mn	9.8	10.0	52	0.8	1.6	100	106	0.1	0.2
Mo	<2	20.0	109	1.2	2.3	200	104	0.2	0.4
Ni	<0.7	10.0	113	2.0	3.5	100	105	0.4	0.8
Pb	<4	15.0	95	1.7	3.5	400	109	0.9	1.7
Sb	<3	30.0	118	3.3	5.6	300	114	0.1	0.1
Se	<5	50.0	100	2.7	5.4	500	112	1.2	2.1
Sn	7.3	40.0	114	3.5	2.7	400	110	1.4	2.4
Ti	0.39	20.0	108	0.7	1.2	200	108	0.1	0.1
Tl	8.2	40.0	105	6.4	7.2	400	110	1.4	2.4
V	<2	20.0	106	2.5	4.7	200	104	0.4	0.9
Zn	<0.5	20.0	110	0.0	0.0	200	110	0.3	0.5

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

REGION 5 – RIVER WATER

Analyte	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.6	5.0	98	2.0	4.1	50	102	0.8	1.6
Al	780	20.0	*	*	*	200	*	*	*
As	<3	15.0	108	3.7	6.8	150	105	1.0	2.0
B	38.8	10.0	*	*	*	100	104	3.6	1.5
Ba	51.7	10.0	*	*	*	100	100	1.3	0.9
Be	0.12	2.0	100	0.8	0.5	20	107	2.0	3.7
Cd	<0.4	2.0	98	1.3	2.5	20	94	1.5	3.2
Ce	<5	25.0	118	3.0	5.1	250	105	0.9	1.8
Co	1.8	10.0	96	1.8	1.8	100	100	0.8	1.6
Cr	<2	10.0	101	0.5	1.0	100	103	0.8	1.6
Cu	3.8	10.0	98	2.6	1.5	100	101	0.8	1.4
Fe	1240	10.0	*	*	*	100	*	*	*
Hg	<3	15.0	102	0.7	1.3	150	107	1.5	2.8
Li	7.0	10.0	93	14.9	4.9	100	106	1.7	1.5
Mn	191	5.0	*	*	*	50	93	10.4	3.7
Mo	<2	10.0	109	3.0	5.5	100	102	1.2	2.3
Ni	5.5	5.0	79	13.5	7.4	50	105	1.7	2.2
Pb	8.0	7.5	91	45.8	9.4	200	104	2.1	2.4
Sb	3.5	15.0	84	5.3	0.6	150	107	0.9	1.4
Se	<5	25.0	97	1.4	2.9	250	107	2.7	5.1
Sn	<5	20.0	120	3.5	5.9	200	94	2.5	5.4
Ti	3.9	10.0	79	13.4	2.6	100	96	1.4	1.0
Tl	<6	20.0	87	0.5	1.2	200	105	0.7	1.2
V	<2	10.0	102	0.0	0.0	100	97	0.8	1.5
Zn	16.8	10.0	62	3.5	2.2	100	102	0.4	0.6

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <25% of sample background concentration.

TABLE 7. AQUEOUS MATRIX ELEMENT CONCENTRATIONS[1]

DRINKING WATER

REGION 2

Matrix Elements	Sample Conc. mg/L	% RSD
Ca	4.08	0.8
K	0.786	5.4
Mg	0.626	1.4
Na	7.83	0.6
SiO_2	3.09	0.5
Sr	0.029	0.6

REGION 5

Matrix Elements	Sample Conc. mg/L	% RSD
Ca	27.4	0.9
K	1.62	1.8
Mg	7.18	0.9
Na	9.97	0.4
SiO_2	6.22	1.0
Sr	0.146	0.6

REGION 6

Matrix Elements	Sample Conc. mg/L	% RSD
Ca	253	n.a.
K	4.60	0.9
Mg	36.3	1.0
Na	39.9	0.9
SiO_2	32.6	0.9
Sr	4.06	1.4

REGION 10

Matrix Elements	Sample Conc. mg/L	% RSD
Ca	19.9	0.6
K	1.84	1.4
Mg	1.43	0.4
Na	19.4	0.4
SiO_2	37.3	0.4
Sr	0.063	0.4

RIVER WATER

REGION 5

Matrix Elements	Sample Conc. mg/L	% RSD
Ca	31.5	1.1
K	2.27	1.2
Mg	9.38	1.6
Na	12.1	0.9
SiO_2	1.54	18.4
Sr	0.220	1.5

1Mean sample concentration and relative standard deviation were determined from five replicate aliquots of each sample.