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METHOD 200.5 DETERMINATION OF TRACE ELEMENTS IN DRINKING WATER BY AXIALLY VIEWED INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY

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METHOD 200.5

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1.0 SCOPE AND APPLICATION

1.1 Axially viewed inductively coupled plasma-atomic emission spectrometry (AVICP-AES) is used to determine trace elements, as well as water matrix elements, in drinking water and drinking water supplies. This method is applicable to the following analytes:

Analyte	Abbreviation	Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony*	(Sb)	7440-36-0
Arsenic*	(As)	7440-38-2
Barium*	(Ba)	7440-39-3
Beryllium*	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium*	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium*	(Cr)	7440-47-3
Copper*	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead*	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Nickel	(Ni)	7440-02-0
Selenium*	(Se)	7782-49-2
Silica	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Tin	(Sn)	7440-31-5
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

* Designated primary drinking water contaminant.

1.2 For reference where this method is approved for use in compliance monitoring program (e.g., Safe Drinking Water Act [SDWA]) consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 141 § 141.23) and the latest Federal Register announcements.

1.3 This method provides a specific procedure utilizing axially-viewed plasma atomic emission signals generated only by pneumatic nebulization for the analysis of all analytes. Some AVICP-AES instruments are so configured that the emitted signal can also be viewed alternately or simultaneously in a radial manner. Radially-viewed signals for the determination of drinking water matrix elements (Ca, Mg and Na) and silica are acceptable. The Ca and Mg data can be used in the calculation of hardness.

1.4 When viewing sodium emission from the axial configuration, the ratio of signal intensity to analyte concentration is not a linear response. Therefore, sodium should be calibrated using multiple standard solutions of increasing concentration to properly define the response ratio at various levels of concentration (see Sect. 7.8.2).

1.5 For drinking water compliance monitoring, a "total" element determination (dissolved + suspended fractions) is required. When the measured turbidity on an acid preserved sample is < 1 NTU, direct analysis, without sample digestion, is permitted with the use of some approved spectrochemical methods. However, when using this method, all samples are digested and preconcentrated prior to analysis using the total recoverable digestion(T) step described in Section 11.1. Preconcentrating the sample prior to analysis increases analytical sensitivity for meeting the method detection limit (MDL) requirements given in Section 1.12. Thus, when using this method, the need to measure sample turbidity prior to metal analysis is eliminated.

1.6 Operative matrix effects can occur from elevated dissolved solids. Using this technique, matrix effects have been observed when the concentration of calcium and/or the combined concentrations of the matrix elements (Ca, Mg, and Na) and silica exceed 125 mg/L and 250 mg/L, respectively. To verify that a matrix effect is not operative, an LFM (see Sect. 9.4) must be analyzed when a primary contaminant (see Sect. 1.1) concentration exceeds 80% of the established maximum contaminant level (MCL) or action level. If the absence of a matrix interference can not be verified, the sample must be analyzed by method of standard additions (MSA; see Sect. 11.3) or another approved method (see Sect. 1.7 for special requirements for lead).

1.7 When determining lead by this method, the instrument must be capable of analyzing silica as well. Levels of silica that exceed 30 mg/L, when preconcentrated 2X, cause a suppressive effect on lead determinations. For samples containing silica above 30 mg/L and lead concentrations ≥ 10 µg/L, lead must be determined by method of standard additions (MSA; see Sect. 11.3) or by another approved compliance monitoring method. If the laboratory can not determine silica when using this method, this method can not be used for compliance monitoring of lead.

1.8 When determining boron and silica, only plastic or PTFE labware should be used from time of sample collection to completion of analysis. In this method, glassware is specifically avoided and only the use of metal-free plastic labware is recommended. Borosilicate glass should be avoided to prevent contamination of these analytes.

1.9 The total recoverable sample digestion procedure given in Section 11.1 is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. Also, samples prepared using the procedure may be analyzed for thallium using EPA Method 200.9[2].

1.10 Compliance monitoring data for metal contaminants are normally reported in units of mg/L; however, the data for the total recoverable analytes in this method are noted in units of µg/L. This difference is done to reduce or eliminate the listing of non-significant zeros. When data are reported for compliance monitoring, the data should be reported in the same units used to express the established MCL and to the appropriate numerical level of significance.

1.11 MDLs for trace elements and linear ranges for the drinking water matrix elements will vary with the wavelength selected and the spectrometer configuration and operating conditions. Table 4 provides determined MDLs for the listed wavelengths utilizing the instrument operating conditions given in Table 3. These values are provided for comparative purposes for user self-evaluation when completing the mandatory initial demonstration of performance. Meeting the exact same limits listed in Table 4 is not necessarily a requirement for the use of this method. Users of this 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 (see Sect. 1.12).

1.12 Users of this method for the purpose of SDWA compliance monitoring must achieve and document MDLs for As, Be, Cd, Sb, Se, and Pb that are ≤ a value of 1/5 their respective MCL or action level.

2.0 SUMMARY OF METHOD

2.1 A 50 mL aliquot of a well-mixed, non-filtered, acid preserved aqueous sample is accurately transferred to a clean 50-mL plastic disposable digestion tube containing a mixture of nitric and hydrochloric acids. The aliquot is heated to 95 °C (± 2 °C), evaporated to approximately 25 mL, covered with a ribbed plastic watch glass and subjected to total recoverable solubilization with gentle refluxing for 30 minutes. The sample is allowed to cool and diluted to 25 mL with reagent water to effect a 2X preconcentration. The sample is capped, mixed and now ready for analysis (The time required to complete the sample preparation step is approximately 2.5 hours).

2.2 The analytical determinative step described in this method involves multi-elemental determinations by AVICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Standard and sample solutions are nebulized by pneumatic nebulization and the resulting aerosol is transported by argon carrier-gas 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. Photo currents 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 should be measured adjacent to the analyte wavelength during analysis. Possible interferences that can occur must be considered and addressed appropriately as discussed in Section 4.

3.0 DEFINITIONS

3.1 CALIBRATION BLANK - A volume of reagent water acidified with the same acid matrix reagents as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the AVICP instrument (Sects. 7.9.1).

3.2 CALIBRATION STANDARD (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions contain the acid matrix reagents and are used to calibrate the instrument response with respect to analyte concentration (Sect. 7.8.1).

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.

3.4 FIELD REAGENT BLANK (FRB) - An aliquot of reagent water 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, acid preservation, and all analytical procedures. The FRB is used to determine if method analytes or interferences are present in the field environment (Sect. 8.2).

3.5 INSTRUMENT DETECTION LIMIT (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.

3.6 INSTRUMENT PERFORMANCE CHECK (IPC) SOLUTION - A solution of method analytes in the acid matrix reagents used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sects. 7.10.3 & 9.3.4).

3.7 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.

3.8 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 (Sects. 7.9.3 & 9.3.2).

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An aliquot of a drinking water or drinking water supply 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 (Sects. 1.6, 1.7 & 9.4).

3.10 LABORATORY REAGENT BLANK (LRB) - An aliquot of reagent water that is treated exactly as a sample including exposure to all labware, equipment, and reagents, 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 (Sects. 7.9.2 & 9.3.1).

3.11 LINEAR DYNAMIC RANGE (LDR) - The concentration range over which the instrument response to an analyte is linear (Sect. 9.2.2).

3.12 MAXIMUM CONTAMINANT LEVEL (MCL) - The maximum permissible level of a contaminant in water which is delivered to any user of a public water system.

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 (Sects. 1.11, 1.12, 9.2.5 and Table 4).

3.14 PLASMA SOLUTION - A solution used to determine the nebulizer argon flow rate or gas pressure that will produce the optimum net-signal-to-noise (S-B/B) needed for the most requiring analyte included in the analytical scheme (Sects. 7.11 & 10.2).

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 (Sects. 7.10.4 & 9.2.4).

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 (Sects. 4.1 & 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 (Sects. 1.6 & 11.3).

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 (Sect. 7.7).

3.19 TOTAL RECOVERABLE ANALYTE - For this method, the concentration of analyte determined by the analysis of an unfiltered acid preserved drinking water

sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 1.5 & 11.1). Data are reported as a "total" element determination - the combined concentrations of the dissolved and suspended fractions of the sample.

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. Except for interference from background emission and possible stray light, which can usually be compensated for by subtracting the background emission adjacent to the analyte wavelength peak, spectral interferences associated with the analysis of drinking water are minimal. However, the absence of interelement spectral interference should be verified. **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.** When an instrument equipped with a conventional diffraction grating that provides 0.016 nm first order resolution is used with the wavelengths in the noted spectral order and background correction locations given in Table 1, no detectable concomitant interelement spectral interferences occurs between the trace element analytes listed in this method at concentrations ≤ 20 mg/L. Since concentrations of trace elements in drinking water and drinking water supplies are far below the level of 20 mg/L, an interelement correction routine for trace analytes would be unnecessary for an instrument so configured. On the other hand, the concentration of the water matrix elements can be in excess of 100 mg/L. Fortunately, the matrix elements are not spectrally rich and have few prominent lines to cause interelement spectral interference. Using this method and analyzing single element solutions of 300 mg/L Ca, 200 mg/L Mg, 200 mg/L Na, and 100 mg/L Si, no spectral enhancement of other method analytes were observed, thus not requiring interelement corrections. However, there are three concerns worth noting: (1) yttrium, a commonly used internal standard, proved an interference in the spectral region recommended for background correction on the listed Ag wavelength (328.068 nm), (2) a similar situation occurs from molybdenum on the spectral region recommended for background correction on the V wavelength (292.402 nm), and (3) the listed Fe wavelength (271.441 nm) experiences an apparent concentration increase of approximately 8% from cobalt (271.442 nm) when the two analytes are present in equal concentration. Therefore, a quality control check sample containing both iron and cobalt or both vanadium and molybdenum should **not** be used to confirm the calibration standards when the Fe 271.441 nm and V 292.402 nm wavelengths are utilized.

Note: If wavelengths, noted spectral order, and background correction locations different from those listed in Table 1 are used with this method, and/or the optical resolution of the instrument utilized does not provide 0.016 nm first order resolution or better, the absence of interelement spectral interference must be confirmed by completing spectral scans over the wavelength area and background correction locations to be utilized. The spectral scans should be completed using single

element solutions of both trace and water matrix elements of concentrations noted above that will verify nonexistent apparent analyte concentrations. If an interelement spectral interference is detected, a correction routine that is operative during analysis must be used with daily verification using SIC solutions, to demonstrate that the routine meets the above criteria.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Physical interferences of the types described above have not been evident in the analysis of most drinking waters. However, the use of a peristaltic pump to regulate solution uptake rate and the use of mass flow controllers that provide better control of the argon flow rates, especially for the nebulizer, improve instrument stability and precision.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. In general, chemical interferences are highly dependent on matrix type and the specific element. In radial ICP-AES, one way of controlling these effects is careful selection of the observation height in the plasma. However, for increased sensitivity, the total emission of the plasma is observed in AVICP-AES, thus eliminating this useful option. To counteract ionization and matrix interferences in AVICP-AES, some laboratories routinely use an ionization buffer along with an internal standard added to both standards and samples alike in the sample train using a peristaltic pump and mixing tee. Use of an ionization buffer is permitted with this method provided the addition does not cause an interelement spectral interference with a method analyte. However, in drinking water analyses the use of an internal standard with pneumatic nebulization is discouraged because it is not necessary and adds additional variance to the determination. The above stated chemical interferences have not been observed using this method for drinking water analyses when the operating conditions and preparations procedures are followed as written.

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. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Sect. 7.9.4). The rinse times necessary for a particular element should be estimated prior to analysis. For the water matrix elements this may be achieved by aspirating a single element standard solution corresponding to their LDRs (Sect. 3.11), while for the trace contaminants single element solutions containing 10 mg/L are sufficient. The aspiration 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 signal to within a factor of 10 times the calibration blank should be noted. Until the required rinse time is established, this method requires a rinse period using the rinse blank of at least 30 sec between samples and standards. If a memory interference is suspected, the sample should 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 [3-5]. 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 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 Acidification of samples should be done in a fume hood.

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

5.4 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 Axially viewed 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 (optional) A mass flow controller to regulate or monitor the argon flow rate of the aerosol transport gas is highly recommended. Use of a mass flow controller will provide more exacting control of reproducible plasma conditions.

6.2 An analytical balance with capability to measure to 0.1 mg, for use in preparing

standards and for weighing samples as may be required.

6.3 A temperature adjustable hot plate for preparing stock standard solutions.

6.4 A temperature adjustable block digester capable of maintaining a temperature of 95 °C for use with 50-mL plastic disposable digestion tube.

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

6.6 Air displacement pipetters capable of delivering volumes ranging from 50 µL to 10.0 mL with an assortment of high quality disposable pipet tips.

6.7 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling should be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All reusable labware (polyethylene, polymethylpentene, PTFE, FEP, etc.) and plastic disposable digestion tubes, caps, and watch glasses should be sufficiently clean for the task objectives. Several cleaning procedures can provide clean labware. The procedure recommended for reusable labware includes washing with a detergent solution, rinsing with tap water, and soaking for 4 h or more in a mixture of 5% (v/v) HNO_3 and 5% (v/v) HCl, rinsing with reagent water and storing clean. (If digested LRBs indicate random contamination, the plastic disposable digestion tubes, caps, and watch glasses should be cleaned with 2% (v/v) HNO_3 and rinsed with reagent water prior to use.) Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.7.1 Plastic volumetric labware - PMP (polymethylpentene) or equivalent metal free plastic volumetric flasks (50-mL to 500-mL capacities), graduated cylinders (50-mL), and disposable metal-free plastic digestion tubes with caps and watch glass covers.

6.7.2 (optional) PTFE Griffin beakers, 250-mL with PTFE covers for preparing stock standards and reagents.

6.7.3 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) and LDPE (low density polyethylene) with screw closure, 60-mL to 500-mL capacities.

6.7.4 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 must be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method should be of ultra high-purity grade or equivalent. Trace metal grade acid may also be used if it can be verified by analysis to be free of contamination. 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 250 mL concentrated HCl to 200 mL reagent water and dilute to 500 mL.

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 250 mL concentrated HNO_3 to 200 mL reagent water and dilute to 500 mL.

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 reagent water in this method refer to ASTM Type I grade water[6].

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

7.6 Tartaric acid, ACS reagent grade.

7.7 Standard Stock Solutions - Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99 to 99.999% pure). All compounds must be dried for 1 h at 105 °C, unless otherwise specified. It is recommended that stock solutions be stored in acid-cleaned, never-used LDPE bottles for storage. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified (see Sect. 9.2.4).

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

Typical stock solution preparation procedures follow for 500-mL 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.

7.7.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 0.500 g of aluminum metal, weighed accurately to at least three 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 500-mL PMP flask, add an additional 5.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.7.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 0.500 g of antimony powder, weighed accurately to at least three significant figures, in 10.0 mL (1+1) HNO_3 and 5.0 mL concentrated HCl in a beaker. Add 50 mL reagent water and 0.75 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool solution and add reagent water to volume in a 500-mL PMP volumetric flask.

7.7.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 0.660 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least three significant figures, in 50 mL of reagent water containing 5.0 mL concentrated NH_4OH in a beaker. Warm the solution gently to effect dissolution. Acidify the solution with 10.0 mL concentrated HNO_3 and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 0.719 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least three significant figures, in a beaker containing 75 mL (1+2) HNO_3 with heating and stirring to degas and dissolve compound. Let solution cool and dilute with reagent water in 500-mL PMP volumetric flask.

7.7.5 Beryllium solution, stock, 1 mL = 1000 µg Be: <u>DO NOT DRY</u>. Dissolve 9.823 g $BeSO_4 \cdot 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 5.0 mL concentrated HNO_3, and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.6 Boron solution, stock, 1 mL = 1000 µg B: <u>DO NOT DRY</u>. Dissolve 2.859 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 0.500 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least three significant figures, in 25 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool and dilute with reagent water in a 500-mL PMP volumetric flask.

7.7.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 1.249 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180 °C for 1 h 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 5.0 mL concentrated HNO_3 and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 0.962 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least three significant figures, in 60 mL (1+5) HNO_3. When dissolution is complete, dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.10 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 0.500 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least three significant figures, in 25 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.11 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 0.500 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to three significant figures, in 50 mL (1+1) HCl in a beaker with heating to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.12 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 0.799 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least three significant figures, in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HNO_3 and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.13 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 0.500 g of cleanly polished Mg ribbon, accurately weighed to at least three significant figures, in **slowly** added 2.5 mL (1+1) HCl (**CAUTION:** reaction is vigorous). Add 10.0 mL (1+1) HNO_3 and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.14 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 0.500 g of manganese metal, weighed accurately to at least three significant figures, in 25 mL (1+1) HNO_3 and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.15 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 0.500 g of nickel metal, weighed accurately to at least three significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.16 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 0.703 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least three significant figures, in 100 mL reagent water and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.17 Silica solution, stock, 1 mL = 1000 µg SiO_2: <u>DO NOT DRY</u>. Dissolve

1.482 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 100 mL (1+20) HCl in a beaker with heating at 85 °C to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.18 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 0.500 g Ag metal, weighed accurately to at least three significant figures, in 50 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.19 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 1.271 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 5.0 mL concentrated HNO_3 and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.20 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 0.500 g Sn shot, weighed accurately to at least three significant figures, in an acid mixture of 5.0 mL concentrated HCl and 1.0 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool, add 100 mL concentrated HCl, and dilute to volume in a 500-mL PMP volumetric flask with reagent water.

7.7.21 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 0.500 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least three significant figures, in 25 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.7.22 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 0.500 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least three significant figures, in 25 mL (1+1) HNO_3 in a beaker with heating to effect dissolution. Let solution cool and dilute in a 500-mL PMP volumetric flask with reagent water.

7.8 Calibration Standard Solutions.

7.8.1 Mixed Calibration Standard Solutions - For total recoverable analyses prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in 500-mL PMP volumetric flasks containing 20 mL (1+1) HNO_3 and 10 mL (1+1) HCl 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. Recommended wavelengths and calibration concentrations are listed in Table 1. Typical calibration standard combinations are given in Table 2.

7.8.2 Sodium Multi-point Calibration Standards - To determine elevated concentrations of Na in drinking water and drinking water supplies using the recommended wavelength, Na is determined using a multi-point analytical calibration usable to 160 mg/L. Prepare in a mixture of 2% HNO_3 (v/v) and 1% HCl (v/v) a calibration blank and six calibration standards at concentrations of 5, 10, 20, 40, 80, and 160 mg/L, respectively. To create the multi-point calibration, curve-fit the response of the blank and standards and store as a computer file. This calibration is standardized before each period of analysis using the calibration blank and the mixed calibration standard solution containing 20 mg/L Na (Sect. 7.8.1). A new multi-point calibration should be prepared whenever there is a change in analytical performance caused by either a change in instrument hardware or operating conditions. (Of the 990 ground water samples analyzed in the National Inorganic Radionuclide Survey, Na was reported below 90 mg/L in 84% of the samples.)

7.9 Blanks - Four types of blanks are required for this method. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the laboratory procedure, the laboratory fortified blank is used to assess routine laboratory performance and a rinse blank is used to flush the uptake system to reduce memory interferences.

7.9.1 The calibration blank is prepared by diluting 20 mL (1+1) HNO_3 and 10 mL (1+1) HCl in a 500-mL PMP volumetric flask to volume with reagent water. Store the prepared blank solution to an acid-cleaned, never-used 500-mL FEP bottle. This bottle should be dedicated for reuse and storage of this solution.

7.9.2 The laboratory reagent blank (LRB) is prepared by carrying 50 mL of reagent water through the entire analytical procedure. The LRB must contain all the reagents in the same volumes as used in processing the samples.

7.9.3 The laboratory fortified blank (LFB) is prepared in the same manner as the LRB, and fortified by adding 1.0 mL of the fortifying solution (7.10.1) to 50 mL of LRB. The LFB must be carried through the entire analytical procedure. The analyte concentrations fortified in the LFB are as follows: 4 µg/L Be; 5 µg/L Cd; 6 µg/L Sb; 10 µg/L As; 15 µg/L Pb; 50 µg/L Ag, Mn, Se, Sn and V; 100 µg/L B, Cr and Ni; 200 µg/L Al; 300 µg/L Fe; 1000 µg/L Ba, Cu and Zn.

7.9.4 The rinse blank is prepared by acidifying reagent water in an acid-cleaned LDPE bottle to concentrations of 2% (v/v) HNO_3 + 2% (v/v) HCl.

7.10 Quality Control Solutions.

7.10.1 Fortifying solution - The fortifying solution is used to prepare the laboratory fortified blank (LFB) and laboratory fortified matrix (LFM) solutions. The fortifying solution should be prepared in a 100-mL PMP volumetric flask, containing a mixture of 4 mL (1+1) HNO_3 and 2 mL (1+1) HCl, by combining the following listed aliquot volumes of each stock standard and the low-level stock fortifying solution (7.10.2) and diluting to volume with reagent water: 5 mL Ba, Cu & Zn and the low-level stock fortifying solution; 1.5 mL Fe; 1.0 mL Al; 0.5 mL B, Cr & Ni; and 0.25 mL Ag, Mn, Se, Sn & V. Store in a new, acid-cleaned LDPE bottle. The analyte concentrations in the fortifying solution are as follows: 50 mg/L Ba, Cu & Zn; 15 mg/L Fe; 10 mg/L Al ; 5.0 mg/L B, Cr & Ni; 2.5 mg/L Ag, Mn, Se, Sn & V; 0.75 mg/L Pb; 0.50 mg/L As; 0.30 mg/L Sb; 0.25 mg/L Cd; and 0.20 mg/L Be.

7.10.2 Low-level stock fortifying solution - The low-level stock fortifying solution is used to prepare the fortifying solution described in Section 7.10.1. The low-level stock fortifying solution is prepared in a 50-mL PMP volumetric flask, containing a mixture of 2 mL (1+1) HNO_3 and 1 mL (1+1) HCl, by combining the following listed aliquot volumes of each stock standard and diluting to volume with reagent water: 750 µL Pb (15 mg/L); 500 µL As (10 mg/L); 300 µL Sb (6 mg/L); 250 µL Cd (5 mg/L); and 200 µL Be (4 mg/L). (The concentration in parenthesis is that of the analyte in the low-level stock.) Store in a new, acid-cleaned LDPE bottle dedicated for reuse and repeated storage of this solution.

7.10.3 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared by combining method analytes at appropriate concentrations in the same acid mixture (2% HNO_3 + 1% HCl) as the calibration standards. Silver should be limited to < 100 µg/L; while Al and Fe should be made to a concentration of 2 mg/L; Ca, Mg, and SiO_2 made to 5 mg/L; and Na to a concentration of 10 mg/L. For all other analytes, a concentration of 200 µg/L is recommended. The IPC should be prepared in a PMP (metal-free plastic) volumetric flask to avoid B and SiO_2 contamination. Store the IPC solution in a new, acid-cleaned FEP bottle dedicated for reuse and repeated storage of this solution.

NOTE: If the instrument readout system incorporates the use of a dilution factor (0.5) to report original sample concentration prior to processing, and the IPC solution is analyzed in the same manner as the samples, the reported IPC concentrations will be half the concentrations listed above.

7.10.4 Quality Control Sample (QCS) - Analysis of a QCS is required for initial

and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The QCS must be obtained from outside source different from the standard stock solutions and prepared in a PMP volumetric flask using the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be sufficient to meet the data quality objectives given in Section 9.2.4. The concentrations may range from 200 µg/L for sensitive analytes such as Be and Cd to > 2.0 mg/L for Al, Ca, Fe, Mg, Na, and SiO_2. However, the concentration of Ag should be limited to 0.1 mg/L or less to ensure complete solubility and stability. The QCS solution should be stored in a new, acid-cleaned LDPE bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.11 Plasma Solution - The plasma solution is used for determining the nebulizer argon flow rate or gas pressure that will produce the optimum net-signal-to-background noise (S-B/B) ratio needed for the most requiring analytes included in the method without degrading the performance of the other analytes. The two analytes that present the greatest challenge are Sb and As because of the low MCLs and limited analytical sensitivity. The combined 1 mg/L solution is prepared by adding 100 µL of the Sb stock standard (7.7.2) and a 100 µL of the As stock standard (7.7.3) to a mixture of 4 mL (1+1) HNO_3 and 2 mL (1+1) HCL in a 100-mL PMP volumetric and diluting to volume with reagent water. Store the solution in a new, acid-cleaned LPDE bottle for repeated use as necessary.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 For the determination of trace and water matrix elements in drinking water and drinking water supplies, samples are **not** filtered, but acidified with (1+1) nitric acid to a pH < 2 (3 mL of [1+1] acid per liter of sample should be sufficient). 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 sixteen hours, and then verified to be pH < 2 just prior to withdrawing an aliquot for sample processing. 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 sixteen hours until verified to be pH < 2. If properly preserved, the sample can be held up to 6 months.

8.2 If required by the data user, a field reagent blank (Sect. 3.4) should be prepared and analyzed in the same manner as a collected sample. Use the same type of 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 consists 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 used for the analysis of the drinking water matrix analytes: Ca, Mg and silica. It must be determined from a linear calibration prepared using the established instrument operating conditions. 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 upper LDR limit must be diluted and reanalyzed. The LDRs should be verified as required for certification or whenever, in the judgment 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 Non-linear dynamic range - The upper limit of the non-linear calibration used for the determination of Na is the highest standard used to describe the calibration curve. The non-linear calibration must be established using the same instrument operating conditions used for analysis. Determined sample concentrations that are > 10% above the upper limit for Na must be diluted and reanalyzed. The upper limit should be verified as required for certification or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.4 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 analysis of a QCS (Sect. 7.10.4.) To verify the calibration standards, the determined mean concentrations from 3 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.

9.2.5 Method detection limit (MDL) - MDLs must be established for all wavelengths utilized for trace element determinations in total recoverable digestates. MDLs are determined using reagent water (blank) fortified to a concentration ranging from the instrument detection limit (IDL) to approximately two times the IDL[7] (see Table 4 for typical levels). To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire total recoverable analytical procedure. 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 = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates).

S = standard deviation of the replicate analyses.

Note: If the relative standard deviation (RSD) from the analyses of the seven aliquots is < 10% and neither random nor reagent contamination is operative, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. In this case the MDL determination should be repeated using a lower concentration. Although data can be reported down to the MDL, the associated variability (RSD $\geq$ 30%) at the MDL concentration is very high. A more realistic reporting limit is the estimated upper limit of the 95% confidence interval about the MDL. This limit is based on the 97.5 percentile of chi square over associated 6 degrees of freedom and is computed by multiplying the MDL by a factor of 2.2[8]. Typical single laboratory MDLs and reporting limits values using this method are given in Table 4.

The MDLs must be sufficient to meet data quality needs and detect analytes at the required levels according to compliance monitoring regulation (Sect. 1.2). Specifically, the determined MDLs for the analytes: As, Be, Cd, Sb, Se and Pb must be $\leq$ 1/5 their respective MCL or action level before this method can be used for compliance monitoring. MDLs should be determined as required for laboratory certification, when a new operator begins work or whenever, in the judgment 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 (Sect. 7.9.2) with each batch of 20 or fewer samples. 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 for the trace analytes are above the calculated reporting limit (2.2 times the analyte MDL), 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 (Sect. 7.9.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

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

where: R = percent recovery.
LFB = laboratory fortified blank determined concentration.
s = concentration equivalent of analyte added to fortify the LRB solution.

If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged to be 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 appropriate required control limits of 90-110% (see Sect.9.3.2). When sufficient internal performance data become available (usually a minimum of twenty to thirty 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 appropriate required control limits. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent twenty to thirty data points. Also, the standard deviation (S) data should be used to establish 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 - The laboratory must initially and periodically verify that the instrument calibration is within required control limits. For all determinations the laboratory must analyze the IPC solution (Sect. 7.10.3) and a portion of the calibration blank immediately

following calibration, after every tenth sample and at the end of the sample run. Analysis of the calibration blank should always be less than the calculated reporting limit (2.2 times the analyte MDL) for the trace elements. Analysis of the IPC solution immediately following calibration must verify that the instrument is within ± 5% of calibration. Subsequent analyses of the IPC solution must be within ± 10% of calibration. If the calibration can not be verified within the specified limits, reanalyze both the IPC solution and the calibration blank. If the second analysis confirms 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 analysis must be reanalyzed. The analyses data of the IPC solution should be kept on file with the sample analyses data.

9.3.5 Spectral interference check (SIC) solution - For this method using the listed wavelengths, the specified background locations, and an instrument with first order resolution of 0.016 nm or better, verification of interelement spectral interference is not required. However, if method flexibility, allowing the use of different wavelengths, spectral orders, and background correction locations requires an interelement correction routine for spectral interference, it must be verified daily with the use of SIC solutions (see Sect. 4.1 for listed criteria and description of required testing).

9.4 Assessing Total Recoverable Analyte Recovery and Data Quality

9.4.1 Sample non-homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. In the analysis of finished drinking water, these aspects are rarely an issue. However, source water for a drinking water supply can have varying turbidity. 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 (Sect. 9.4.2) is required.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. The LFM aliquot must be a duplicate of the aliquot used for sample analysis and fortified prior to sample preparation. The added analyte concentration must be the same as that used in the laboratory fortified blank (Sect. 7.9.3). Over time, samples from all routine sample sources should be fortified.

9.4.3 Calculate the percent recovery for each analyte, corrected for analyte background concentrations greater than the calculated reporting limit measured in the unfortified sample, and compare these values to the designated LFM recovery range of 85-115%. 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 (>2.2 X MDL).
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 (Sect. 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. If the analyte in question is a primary contaminant (Sect. 1.1), under certain circumstances additional analyses may be required (see Sects. 1.6 and 1.7). For a primary contaminant not requiring additional analysis, for a secondary contaminant, or non-regulated analyte, the data user should be informed that the result for that analyte is suspect due to matrix effects.

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.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Specific wavelengths and calibration concentrations are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference (see Sect. 4.1). However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions are not required. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality (see Sect. 1.12) to the drinking water program and data user. The analyst should follow the instructions provided by the instrument manufacturer; however, instrument operating conditions used to collect the single laboratory performance data included in this method are listed in Table 3 and are provided as a recommendation. Once operating conditions are established, it is intended that daily calibration will be accomplished using a calibration blank and a single analyte concentration.

10.2 Prior to using this method, optimize the plasma operating conditions. The purpose of plasma optimization is to provide a maximum net signal-to-background ratio (S-B/B) for the determination of As and Sb, the most requiring elements in the analytical array. The use of a mass flow controller to regulate or monitor the nebulizer gas flow rate greatly facilitates the procedure. The following procedure is recommended:

10.2.1 Ignite the plasma, and using the conditions listed in Table 3 as a guide, select appropriate incident rf power and plasma gas flows. Allow the instrument to become thermally stable before beginning. This usually requires approximately 30 minutes of operation. Set the aerosol argon flow rate through the nebulizer at approximately 650 mL per minute or at the instrument manufacturer's recommended pressure setting if the flow rate can not be measured. Following the instrument manufacture's instructions, optically profile the instrument to provide maximum signal for all wavelengths. While aspirating reagent water and using the As channel signal, adjust the horizontal and vertical position of the torch to provide minimum signal intensity. This should align the optics with the center of the sample channel of the plasma and minimize background noise.

10.2.2 After profiling the torch, aspirate the plasma solution (Sect. 7.11) and while following the instrument manufacturer's instructions, adjust the aerosol carrier gas flow rate through the nebulizer and collect signal intensity readings (S) at equal incremental flow settings on either side of the initial flow rate setting. Suggested flow rates (mL/min) settings are: 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690 and 700. (NOTE: If nebulizer flow rates can not be measured, incremental pressure settings that control flow should be used.) After acid rinsing to eliminate any possible memory effect, repeat the same operation using an acid blank solution and collect the blank signal intensity readings (B) at the same respective flow settings. Calculate the S-B/B ratio for As and Sb at each flow setting. Plot, on the same graph, the calculated ratios and the blank intensity readings versus the argon flow rates. The intensity counts for the blank signal should decrease at a uniform rate as the argon flow rate increases, while the calculated S-B/B ratios for Sb should increase. At the lower flow rate settings, the As ratios should remain nearly constant; however, at some point the As ratio will start to decrease with an increase in flow rate. The flow rate where the As ratio begins to decrease (2% or more) is the limiting flow and the flow rate just prior to the limiting flow should be selected for routine operation. Record the nebulizer gas flow rate or pressure setting for future reference. If the nebulizer is replaced with a new or different nebulizer, repeat this optimization procedure.

10.2.3 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume calibration blank for a period of at least 3 minutes. Divide the spent volume by the aspiration time (in minutes) and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

10.2.4 The final instrument operating condition, selected as being optimum, should provide acceptable instrument detection limits and method detection limits for all trace analytes. Refer to Table 4 for comparison of IDLs and MDLs, respectively.

10.2.5 Before daily calibration and after the instrument warmup period, the

nebulizer gas flow should 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 reliable MDLs, the nebulizer gas flow rate should be the same from day-to-day (<2% change).

10.3 Before using the procedure (Sect. 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedures are described in Sections 9.2.2, 9.2.3, 9.2.4, and 9.2.5. These data must be generated using the same instrument operating conditions and respective calibration routines used for sample analysis (see Sect. 11.2). 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, if needed, must establish and initially verify the interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction are given in Sections 4.1 and 9.3.5. Once established, the entire routine must be verified on a daily basis by analyzing SIC solution(s) resulting in response data that falls within the 3-sigma control limits of the calibration blank of the analyte (Sect. 4.1).

11.0 PROCEDURE

11.1 Sample Preparation (Total Recoverable Digestion) - For the determination of trace analytes and water matrix elements in drinking water and source water supply, using a 50-mL PMP graduated cylinder, transfer a 50 mL (± 0.5 mL) aliquot from a well-mixed, acid preserved sample to a 50-mL clean digestion tube containing a mixture of 1.0 mL (1+1) HNO_3 (Sect. 7.3.1) and 0.5 mL (1+1) HCl (Sect. 7.2.1). (The acids should be added to the digestion tube using an air displacement pipetter - see Sect. 6.6.) Place the digestion tube in the block digester (Sect. 6.4). (The block digester should be located in a **clean** fume hood.) Power the digestion block to preselected settings to evaporate the sample at a temperature of 95 °C (± 2 °C). Preconcentrate the sample until the volume has been reduced to approximately 25 mL. Cover the digestion tube with a plastic watch glass and reflux the sample for 30 minutes. (The time required to complete this step should approximate 2.5 h.) Once the refluxing step is complete, remove the digestion tube from the block digester and allow the sample to cool. When cool, using the volume gradation marks on the digestion tube, adjust the sample volume to 25 mL with reagent water (Sect. 7.4). Cap the digestion tube and mix. The sample is now ready for analysis. Because the effects of various matrices on the stability of analytes in low concentration can not be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.2 Sample Analysis

11.2.1 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.

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

11.2.3 The instrument should be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 minutes of operation. After instrument warmup, complete any required optical profiling or alignment routines particular to the instrument.

11.2.4 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Sect. 7.8.1) and the calibration blank (Sect. 7.9.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 20 sec after reaching the plasma before beginning integration of the background corrected signal to accumulate data. To reduce measurement variance, use the average value of replicate integration periods of the signal to be correlated to analyte concentration. (Suggested data collection period for all determinations: 5 replicate 24 sec periods [8 sec on the wavelength peak and 8 sec on each BKGD location] = 120 sec.) Flush the system with the rinse blank (Sect. 7.9.4) for a minimum of 30 seconds (Sect. 4.4) between each standard.

11.2.5 After completion of the initial requirements of this method (Sects. 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 and quality control check solutions.

11.2.6 During sample analysis the laboratory must comply with the required quality control described in Sections 9.3 and 9.4.

11.2.7 Determined water matrix element concentrations that are 90% or more of the upper limit of the analyte LDR, or in the case of Na above the multi-point calibration range, must be diluted with reagent water that has been acidified in the same manner as the calibration blank and reanalyzed.

11.2.8 To ensure an accurate determination for compliance monitoring, a primary contaminant must be reanalyzed by either method of standard additions (see Sect.11.3), or by another approved method, when the concentration of that primary contaminant determined by the normal analytical routine (Sect. 11.2) is $\geq$ 80% of the established MCL, or action level, and the required LFM analysis does not verify the absence of a matrix interference (see Sects. 1.6 & 9.4).

11.2.9 Report data as directed in Section 12.

11.3 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[9] 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:

$$\text{Sample Conc } \mu g/L = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where: C = Concentration of the standard solution (µg/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

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data for the water matrix elements (Ca, Mg and Na) and silica should be reported in units of mg/L. For compliance monitoring, total recoverable trace elements should be reported in the same units used to express the MCL or action level. If there is no established MCL, the trace element should be reported in µg/L.

12.2 For water matrix analytes, multiply the solution analyte concentrations by the dilution factor, 0.5, and report the data with allowance for sample dilution when analyte concentrations exceed 90% or more of the LDR upper limit, and in the case of Na when the analytical range is exceeded. Round the data to the thousandth place and report up to three significant figures. Do not report analyte concentrations below the IDL.

12.3 For total recoverable trace element analytes, multiply solution analyte concentrations by the dilution factor 0.5, round off the data values (µg/L) to the nearest tenths place and report analyte concentrations up to three significant figures. For drinking water compliance monitoring, do not report data below the analyte reporting limit calculated from the laboratory determined MDL data (see Sect. 9.2.5). Typical MDLs and calculated reporting limits are given in Table 4.

12.4 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 total recoverable MDLs for the sample procedure given in Sections 11.1, followed by analysis using pneumatic nebulization. They were determined for the recommended wavelengths using simultaneous AVICP-AES and the operating conditions given in Table 3. The MDLs were determined in reagent blank matrix (best case situation) fortified with the respective analyte concentration also listed in Table 4.

13.2 Data obtained from single laboratory method testing are summarized in Tables 5 and 6. Table 5 lists precision (RSD) and average recovery data for SRM 1643c that was analyzed along with the drinking water samples listed in Table 6. The drinking water samples were prepared using the procedure given in Section 11.1. Table 6 lists data for 4 different tap water matrices (two well water supplies, one surface water supply, and a home cistern supply). Five unfortified aliquots were prepared to determine sample background concentrations and four aliquots for each LFM. For primary and secondary contaminants, the LFMs were fortified to a concentration equivalent to the respective analyte MCL. Data for the analysis of the water matrix elements and silica are listed at the bottom of sample data sheet.

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., Sect. 7.7). 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, or on-line at http://membership.acs.org/c/ccs/pub_9.htm.

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

1. U.S. Environmental Protection Agency. Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements - Method 200.2, Revision 2.8, May 1994 (EPA-600/R-94/111).

2. U.S. Environmental Protection Agency. Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption - Method 200.9, Revision 2.2, May 1994 (EPA-600/R-94/111).

3. Carcinogens - Working With Carcinogens, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977. Available from the National Technical Information Service (NTIS) as PB-277256.

4. OSHA Safety and Health Standards, General Industry, (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. Safety in Academic Chemistry Laboratories, American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

6. American Society for Testing and Materials. Standard Specification for Reagent Water, D1193-77. Annual Book of ASTM Standards, Vol. 11.01. Philadelphia, PA, 1991.

7. Code of Federal Regulations 40, Ch. 1, Pt. 136 Appendix B.

8. Glaser, J.A.,D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde, "Trace Analyses for Wastewaters," Environ. Sci. Technol., **15** (1981) 1426-1435.

9. Winefordner, J.D., Trace Analysis: Spectroscopic Methods for Elements, Chemical Analysis, Vol. 46, pp. 41-42.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. WAVELENGTHS, BACKGROUND CORRECTION LOCATIONS, AND RECOMMENDED CALIBRATION

Analyte	Wavelength[a] (nm)	Location For BKGD. Correction (nm)	Calibrate[b] to (mg/L)
Aluminum	308.215	+0.033	5
Antimony	206.833x2	-0.009	0.5
Arsenic	189.042x2	-0.009	0.5
Barium	493.409	+0.033	1
Beryllium	313.042	+0.033	0.1
Boron	249.678x2	+0.016	1
Cadmium	226.502x2	+0.016	0.1
Calcium	315.887	+0.033	20
Chromium	267.716	+0.033	0.5
Copper	324.754	+0.033	2
Iron	271.441	+0.033	5
Lead	220.353x2	+0.016	0.5
Magnesium	279.079	+0.033	20
Manganese	257.610	+0.033	0.5
Nickel	231.604x2	+0.016	0.5
Selenium	196.090x2	-0.009	0.5
Silica (SiO_2)	251.611	+0.033	21.4
Silver	328.068	+0.033	0.1
Sodium	330.232	+0.033	20
Tin	189.980	-0.018	0.2
Vanadium	292.402	+0.033	0.5
Zinc	206.200	+0.033	0.5

[a] The wavelengths listed in the noted spectral order 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 Sect. 4.1).

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

TABLE 2. MIXED STANDARD SOLUTIONS

Solution[a]	Analytes
I	As, Be, Cd, Pb, Sb, Se, V, and Zn
II	Ba, Cr, Fe, Mn, Ni, Sn, and SiO_2
III	Al, Cu, Ca, Mg, and Na
IV	Ag and B

[a] See Section 7.8.1

TABLE 3. AXIALLY VIEWED INDUCTIVELY COUPLED PLASMA INSTRUMENT OPERATING CONDITIONS

rf power	950 watts
Argon supply	liquid argon
Argon pressure	60 psi
Coolant argon flow rate	20 L/min
Aerosol carrier argon	
pressure	27 psi
flow rate	635 mL/min
Auxiliary (plasma) argon flow rate	0.5 L/min
Sample uptake rate controlled to	1.6 mL/min

TABLE 4. DETECTION AND REPORTING LIMITS

ANALYTE	INSTRUMENT[a] DETECT. LIMIT mg/L	µg/L	MDL SPIKE µg/L	METHOD DETECTION LIMIT (MDL), µg/L	CALCULATED[b] REPORTING LIMIT, µg/L
Ag	-	0.2	0.5	0.2	0.5
Al	-	3	4.0	2.2	4.9
As	-	2	2.5	1.4	3.1
B	-	0.5	0.8	0.3	0.7
Ba	-	0.03	0.08	0.05	0.2
Be	-	0.03	0.04	0.02	0.1
Ca	0.02	-	-	-	-
Cd	-	0.2	0.4	0.1	0.3
Cr	-	0.2	0.4	0.2	0.5
Cu	-	0.2	0.4	0.3	0.7
Fe	-	5	10	3.3	7.3
Mg	0.02	-	-	-	-
Mn	-	0.07	0.08	0.06	0.2
Na	0.4	-	-	-	-
Ni	-	0.6	1.3	0.6	1.4
Pb	-	1	3.0	1.1	2.5
Sb	-	1	2.0	0.9	2.0
Se	-	2	3.0	1.3	2.9
SiO_2	0.01	-	-	-	-
Sn	-	1	1.0	0.5	1.1
V	-	0.2	0.6	0.2	0.5
Zn	-	0.4	0.6	0.4	0.9

[a] Instrument detection limits are used as reporting limits for matrix elements.

[b] The listed calculated reporting limits have been rounded up to the tenths place to fully meet the 2.2 multiple criteria and to eliminate the listing of insignificant numbers. Because of rounding up to the tenths place, the reporting limits listed for Ba and Be are multiples of 4 and 5 times their respective MDLs.

TABLE 5. SRM(1643c) PRECISION AND ACCURACY DATA

ANALYTE	NIST - 1643c CERTIFIED VALUE µg/L	DETERMINED CONC. µg/L	STD. DEV.	AVERAGE RECOVERY %	RSD %
Ag	2.21 ± 0.30	2.1	0.82	95%	3.9%
Al	114.6 ± 5.1	125	5.1	109%	4.1%
As	82.1 ± 1.2	83.7	1.9	102%	2.2%
B	119.0 ± 1.4	114	0.5	96%	0.4%
Ba	49.6 ± 3.1	49.2	0.52	99%	1.0%
Be	23.2 ± 2.2	22.5	0.33	97%	1.5%
Cd	12.2 ± 1.0	11.9	0.13	98%	1.1%
Cr	19.0 ± 0.6	18.0	0.21	103%	1.2%
Cu	22.3 ± 2.8	22.9	0.74	99%	3.2%
Fe	106.9 ± 3.0	106	2.8	99%	2.7%
Mn	35.1 ± 2.2	34.5	0.4	98%	1.2%
Ni	60.6 ± 7.3	57.4	0.58	95%	1.0%
Pb	35.3 ± 0.9	34.4	1.2	97%	3.5%
Se	12.7 ± 0.7	11.9	0.7	94%	5.9%
V	31.4 ± 2.8	28.3	0.15	93%	0.5%
Zn	73.9 ± 0.9	74.4	0.52	101%	0.7%

ANALYTE	NIST - 1643c CERTIFIED VALUE mg/L	DETERMINED CONC. mg/L	STD. DEV.	AVERAGE RECOVERY %	RSD %
Ca	36.8 ± 1.4	37.0	0.32	101%	0.9%
Mg	9.45 ± 0.27	9.61	0.16	102%	1.6%
Na	12.19 ± 0.36	12.6	0.09	103%	0.7%

TABLE 6. TRACE ELEMENT PRECISION AND RECOVERY DATA

TAP WATER - REGION 5 SURFACE WATER SUPPLY

ANALYTE	SAMPLE CONC. µg/L	STD. DEV.	Spike µg/L	AVERAGE RECOVERY (%)	RSD (%)
Ag	<0.5	-	100	100	1.2
Al	18	1.3	200	105	1.5
As	<3.1	-	10.0	105	4.2
B	34.8	0.9	100	101	1.5
Ba	37.7	0.4	2000	100	1.3
Be	<0.1	-	4.0	100	1.4
Cd	<0.3	-	5.0	98	1.8
Cr	<0.5	-	100	99	1.3
Cu	3.3	0.09	1000	101	1.3
Fe	<7.3	-	300	99	1.5
Mn	0.4	0.01	50	98	1.1
Ni	1.5	0.1	100	99	1.0
Pb	<2.5	-	15.0	100	2.2
Sb	<2.0	-	6.0	100	5.3
Se	<2.9	-	50	104	2.0
Sn	<1.1	-	50	102	2.0
V	<0.5	-	50	100	1.4
Zn	5.6	0.1	2000	99	1.0

< Sample concentration below the calculated reporting limit.

Analysis of Water Matrix Elements

Analyte	Sample Conc. mg/L	RSD (%)
Ca	34.6	1.4
Mg	9.64	1.6
Na	26.4	2.9
SiO_2	5.23	1.6

TABLE 6. TRACE ELEMENT PRECISION AND RECOVERY DATA (Cont'd.)

TAP WATER - REGION 5 WELL WATER SUPPLY

ANALYTE	SAMPLE CONC. µg/L	STD. DEV.	Spike µg/L	AVERAGE RECOVERY (%)	RSD (%)
Ag	<0.5	-	100	97	1.2
Al	<4.9	-	200	103	1.1
As	17.7	0.3	10.0	101	1.2
B	96.0	0.7	100	102	0.9
Ba	107	0.7	2000	97	1.0
Be	<0.1	-	4.0	97	1.4
Cd	<0.3	-	5.0	96	1.9
Cr	<0.5	-	100	93	1.3
Cu	<0.7	-	1000	98	1.1
Fe	552	2.7	300	103	1.1
Mn	15.0	0.1	50	95	1.1
Ni	<1.4	-	100	94	1.3
Pb	<2.5	-	15.0	97	4.7
Sb	<2.0	-	6.0	97	7.4
Se	<2.9	-	50	101	1.2
Sn	<1.1	-	50	102	1.2
V	<0.5	-	50	95	1.3
Zn	6.2	0.36	2000	95	1.5

< Sample concentration below the calculated reporting limit.

Analysis of Water Matrix Elements

Analyte	Sample Conc. mg/L	RSD (%)
Ca	69.9	0.6
Mg	28.0	0.7
Na	57.9	1.9
SiO_2	12.3	0.8

TABLE 6. TRACE ELEMENT PRECISION AND RECOVERY DATA (Cont'd.)

TAP WATER - REGION 6 WELL WATER SUPPLY

ANALYTE	SAMPLE CONC. µg/L	STD. DEV.	Spike µg/L	AVERAGE RECOVERY (%)	RSD (%)
Ag	<0.5	-	100	100	1.2
Al	<4.9	-	200	102	1.6
As	<3.1	-	10.0	101	2.3
B	56.4	1.2	100	104	1.4
Ba	203	3.6	2000	100	1.4
Be	<0.1	-	4.0	102	1.4
Cd	<0.3	-	5.0	96	1.9
Cr	1.3	0.07	100	96	1.1
Cu	155	2.7	1000	100	1.3
Fe	8.6	1.9	300	96	1.7
Mn	0.6	0.02	50	97	1.3
Ni	3.3	0.2	100	98	1.4
Pb	<2.5	-	15.0	105	2.5
Sb	<2.0	-	6.0	98	3.6
Se	4.1	0.5	50	100	1.1
Sn	4.4	0.1	50	102	1.0
V	11.5	0.2	50	98	1.4
Zn	26.4	0.5	2000	98	1.4

< Sample concentration below the calculated reporting limit.

Analysis of Water Matrix Elements

Analyte	Sample Conc. mg/L	RSD (%)
Ca	44.6	1.6
Mg	9.26	1.6
Na	41.0	1.7
SiO_2	26.2	1.6

TABLE 6. TRACE ELEMENT PRECISION AND RECOVERY DATA (Cont'd.)

TAP WATER - CISTERN WATER SUPPLY

ANALYTE	SAMPLE CONC. µg/L	STD. DEV.	Spike µg/L	AVERAGE RECOVERY (%)	RSD (%)
Ag	<0.5	-	100	98	1.2
Al	31.3	0.9	200	104	1.7
As	<3.1	-	10.0	102	7.8
B	6.6	0.2	100	100	1.2
Ba	3.3	0.05	2000	98	1.4
Be	<0.1	-	4.0	96	1.2
Cd	<0.3	-	5.0	94	1.1
Cr	<0.5	-	100	95	1.1
Cu	262	1.5	1000	99	1.7
Fe	13	1.9	300	95	1.3
Mn	0.6	0.01	50	94	1.2
Ni	<1.4	-	100	95	1.7
Pb	<2.5	-	15.0	101	1.6
Sb	<2.0	-	6.0	103	3.2
Se	<2.9	-	50	95	1.2
Sn	<1.1	-	50	95	1.6
V	<0.5	-	50	97	1.3
Zn	14.2	3.4	2000	95	1.2

< Sample concentration below the calculated reporting limit.

Analysis of Water Matrix Elements

Analyte	Sample Conc. mg/L	RSD (%)
Ca	10.1	0.7
Mg	0.68	1.0
Na	2.3	1.1
SiO_2	2.07	0.6