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METHODS FOR THE DETERMINATION OF METALS IN ENVIRONMENTAL SAMPLES

SUPPLEMENT I

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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DISCLAIMER

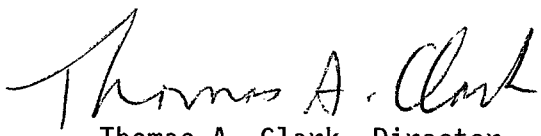
This manual has been reviewed by the Environmental Monitoring Systems Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-Cincinnati) conducts research to:

- Develop and evaluate analytical methods to identify and measure the concentration of chemical pollutants in drinking waters, surface waters, groundwaters, wastewaters, sediments, sludges, and solid wastes.
- Investigate methods for the identification and measurement of viruses, bacteria and other microbiological organisms in aqueous samples and to determine the responses of aquatic organisms to water quality.
- Develop and operate a quality assurance program to support the achievement of data quality objectives in measurements of pollutants in drinking water, surface water, groundwater, wastewater, sediment and solid waste.

This supplement to the EMSL-Cincinnati publication, "Methods for the Determination of Metals in Environmental Samples" was prepared to revise and place in the Environmental Monitoring Management Council (EMMC) format certain spectrochemical methods used for metals analyses in regulatory compliance monitoring programs. Also, included in this supplement is a new method, Method 200.15 Determination of Metals and Trace Elements in Water by Ultrasonic Nebulization Inductively Coupled Plasma-Atomic Emission Spectrometry. This method is intended for analysis of ambient waters with possible limited use in regulatory compliance monitoring. We are pleased to provide this updated supplement to the manual and believe that it will be of considerable value to many public and private laboratories that wish to determine metals in environmental media for regulatory or other reasons.



Thomas A. Clark, Director
Environmental Monitoring Systems
Laboratory - Cincinnati

ABSTRACT

This manual includes seven analytical methods four of which are considered multi-analyte methods, two are single analyte methods, and the total recoverable sample preparation procedure is given as a separate method write up. These methods utilize inductively coupled plasma (ICP)/atomic emission spectrometry (AES), ICP/mass spectrometry (MS), graphite furnace atomic absorption (GFAA), cold vapor atomic absorption (CVAA), and ion chromatography (IC). Application of these methods is directed primarily toward aqueous samples such as wastewater, drinking and ambient waters. However, procedures for the analysis of solid samples such sludges and soils also are included in the multi-analyte methods 200.7, 200.8, and 200.9.

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ACKNOWLEDGEMENT

The methods included in this manual have been for the most part prepared and assembled by former and present staff members of the Inorganic Chemistry Branch of the Chemistry Research Division, Environmental Monitoring Systems Laboratory - Cincinnati. However, others have contributed as prime authors or have provided review comments as a function of work group participation. To recognize those efforts and give a historical perspective to the method, listed on the title page of each method are the significant versions of the method and the persons or groups responsible. Finally, all method authors and contributors wish to thank William L. Budde, Director of the Chemistry Research Division, and Thomas A. Clark, Director of the Environmental Monitoring Systems Laboratory - Cincinnati, for their cooperation and support during this project.

INTRODUCTION

Six of the seven methods appearing in this supplement were included in the first publication of the manual "Determination of Metals in Environmental Samples", EPA 600 4-91/010, June, 1991. The one new method appearing in this supplement is Method 200.15, Determination of Metals and Trace Elements in Water by Ultrasonic Nebulization Inductively Coupled Plasma-Atomic Emission Spectrometry. Method 200.15 was developed to extend the analytical range of the ICP-AES technique to lower concentrations. Its usefulness for the analysis of drinking water is evident by the performance data included in the method.

Unlike the 1991 manual (EPA 600 4-91/010) which contains 13 methods for a variety of sample matrices, this supplement is focused more on the analysis of water and wastes. Its purpose is for use in compliance monitoring of National Pollution Discharge Elimination System (NPDES) effluents as required under the Clean Water Act and compliance monitoring of drinking water as required under the Safe Drinking Water Act. These methods are also useful for the analysis of ambient waters with the exclusion of marine water.

The methods included in this supplement have been prepared in the format adopted by the Environmental Monitoring Management Council (EMMC). In this format method sections are ordered in a specific manner and purpose with the addition of two new sections on pollution prevention and waste management.

All methods have the same approach to analytical quality control in that initial demonstration of performance is required prior to method use, and assessing ongoing laboratory performance is mandatory. However, the required frequency of demonstration has been lessened and the acceptance control limits have been widened. Also, the required limits used in assessing recovery data from fortified matrices have been widened. Where available multi-laboratory data and regression equations have been included in the methods.

The multi-analyte methods (200.7, 200.8, 200.9, and 200.15) all utilize the same total recoverable sample digestion procedure that is described in Method 200.2 as a stand-alone procedure. This procedure also is applicable to flame atomic absorption determinations. Using a common sample preparation for all spectrochemical techniques is convenient and can reduce cost of analyses.

Changes to previous versions of specific methods are as follows:

- Cerium has been added to Method 200.7 for correction of potential spectral interferences
- Titanium has been added as an analyte to Method 200.7
- Mercury has been added to Method 200.8 for the analysis of drinking water with turbidity of < 1 NTU
- Zinc has been deleted from Method 200.9 because its determination by the graphite furnace technique is impractical
- Digestion of Method 245.1 mercury calibration standards is no longer required

METHOD 200.2

SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS

Revision 2.8
EMMC Version

T.D. Martin, E.R. Martin, and S.E. Long (Technology Applications, Inc.) - Method 200.2, Revision 1.1 (1989)

T.D. Martin, S.E. Long (Technology Applications Inc.), and J.T. Creed - Method 200.2, Revision 2.3 (1991)

T.D. Martin, J.T. Creed, and C.A. Brockhoff - Method 200.2, Revision 2.8 (1994)

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METHOD 200.2

SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS

1.0 SCOPE AND APPLICATION

1.1 This method provides sample preparation procedures for the determination of total recoverable analytes in groundwaters, surface waters, drinking waters, wastewaters, and, with the exception of silica, in solid type samples such as sediments, sludges and soils.[1] Aqueous samples containing suspended or particulate material ≥ 1% (W/V) should be extracted as a solid type sample. This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Boron	(B)	7440-42-8
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
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
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica[a]	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6

(continues on next page)

[a] This method is not suitable for the determination of silica in solids.

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Tin	(Sn)	7440-31-5
Uranium	(U)	7440-61-1
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 Samples prepared by this method can be analyzed by the following methods given in this supplement: Method 200.7, Determination of Metals and Trace Elements by Inductively Coupled Plasma-Atomic Emission Spectrometry; Method 200.8, Determination of Trace Elements By Inductively Coupled Plasma-Mass Spectrometry; and Method 200.9, Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry. Also, this method can be used prior to analysis by direct aspiration flame atomic absorption for the above list of analytes with the exception of the following: As, B, Hg, P, Se, SiO_2, Th, and U.

1.4 The preparation procedures described in this method are **not** recommended prior to analysis by the conventional graphite furnace technique, commonly refered to as "off-the-wall", non-platform or non-delayed atomization. It is believed that the resulting chloride concentration in the prepared solutions can cause either analyte volatilization loss prior to atomization or an unremediable chemical vapor state interference for some analytes when analyzed using the conventional graphite furnace technique.

1.5 This method is suitable for preparation of aqueous samples containing silver concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots must be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots < 1 g when determined sample concentrations exceed 1%.

1.6 When using this method for determination of boron and silica in aqueous samples, only plastic or quartz labware should be used from

the time of sample collection to the completion of the analysis. For accurate determinations of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 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.

1.8 This method is not suitable for the determination of volatile low boiling point organo-mercury compounds.

2.0 SUMMARY OF METHOD

2.1 Solid and aqueous samples are prepared in a similar manner for analysis. Nitric and hydochloric acids are dispensed into a beaker containing an accurately weighed or measured, well mixed, homogeneous aqueous or solid sample. Aqueous samples are first reduced in volume by gentle heating. Then, metals and toxic elements are extracted from either solid samples or the undissolved portion of aqueous samples by covering the beaker with a watch glass and refluxing the sample in the dilute acid mixture for 30 min. After extraction, the solubilzed analytes are diluted to specified volumes with ASTM type I water, mixed and either centrifuged or allowed to settle overnight before analysis. Diluted samples are to be analyzed by the appropriate mass and/or atomic spectrometry methods as soon as possible after preparation.

3.0 DEFINITIONS

3.1 **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 (Sect 8.3).

3.2 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.3 **Total Recoverable Analyte** - The concentration of analyte determined to be in either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid.

3.4 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 In sample preparation, contamination is of prime concern. The work area, including bench top and fume hood, should be periodically cleaned in order to eliminate environmental contamination.

4.2 Chemical interferences are matrix dependent and cannot be documented previous to analysis.

4.3 Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical determinations of boron and silica, only quartz and/or PTFE plastic labware should be used. When quartz beakers are not available for extraction of solid samples, to reduce boron contamination, immediately transfer an aliquot of the diluted extract to a plastic centrifuge tube for storage until time of analysis. A series of laboratory reagent blanks can be used to monitor and indicate the contamination effect.

5.0 SAFETY

5.1 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.

5.2 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 Material safety data sheets for all chemical reagents should be available to and understood by all personnel using this method. Specifically, concentrated hydrochloric acid and concentrated nitric acid are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a 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 when working with these reagents.[2,3,4]

6.0 EQUIPMENT AND SUPPLIES

6.1 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, and for determining dissolved solids in extracts.

6.2 Single pan balance, with capability of weighing to 0.01 g, for use in rapid weighing solids and liquids or samples in excess of 10 g.

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

6.4 (optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted digestion tubes.

6.5 (optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

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

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

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 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 must 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, (2) depleting element concentrations through adsorption processes. 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 soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 20% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with ASTM Type I grade water and storing clean.

NOTE: Chromic acid must not be used for cleaning glassware.

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

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250-mL with 50-mm watch glasses.

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

6.10.5 (optional) PTFE and/or quartz beakers, 250-mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

6.10.7 Wash bottle - One piece stem, Teflon FEP bottle with Tefzel ETFE screw closure, 125-mL capacity.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities which might affect analytical data. High-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.2 Nitric acid (1+1) - Add 500 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.3 Hydrochloric acid, concentrated (sp.gr. 1.19).

7.1.4 Hydrochloric acid (1+1) - Add 500 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.1.5 Hydrochloric acid (1+4) - Add 200 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

7.2 Reagent water - For all sample preparation and dilutions, ASTM type I water (ASTM D1193)[5] is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 Refer to the appropriate analytical method for the preparation of standard stock solutions, calibration standards, and quality control solutions.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 For determination of total recoverable elements in aqueous samples, the samples must be acid preserved prior to aliquoting for either sample processing or determination by direct spectrochemical analysis. For proper preservation samples are **not** filtered, but acidified with (1+1) nitric acid to pH < 2. Preservation may be done at the time of sample 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 and held for sixteen hours. (Normally, 3 mL of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). The pH of all aqueous samples must be tested immediately prior to withdrawing an aliquot for processing to ensure the sample has been properly preserved. 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 acid preserved, the sample can be held up to 6 months before analysis.

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.

8.2 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.3 For aqueous samples, 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 determining total recoverable elements is required to operate a formal quality control (QC) program. The minimum requirements of a QC program consist of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and quality control samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.

9.2 Specific instructions on accomplishing the described aspects of the QC program are discussed in the analytical methods (Sect. 1.3).

10. CALIBRATION AND STANDARDIZATION

10.1 Not applicable. Follow instructions given in the analytical method selected.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Total Recoverable Analytes

11.1.1 For the determination of total recoverable analytes in aqueous samples, transfer a 100 mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (Sects. 1.2, 1.5, 1.6, 1.7, & 1.8). (When necessary, smaller sample aliquot volumes may be used.)

NOTE: If the sample contains undissolved solids > 1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.2.3 thru 11.2.8.

11.1.2 Add 2 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.)

11.1.3 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about 2 h for a 100 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.)

11.1.4 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 $HCl-H_2O$ azeotrope.)

11.1.5 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask, make to volume with reagent water, stopper and mix.

11.1.6 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 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 by either inductively coupled plasma-atomic emission spectrometry or direct aspiration flame and stabilized temperature graphite furnace atomic absorption spectroscopy (Sects. 1.3 & 1.4).

11.1.7 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Sect. 1.3), adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 50-mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. Internal standards are added at the time of analysis.)

11.1.8 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.

11.2 Solid Sample Preparation - Total Recoverable Analytes

11.2.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion

(> 20 g) to tared weighing dish, weigh the sample and record the wet weight. (For samples with < 35% moisture a 20 g portion is sufficient. For samples with moisture > 35% a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight for calculation of percent solids (Sect. 12.1). (The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.2.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction (Sects. 1.5, 1.6, 1.7, & 1.8).

11.2.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

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.) Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.2.4 Heat the sample and gently reflux for 30 min. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (3 to 4 mL).

11.2.5 Allow the sample to cool and quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.2.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution 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 by either inductively coupled plasma-atomic emission spectrometry or direct aspiration flame and stabilized temperature graphite furnace atomic absorption spectroscopy (Sects. 1.3 & 1.4).

11.2.7 To ready the sample for analyses by inductively coupled plasma-mass spectrometry (Sect. 1.3), adjust the chloride concentration by pipetting 10 mL of the prepared solution into a 50-mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. Internal standards are added at the time of analysis.)

11.2.8 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 - Use an analytical method listed in Sect. 1.3.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 To report percent solids in solid samples (Sect. 11.2) calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 10$$

where: DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 11.2.1 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

12.2 Calculation and treatment of determined analyte data are discussed in analytical methods listed in Sect. 1.3.

13.0 METHOD PERFORMANCE

13.1 Not applicable. Available data included in analytical methods listed in Sect. 1.3.

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. 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

1. Martin, T.D. and E.R. Martin, "Evaluation of Method 200.2 Sample Preparation Procedure for Spectrochemical Analyses of Total Recoverable Elements," December 1989, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268.

2. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

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

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5. Annual Book of ASTM Standards, Volume 11.01.

METHOD 200.7

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

Revision 4.4
EMMC Version

USEPA-ICP Users Group (Edited by T.D. Martin and J.F. Kopp) - Method 200.7, Revision 1.0, (Printed 1979, Published 1982)

T.D. Martin and E.R. Martin - Method 200.7, Revision 3.0 (1990)

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ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 200.7

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

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1-4] (For analysis of petroleum products see references 5 and 6 Sect. 16.0) This method is applicable to the following analytes:

Analyte		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
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)	7439-93-2
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
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica[b]	(SiO_2)	7631-86-9

(continues on next page)

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

[b] This method is <u>not</u> suitable for the determination of silica in solids.

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

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

1.3 ICP-AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be < 0.2% (w/v) (Sect. 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis". However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sects. 11.2.2 thru 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample.

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. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. 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. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater 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. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots < 1 g when determined sample concentrations exceed 1%.

1.8 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.9 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity < 1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided the sample solution is adjusted to contain the same mixed acid (HNO_3 + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.10 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Table 1 provides estimated instrument detection limits for the listed wavelengths.[7] However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.11 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 aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous 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 aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, 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 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 (Sect. 7.10.1).

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 (Sect. 7.9).

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 (Sect. 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 (Sect 8.5).

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 (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 (Sects. 7.11 & 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 (Sect. 11.5).

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 (Sects. 7.10.3 & 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 (Sect. 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 (Sects. 7.10.2 & 9.3.1).

3.12 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Sect. 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 (Sect. 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 (Sects. 7.15 & 10.2.3).

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. 7.12 & 9.2.3).

3.16 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.17 **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. 7.13, 7.14 & 9.3.5).

3.18 **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. 9.5.1 & 11.5).

3.19 **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. 7.8).

3.20 **Total Recoverable Analyte** - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU (Sect. 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 11.2 & 11.3).

3.21 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light 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.[8] 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 7.13. 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.[7,8]

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. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are <u>not</u> used, either on-going SIC solutions (Sect. 7.14) 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, > the analyte IDL, or false negative analyte concentration, < 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 transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using

a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow 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. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

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. 7.10.4). 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 aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. 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 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 sec 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.[9-12] 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 (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 weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

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

6.4 (optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted digestion tubes.

6.5 (optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

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

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

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 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 must 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, (2) depleting element concentrations through adsorption processes. 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.[2,3] Chromic acid cleaning solutions must be avoided because chromium is an analyte.

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

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250-mL with 50-mm watch glasses.

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

6.10.5 (optional) PTFE and/or quartz Griffin beakers, 250-mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

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

6.10.8 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[13] 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+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.3 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.[14]

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

7.6 Tartaric acid, ACS reagent grade.

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

7.8 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 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 (Sect. 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,

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

where:

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

7.8.1 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 HNO_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.

7.8.2 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.

7.8.3 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 the 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.

7.8.4 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.

7.8.5 Beryllium solution, stock, 1 mL = 1000 µg Be: DO NOT DRY. Dissolve 19.66 g $BeSO_4 \cdot 4H_2O$ (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.

7.8.6 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.

7.8.7 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.

7.8.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.498 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 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.8.9 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.

7.8.10 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.

7.8.11 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.

7.8.12 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.

7.8.13 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.

7.8.14 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.

7.8.15 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.

7.8.16 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.

7.8.17 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.

7.8.18 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.

7.8.19 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.

7.8.20 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.

7.8.21 Phosphorus solution, stock, 1 mL = 1000 µg P: Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), 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.

7.8.22 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.

7.8.23 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.

7.8.24 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.

7.8.25 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.

7.8.26 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.

7.8.27 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.

7.8.28 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.

7.8.29 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1-L volumetric flask with reagent water.

7.8.30 Titanium solution, stock, 1 mL = 1000 µg Ti: DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (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.

7.8.31 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.

7.8.32 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 1.270 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.

7.8.33 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.

7.9 Mixed Calibration Standard Solutions - For the analysis of total recoverable digested samples 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 and 20 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. 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 mixed-acid calibration standard 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 0.5 mg/L.

7.10 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.

7.10.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The calibration blank should be stored in a FEP bottle.

7.10.2 The laboratory reagent blank (LRB) must contain all the reagents 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.

7.10.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a suitable concentration using the following recommended criteria: Ag $\leq$ 0.1 mg/L, $\geq$ K 5.0 mg/L and all other analytes 0.2 mg/L or a concentration approximately 100 times their respective MDL, whichever is greater. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

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

7.11 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to < 0.5 mg/L; while potassium and phosphorus because of higher MDLs and silica because of potential contamination should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 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 an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be $\geq$ 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.13 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.

7.13.1 SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L AL; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid 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[3] 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.)

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

7.13.2 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.

7.13.3 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.

7.13.4 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. This 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.

7.13.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for 5 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 10-mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

7.13.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 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.

7.14 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., $\geq$ 10 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 $\geq$ 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.

7.15 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 (Sect. 10.2). The solution is prepared by adding a 5-mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) nitric acid and 20 mL (1+1) hydrochloric acid and diluting to 500 mL 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 processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 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 sixteen 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 sixteen 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 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, 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 upper 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 a QCS (Sect. 7.12). 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 cannot 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.[15] 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 = 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 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 inappropriately 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 (Sect. 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 (Sect. 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 (Sect. 7.10.2) 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 (Sect. 7.10.3) 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 LBR 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% (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:

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

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits 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 - For all determinations the laboratory must analyze the IPC solution (Sect. 7.11) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the analyte IDL, but > 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 ± 5% of calibration with a relative standard deviation < 3% from replicate integrations ≥ 4. Subsequent analyses of the IPC solution 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 7.13. Special cases where on-going verification is required are described in Section 7.14.

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 (Sect 9.4.2) is required. Also, other tests such as the analyte addition test (Sect. 9.5.1) and sample dilution test (Sect. 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. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Sect. 7.10.3). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Sect. 12.5). (For notes on Ag, Ba, and Sn see Sects. 1.7 & 1.8.) Over time, samples from all routine sample sources should be fortified.

NOTE: The concentration of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids 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 higher concentrations, but even major constituents should be limited to < 25 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% or a 3 sigma recovery range calculated from the regression equations given in Table 9.[16] Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, 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 (Sect. 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) (Sect. 11.5) 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 11.5.

9.5.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is < 20% of the sample analyte concentration, the following dilution 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 for aqueous solutions usually vary from 1100 to 1200 watts forward power, 15-to 16-mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1 L/min argon aerosol flow, 1 to 1.8 mL/min sample pumping rate with a 1-min preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors.[17]

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. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000-μg/mL solution of yttrium (Sect. 7.8.32), 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 to 20 mm above the top of the work coil.[18] Record the nebulizer gas flow rate or pressure setting for future reference.

10.2.2 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.

10.2.3 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 10.2.1 and 10.2.2, and aspirate the plasma solution (Sect. 7.15), containing 10 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 to 18 mm above the top of the work coil. (This region of the plasma is commonly

referred to as the analytical zone.)[19] 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.

10.2.4 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.

10.2.5 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.

10.2.6 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). The change in signal intensity with a change in nebulizer gas flow rate for both "hard" (Pb 220.353 nm) and "soft" (Cu 324.754) lines is illustrated in Figure 1.

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 (Sect. 11.4) 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 (Sect 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 7.13. 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 7.14.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥ 20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Sect. 1.3). Allowance for sample dilution should be made in the calculations. (If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects. Sect. 1.9)

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 thru 11.2.7 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 (Sect. 1.2). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis 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), transfer a 100-mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (Sects. 1.2, 1.3, 1.6, 1.7, 1.8, & 1.9). (When necessary, smaller sample aliquot volumes may be used.)

NOTE: If the sample contains <u>undissolved</u> solids > 1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously

evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 thru 11.3.6.

11.2.3 Add 2 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 2 h for a 100 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 $HCl-H_2O$ azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask, 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 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 Solid Sample Preparation - Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (> 20 g) to tared weighing dish, weigh the sample and record

the wet weight (WW). (For samples with < 35% moisture a 20 g portion is sufficient. For samples with moisture > 35% a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight (DW) for calculation of percent solids (Sect. 12.6). (The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction (Sects.1.6, 1.7, 1.8, & 1.9).

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

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.) Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 min. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (3 to 4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract 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.

11.4 Sample Analysis

11.4.1 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.

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

11.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Sect. 7.9) and the calibration blank (Sect. 7.10.1). 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 30 sec 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 (Sect. 7.10.4) for a minimum of 60 seconds (Sect. 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.[20]

11.4.5 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, LFBs, LFMs, and check solutions (Sect. 7.10.4).

11.4.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.7 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 Sect. 11.4.8). 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 that is either more sensitive and/or interference free is recommended.

11.4.8 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.

11.4.9 Report data as directed in Section 12.

11.5 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[21] 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 mg/L for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Sect. 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

12.3 For total recoverable aqueous analytes (Sect. 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data as instructed in Section 12.4. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. 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 determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.4 For analytes with MDLs < 0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs ≥ 0.01 mg/L round the data values to the hundredth place and report analyte concentrations up to three significant figures. Extract concentrations for solids data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid samples (Sect. 11.3), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

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

where: C = Concentration in extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.6 To report percent solids in solid samples (Sect. 11.3) calculate as follows:

$$\% \text{ solids } (S) = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 11.3 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

12.7 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 determined for the recommended wavelengths using simultaneous ICP-AES and the operating conditions given in Table 5. The MDLs were determined in reagent blank matrix (best case situation). PTFE beakers were used to avoid boron and silica contamination from glassware with the final dilution to 50 mL completed in polypropylene centrifuged tubes. The listed MDLs for solids are estimates and were calculated from the aqueous MDL determinations.

13.2 Data obtained from single laboratory method testing are summarized in Table 6 for five types of water samples consisting of drinking water, surface water, ground water, and two wastewater effluents. The data presented cover all analytes except cerium and titanium. Samples were prepared using the procedure described in Sect. 11.2. 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 pairs of duplicates were fortified at different concentration levels. For each method analyte, the sample background concentration, mean percent recovery, standard deviation of the percent recovery, and 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. The tap and well waters were processed in Teflon and quartz beakers and diluted in polypropylene centrifuged tubes. The nonuse of borosilicate glassware is reflected in the precision and recovery data for boron and silica in those two sample types.

13.3 Data obtained from single laboratory method testing are summarized in Table 7 for three solid samples consisting of EPA 884 Hazardous Soil, SRM 1645 River Sediment, and EPA 286 Electroplating Sludge. Samples were prepared using the procedure described in Sect. 11.3. For each method analyte, the sample background concentration, mean percent

recovery of the fortified additions, the standard deviation of the percent recovery, and relative percent difference between duplicate additions were determined as described in Sect. 13.2. Data presented are for all analytes except cerium, silica and titanium. Limited comparative data to other methods and SRM materials are presented in reference 23 of Section 16.0.

13.4 Performance data for aqueous solutions independent of sample preparation from a multilaboratory study are provided in Table 8.[22]

13.5 Listed in Table 9 are regression equations for precision and bias for 25 analytes abstracted from EPA Method Study 27, a multilaboratory validation study of Method 200.7.[1] These equations were developed from data received from 12 laboratories using the total recoverable sample preparation procedure on reagent water, drinking water, surface water and 3 industrial effluents. For a complete review and description of the study see reference 16 of Section 16.0.

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. 7.8). 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)	Estimated Detection Limit[b] (µg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	45	10
Antimony	206.833	32	5
Arsenic	193.759	53	10
Barium	493.409	2.3	1
Beryllium	313.042	0.27	1
Boron	249.678	5.7	1
Cadmium	226.502	3.4	2
Calcium	315.887	30	10
Cerium	413.765	48	2
Chromium	205.552	6.1	5
Cobalt	228.616	7.0	2
Copper	324.754	5.4	2
Iron	259.940	6.2	10
Lead	220.353	42	10
Lithium	670.784	3.7[d]	5
Magnesium	279.079	30	10
Manganese	257.610	1.4	2
Mercury	194.227	2.5	2
Molybdenum	203.844	12	10
Nickel	231.604	15	2
Phosphorus	214.914	76	10
Potassium	766.491	700[e]	20
Selenium	196.090	75	5
Silica (SiO_2)	251.611	26[d] (SiO_2)	10
Silver	328.068	7.0	0.5
Sodium	588.995	29	10
Strontium	421.552	0.77	1
Thallium	190.864	40	5
Tin	189.980	25	4
Titanium	334.941	3.8	10
Vanadium	292.402	7.5	2
Zinc	213.856	1.8	5

[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] These estimated 3-sigma instrumental detection limits[16] are provided only as a guide to instrumental limits. The method detection limits are

sample dependent and may vary as the sample matrix varies. Detection limits for solids can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

[c] Suggested concentration for instrument calibration.[2] Other calibration limits in the linear ranges may be used.

[d] Calculated from 2-sigma data.[5]

[e] Highly dependent on operating conditions and plasma position.

TABLE 2: ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 100-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
P	214.914	Cu,Mo
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 Sect. 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

TABLE 3: MIXED STANDARD SOLUTIONS

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

TABLE 4: TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)

Analyte	MDLs Aqueous, mg/L[1]	Solids, mg/kg[2]
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B	0.003	-
Ba	0.001	0.2
Be	0.0003	0.1
Ca	0.01	2
Cd	0.001	0.2
Ce	0.02	3
Co	0.002	0.4
Cr	0.004	0.8
Cu	0.003	0.5
Fe	0.03*	6
Hg	0.007	2
K	0.3	60
Li	0.001	0.2
Mg	0.02	3
Mn	0.001	0.2
Mo	0.004	1
Na	0.03	6
Ni	0.005	1
P	0.06	12
Pb	0.01	2
Sb	0.008	2
Se	0.02	5
SiO_2	0.02	-
Sn	0.007	2
Sr	0.0003	0.1
Ti	0.001	0.2
Tl	0.02	3
V	0.003	1
Zn	0.002	0.3

(1) 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.

(2) Estimated, calculated from aqueous MDL determinations.

\- Boron not reported because of glassware contamination. Silica not determined in solid samples.

* Elevated value due to fume-hood contamination.

TABLE 5: INDUCTIVELY COUPLED PLASMA INSTRUMENT OPERATING CONDITIONS

Incident rf power	1100 watts
Reflected rf power	< 5 watts
Viewing height above 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
Aerosol carrier argon flow rate	620 mL/min
Auxiliary (plasma) argon flow rate	300 mL/min
Sample uptake rate controlled to	1.2 mL/min

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

TAP WATER

ANALYTE	SAMPLE CONC mg/L	LOW SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	<0.002	0.05	95	0.7	2.1	0.2	96	0.0	0.0
Al	0.185	0.05	98	8.8	1.7	0.2	105	3.0	3.1
As	<0.008	0.05	108	1.4	3.7	0.2	101	0.7	2.0
B	0.023	0.1	98	0.2	0.0	0.4	98	0.2	0.5
Ba	0.042	0.05	102	1.6	2.2	0.2	98	0.4	0.8
Be	<0.0003	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Ca	35.2	5.0	101	8.8	1.7	20.0	103	2.0	0.9
Cd	<0.001	0.01	105	3.5	9.5	0.1	98	0.0	0.0
Co	<0.002	0.02	100	0.0	0.0	0.2	99	0.5	1.5
Cr	<0.004	0.01	110	0.0	0.0	0.1	102	0.0	0.0
Cu	<0.003	0.02	103	1.8	4.9	0.2	101	1.2	3.5
Fe	0.008	0.1	106	1.0	1.8	0.4	105	0.3	0.5
Hg	<0.007	0.05	103	0.7	1.9	0.2	100	0.4	1.0
K	1.98	5.0	109	1.4	2.3	20.0	107	0.7	1.7
Li	0.006	0.02	103	6.9	3.8	0.2	110	1.9	4.4
Mg	8.08	5.0	104	2.2	1.5	20.0	100	0.7	1.1
Mn	<0.001	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Mo	<0.004	0.02	95	3.5	10.5	0.2	108	0.5	1.4
Na	10.3	5.0	99	3.0	2.0	20.0	106	1.0	1.6
Ni	<0.005	0.02	108	1.8	4.7	0.2	104	1.1	2.9
P	0.045	0.1	102	13.1	9.4	0.4	104	3.2	1.3
Pb	<0.01	0.05	95	0.7	2.1	0.2	100	0.2	0.5
Sb	<0.008	0.05	99	0.7	2.0	0.2	102	0.7	2.0
Se	<0.02	0.1	87	1.1	3.5	0.4	99	0.8	2.3
SiO_2	6.5	5.0	104	3.3	3.4	20.0	96	1.1	2.3
Sn	<0.007	0.05	103	2.1	5.8	0.2	101	1.8	5.0
Sr	0.181	0.1	102	3.3	2.1	0.4	105	0.8	1.0
Tl	<0.02	0.1	101	3.9	10.9	0.4	101	0.1	0.3
V	<0.003	0.05	101	0.7	2.0	0.2	99	0.2	0.5
Zn	0.005	0.05	101	3.7	9.0	0.2	98	0.9	2.5

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

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

POND WATER

ANALYTE	SAMPLE CONC mg/L	LOW SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	<0.002	0.05	92	0.0	0.0	0.2	94	0.0	0.0
Al	0.819	0.2	88	10.0	5.0	0.8	100	2.9	3.7
As	<0.008	0.05	102	0.0	0.0	0.2	98	1.4	4.1
B	0.034	0.1	111	8.9	6.9	0.4	103	2.0	0.0
Ba	0.029	0.05	96	0.9	0.0	0.2	97	0.3	0.5
Be	<0.0003	0.01	95	0.4	1.1	0.1	95	0.0	0.0
Ca	53.9	5	*	*	0.7	20.0	100	2.0	1.5
Cd	<0.001	0.01	107	0.0	0.0	0.1	97	0.0	0.0
Co	<0.002	0.02	100	2.7	7.5	0.2	97	0.7	2.1
Cr	<0.004	0.01	105	3.5	9.5	0.1	103	1.1	2.9
Cu	0.003	0.02	98	2.1	4.4	0.2	100	0.5	1.5
Fe	0.875	0.2	95	8.9	2.8	0.8	97	3.2	3.6
Hg	<0.007	0.05	97	3.5	10.3	0.2	98	0.0	0.0
K	2.48	5	106	0.3	0.1	20.0	103	0.2	0.4
Li	<0.001	0.02	110	0.0	0.0	0.2	106	0.2	0.5
Mg	10.8	5	102	0.5	0.0	20.0	96	0.7	1.3
Mn	0.632	0.01	*	*	0.2	0.1	97	2.3	0.3
Mo	<0.004	0.02	105	3.5	9.5	0.2	103	0.4	1.0
Na	17.8	5	103	1.3	0.4	20.0	94	0.3	0.0
Ni	<0.005	0.02	96	5.6	9.1	0.2	100	0.7	1.5
P	0.196	0.1	91	14.7	0.3	0.4	108	3.9	1.3
Pb	<0.01	0.05	96	2.6	7.8	0.2	100	0.7	2.0
Sb	<0.008	0.05	102	2.8	7.8	0.2	104	0.4	1.0
Se	<0.02	0.1	104	2.1	5.8	0.4	103	1.6	4.4
SiO_2	7.83	5	151	1.6	1.3	20.0	117	0.4	0.6
Sn	<0.007	0.05	98	0.0	0.0	0.2	99	1.1	3.0
Sr	0.129	0.1	105	0.4	0.0	0.4	99	0.1	0.2
Tl	<0.02	0.1	103	1.1	2.9	0.4	97	1.3	3.9
V	0.003	0.05	94	0.4	0.0	0.2	98	0.1	0.0
Zn	0.006	0.05	97	1.6	1.8	0.2	94	0.4	0.0

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

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

WELL WATER

ANALYTE	SAMPLE CONC mg/L	LOW SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	<0.002	0.05	97	0.7	2.1	0.2	96	0.2	0.5
Al	0.036	0.05	107	7.6	10.1	0.2	101	1.1	0.8
As	<0.008	0.05	107	0.7	1.9	0.2	104	0.4	1.0
B	0.063	0.1	97	0.6	0.7	0.4	98	0.8	2.1
Ba	0.102	0.05	102	3.0	0.0	0.2	99	0.9	1.0
Be	<0.0003	0.01	100	0.0	0.0	0.1	100	0.0	0.0
Ca	93.8	5.0	*	*	2.1	20.0	100	4.1	0.1
Cd	0.002	0.01	90	0.0	0.0	0.1	96	0.0	0.0
Co	<0.002	0.02	94	0.4	1.1	0.2	94	0.4	1.1
Cr	<0.004	0.01	100	7.1	20.0	0.1	100	0.4	1.0
Cu	0.005	0.02	100	1.1	0.4	0.2	96	0.5	1.5
Fe	0.042	0.1	99	2.3	1.4	0.4	97	1.4	3.3
Hg	<0.007	0.05	94	2.8	8.5	0.2	93	1.2	3.8
K	6.21	5.0	96	3.4	3.6	20.0	101	1.2	2.3
Li	0.001	0.02	100	7.6	9.5	0.2	104	1.0	1.9
Mg	24.5	5.0	95	5.6	0.3	20.0	93	1.6	1.2
Mn	2.76	0.01	*	*	0.4	0.1	*	*	0.7
Mo	<0.004	0.02	108	1.8	4.7	0.2	101	0.2	0.5
Na	35.0	5.0	101	11.4	0.8	20.0	100	3.1	1.5
Ni	<0.005	0.02	112	1.8	4.4	0.2	96	0.2	0.5
P	0.197	0.1	95	12.7	1.9	0.4	98	3.4	0.9
Pb	<0.01	0.05	87	4.9	16.1	0.2	95	0.2	0.5
Sb	<0.008	0.05	98	2.8	8.2	0.2	99	1.4	4.0
Se	<0.02	0.1	102	0.4	1.0	0.4	94	1.1	3.4
SiO_2	13.1	5.0	93	4.8	2.8	20.0	99	0.8	0.0
Sn	<0.007	0.05	98	2.8	8.2	0.2	94	0.2	0.5
Sr	0.274	0.1	94	5.7	2.7	0.4	95	1.7	2.2
Tl	<0.02	0.1	92	0.4	1.1	0.4	95	1.1	3.2
V	<0.003	0.05	98	0.0	0.0	0.2	99	0.4	1.0
Zn	0.538	0.05	*	*	0.7	0.2	99	2.5	1.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

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

SEWAGE TREATMENT PRIMARY EFFLUENT

ANALYTE	SAMPLE CONC mg/L	LOW SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	0.009	0.05	92	1.5	3.6	0.2	95	0.1	0.0
Al	1.19	0.05	*	*	0.9	0.2	113	12.4	2.1
As	<0.008	0.05	99	2.1	6.1	0.2	93	2.1	6.5
B	0.226	0.1	217	16.3	9.5	0.4	119	13.1	20.9
Ba	0.189	0.05	90	6.8	1.7	0.2	99	1.6	0.5
Be	<0.0003	0.01	94	0.4	1.1	0.1	100	0.4	1.0
Ca	87.9	5.0	*	*	0.6	20.0	101	3.7	0.0
Cd	0.009	0.01	89	2.6	2.3	0.1	97	0.4	1.0
Co	0.016	0.02	95	3.1	0.0	0.2	93	0.4	0.5
Cr	0.128	0.01	*	*	1.5	0.1	97	2.4	2.7
Cu	0.174	0.02	98	33.1	4.7	0.2	98	3.0	1.4
Fe	1.28	0.1	*	*	2.8	0.4	111	7.0	0.6
Hg	<0.007	0.05	102	1.4	3.9	0.2	98	0.5	1.5
K	10.6	5.0	104	2.8	1.3	20.0	101	0.6	0.0
Li	0.011	0.02	103	8.5	3.2	0.2	105	0.8	0.5
Mg	22.7	5.0	100	4.4	0.0	20.0	92	1.1	0.2
Mn	0.199	0.01	*	*	2.0	0.1	104	1.9	0.3
Mo	0.125	0.02	110	21.2	6.8	0.2	102	1.3	0.9
Na	236	5.0	*	*	0.0	20.0	*	*	0.4
Ni	0.087	0.02	122	10.7	4.5	0.2	98	0.8	1.1
P	4.71	0.1	*	*	2.6	0.4	*	*	1.4
Pb	0.015	0.05	91	3.5	5.0	0.2	96	1.3	2.9
Sb	<0.008	0.05	97	0.7	2.1	0.2	103	1.1	2.9
Se	<0.02	0.1	108	3.9	10.0	0.4	101	2.6	7.2
SiO_2	16.7	5.0	124	4.0	0.9	20.0	108	1.1	0.8
Sn	0.016	0.05	90	3.8	0.0	0.2	95	1.0	0.0
Sr	0.515	0.1	103	6.4	0.5	0.4	96	1.6	0.2
Tl	<0.02	0.1	105	0.4	1.0	0.4	95	0.0	0.0
V	0.003	0.05	93	0.9	2.0	0.2	97	0.2	0.5
Zn	0.160	0.05	98	3.3	1.9	0.2	101	1.0	1.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

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

INDUSTRIAL EFFLUENT

ANALYTE	SAMPLE CONC mg/L	LOW SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH SPIKE mg/L	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	<0.003	0.05	88	0.0	0.0	0.2	84	0.9	3.0
Al	0.054	0.05	88	11.7	12.2	0.2	90	3.9	8.1
As	<0.02	0.05	82	2.8	9.8	0.2	88	0.5	1.7
B	0.17	0.1	162	17.6	13.9	0.4	92	4.7	9.3
Ba	0.083	0.05	86	8.2	1.6	0.2	85	2.3	2.4
Be	<0.0006	0.01	94	0.4	1.1	0.1	82	1.4	4.9
Ca	500	5.0	*	*	2.8	20.0	*	*	2.3
Cd	0.008	0.01	85	4.7	6.1	0.1	82	1.4	4.4
Co	<0.004	0.02	93	1.8	5.4	0.2	83	0.4	1.2
Cr	0.165	0.01	*	*	4.5	0.1	106	6.6	5.6
Cu	0.095	0.02	93	23.3	0.9	0.2	95	2.7	2.8
Fe	0.315	0.1	88	16.4	1.0	0.4	99	6.5	8.0
Hg	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
K	2.87	5.0	101	3.4	2.4	20.0	100	0.8	0.4
Li	0.069	0.02	103	24.7	5.6	0.2	104	2.5	2.2
Mg	6.84	5.0	87	3.1	0.0	20.0	87	0.9	1.2
Mn	0.141	0.01	*	*	1.2	0.1	89	6.6	4.8
Mo	1.27	0.02	*	*	0.0	0.2	100	15.0	2.7
Na	1500	5.0	*	*	2.7	20.0	*	*	2.0
Ni	0.014	0.02	98	4.4	3.0	0.2	87	0.5	1.1
P	0.326	0.1	105	16.0	4.7	0.4	97	3.9	1.4
Pb	0.251	0.05	80	19.9	1.4	0.2	88	5.0	0.9
Sb	2.81	0.05	*	*	0.4	0.2	*	*	2.0
Se	0.021	0.1	106	2.6	3.2	0.4	105	1.9	4.6
SiO_2	6.83	5.0	99	6.8	1.7	20.0	100	2.2	3.0
Sn	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
Sr	6.54	0.1	*	*	2.0	0.4	*	*	2.7
Tl	<0.03	0.1	87	1.8	5.8	0.4	84	1.1	3.6
V	<0.005	0.05	90	1.4	4.4	0.2	84	1.1	3.6
Zn	0.024	0.05	89	6.0	4.4	0.2	91	3.5	8.9

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

ANALYTE	SAMPLE CONC mg/kg	LOW+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	1.1	20	98	0.7	1.0	100	96	0.2	0.6
Al	5080	20	*	*	7.2	100	*	*	5.4
As	5.7	20	95	5.4	10.6	100	96	1.4	3.6
B	20.4	100	93	2.7	5.3	400	100	2.1	5.5
Ba	111	20	98	71.4	22.2	100	97	10.0	1.0
Be	0.66	20	97	0.7	2.0	100	99	0.1	0.2
Ca	85200	-	-	-	-	-	-	-	-
Cd	2	20	93	0.7	1.0	100	94	0.2	0.4
Co	5.5	20	96	3.5	7.7	100	93	0.8	2.1
Cr	79.7	20	87	28.8	16.5	100	104	1.3	1.1
Cu	113	20	110	16.2	4.4	100	104	4.0	4.2
Fe	16500	-	-	-	-	-	-	-	-
Hg	<1.4	10	92	2.5	7.7	40	98	0.0	0.0
K	621	500	121	1.3	0.0	2000	107	0.9	1.8
Li	6.7	10	113	3.5	4.4	40	106	0.6	0.6
Mg	24400	500	*	*	8.4	2000	*	*	10.1
Mn	343	20	*	*	8.5	100	95	11.0	1.6
Mo	5.3	20	88	5.3	13.2	100	91	1.4	4.1
Na	195	500	102	2.2	2.4	2000	100	1.5	3.7
Ni	15.6	20	100	1.8	0.0	100	94	1.5	3.6
P	595	500	106	13.4	8.0	2000	103	3.2	2.7
Pb	145	20	88	51.8	17.9	100	108	15.6	17.4
Sb	6.1	20	83	3.9	7.5	100	81	1.9	5.9
Se	<5	20	79	14.7	52.4	100	99	0.7	2.1
Sn	16.6	20	91	34.6	5.8	80	112	8.7	2.8
Sr	102	100	84	9.6	10.8	400	94	2.5	4.6
Tl	<4	20	92	4.8	14.6	100	91	1.5	4.6
V	16.7	20	104	4.2	5.4	100	99	0.8	1.7
Zn	131	20	103	31.2	7.3	100	104	7.2	6.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not spiked.
+ Equivalent

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont.)

EPA ELECTROPLATING SLUDGE #286

ANALYTE	SAMPLE CONC mg/kg	LOW+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	6	20	96	0.2	0.4	100	93	0.1	0.4
Al	4980	20	*	*	4.4	100	*	*	5.6
As	32	20	94	1.3	0.8	100	97	0.7	1.6
B	210	100	113	2.0	1.6	400	98	1.9	3.5
Ba	39.8	20	0	6.8	0.3	100	0	1.6	5.7
Be	0.32	20	96	0.2	0.5	100	101	0.7	2.0
Ca	48500	-	-	-	-	-	-	-	-
Cd	108	20	98	2.5	0.8	100	96	0.5	0.5
Co	5.9	20	93	2.9	5.7	100	93	0.6	1.5
Cr	7580	20	*	*	0.7	100	*	*	1.3
Cu	806	20	*	*	1.5	100	94	8.3	0.7
Fe	31100	-	-	-	-	-	-	-	-
Hg	6.1	10	90	2.5	4.0	40	97	1.7	4.3
K	2390	500	75	8.3	4.0	2000	94	2.9	3.8
Li	9.1	10	101	2.8	0.5	40	106	1.6	3.1
Mg	1950	500	110	2.0	0.8	2000	108	2.3	3.2
Mn	262	20	*	*	1.8	100	91	1.2	0.9
Mo	13.2	20	92	2.1	2.9	100	92	0.3	0.0
Na	73400	500	*	*	1.7	2000	*	*	1.4
Ni	456	20	*	*	0.4	100	88	2.7	0.9
P	9610	500	*	*	2.9	2000	114	7.4	3.4
Pb	1420	20	*	*	2.1	100	*	*	1.3
Sb	<2	20	76	0.9	3.3	100	75	2.8	10.7
Se	6.3	20	86	9.0	16.6	100	103	1.6	2.7
Sn	24.0	20	87	4.0	2.7	100	92	0.7	0.0
Sr	145	100	90	8.1	8.1	400	93	2.4	4.6
Tl	16	20	89	4.6	5.3	100	92	0.8	0.9
V	21.7	20	95	1.2	1.0	100	96	0.4	0.9
Zn	12500	20	*	*	0.8	100	*	*	0.8

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not spiked.
+ Equivalent

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont.)

NBS 1645 RIVER SEDIMENT

ANALYTE	SAMPLE CONC mg/kg	LOW+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD	HIGH+ SPIKE mg/kg	AVERAGE RECOVERY R(%)	S(R)	RPD
Ag	1.6	20	92	0.4	1.0	100	96	0.3	0.9
Al	5160	20	*	*	8.4	100	*	*	2.4
As	62.8	20	89	14.4	9.7	100	97	2.9	5.0
B	31.9	100	116	7.1	13.5	400	95	0.6	1.5
Ba	54.8	20	95	6.1	2.8	100	98	1.2	1.3
Be	0.72	20	101	0.4	1.0	100	103	1.4	3.9
Ca	28000	-	-	-	-	-	-	-	-
Cd	9.7	20	100	1.1	0.0	100	101	0.7	1.8
Co	9.4	20	98	3.8	4.8	100	98	0.9	1.8
Cr	28500	20	*	*	0.4	100	*	*	0.7
Cu	109	20	115	8.5	0.0	100	102	1.8	1.0
Fe	84800	-	-	-	-	-	-	-	-
Hg	3.1	10	99	4.3	7.7	40	96	0.7	1.0
K	452	500	98	4.1	2.0	2000	106	1.4	2.3
Li	3.7	10	101	2.0	0.7	40	108	1.3	3.0
Mg	6360	500	*	*	1.8	2000	93	2.7	1.0
Mn	728	20	*	*	3.5	100	97	12.4	2.2
Mo	17.9	20	97	12.5	18.5	100	98	0.6	0.0
Na	1020	500	92	2.6	0.0	2000	97	1.1	1.7
Ni	36.2	20	94	5.9	4.0	100	100	1.1	1.5
P	553	500	102	1.4	0.9	2000	100	0.8	1.6
Pb	707	20	*	*	0.8	100	103	5.9	0.4
Sb	22.8	20	86	2.3	0.0	100	88	0.6	0.9
Se	6.7	20	103	14.3	27.1	100	98	3.1	7.6
Sn	309	20	*	*	1.0	100	101	7.9	2.7
Sr	782	100	91	12.3	3.0	400	96	3.3	2.6
Tl	<4	20	90	0.0	0.0	100	95	1.3	4.0
V	20.1	20	89	5.4	5.8	100	98	0.7	0.0
Zn	1640	20	*	*	1.8	100	*	*	1.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not spiked.
+ Equivalent

TABLE 8: ICP-AES INSTRUMENTAL PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc (mg/L)	N[b]	RSD (%)	Accuracy[c] (% of Nominal)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a] These performance values are independent of sample preparation because the labs analyzed portions of the same solutions using sequential or simultaneous instruments.[22]

[b] N = Number of measurements for mean and relative standard deviation (RSD).

[c] Accuracy is expressed as a percentage of the nominal value for each analyte in the acidified, multi-element solutions.

TABLE 9: MULTILABORATORY ICP PRECISION AND ACCURACY DATA*

Analyte	Concentration µg/L	Total Recoverable Digestion µ/L
Aluminum	69-4792	X = 0.9380(C) + 22.1 SR = 0.0481(X) + 18.8
Antimony	77-1406	X = 0.8908(C) + 0.9 SR = 0.0682(X) + 2.5
Arsenic	69-1887	X = 1.0175(C) + 3.9 SR = 0.0643(X) + 10.3
Barium	9-377	X = 0.8380(C) + 1.68 SR = 0.0826(X) + 3.54
Beryllium	3-1906	X = 1.0177(C) - 0.55 SR = 0.0445(X) - 0.10
Boron	19-5189	X = 0.9676(C) + 18.7 SR = 0.0743(X) + 21.1
Cadmium	9-1943	X = 1.0137(C) - 0.65 SR = 0.0332(X) + 0.90
Calcium	17-47170	X = 0.9658(C) + 0.8 SR = 0.0327(X) + 10.1
Chromium	13-1406	X = 1.0049(C) - 1.2 SR = 0.0571(X) + 1.0
Cobalt	17-2340	X = 0.9278(C) - 1.5 SR = 0.0407(X) + 0.4
Copper	8-1887	X = 0.9647(C) - 3.64 SR = 0.0406(X) + 0.96
Iron	13-9359	X = 0.9830(C) + 5.7 SR = 0.0790(X) + 11.5
Lead	42-4717	X = 1.0056(C) + 4.1 SR = 0.0448(X) + 3.5

* - Regression equations abstracted from Reference 16.
X = Mean Recovery, µg/L
C = True Value for the Concentration, µg/L
SR = Single-analyst Standard Deviation, µg/L

TABLE 9: MULTILABORATORY ICP PRECISION AND ACCURACY DATA* (Cont.)

Analyte	Concentration µg/L	Total Recoverable Digestion µ/L
Magnesium	34-13868	X = 0.9879(C) + 2.2 SR = 0.0268(X) + 8.1
Manganese	4-1887	X = 0.9725(C) + 0.07 SR = 0.0400(X) + 0.82
Molybdenum	17-1830	X = 0.9707(C) - 2.3 SR = 0.0529(X) + 2.1
Nickel	17-47170	X = 0.9869(C) + 1.5 SR = 0.0393(X) + 2.2
Potassium	347-14151	X = 0.9355(C) -183.1 SR = 0.0329(X) + 60.9
Selenium	69-1415	X = 0.9737(C) - 1.0 SR = 0.0443(X) + 6.6
Silicon	189-9434	X = 0.9737(C) - 60.8 SR = 0.2133(X) + 22.6
Silver	8-189	X = 0.3987(C) + 8.25 SR = 0.1836(X) - 0.27
Sodium	35-47170	X = 1.0526(C) + 26.7 SR = 0.0884(X) + 50.5
Thallium	79-1434	X = 0.9238(C) + 5.5 SR = -0.0106(X) + 48.0
Vanadium	13-4698	X = 0.9551(C) + 0.4 SR = 0.0472(X) + 0.5
Zinc	7-7076	X = 0.9500(C) + 1.82 SR = 0.0153(X) + 7.78

* - Regression equations abstracted from Reference 16.
X = Mean Recovery, µg/L
C = True Value for the Concentration, µg/L
SR = Single-analyst Standard Deviation, µg/L

Pb-Cu ICP-AES EMISSION PROFILE

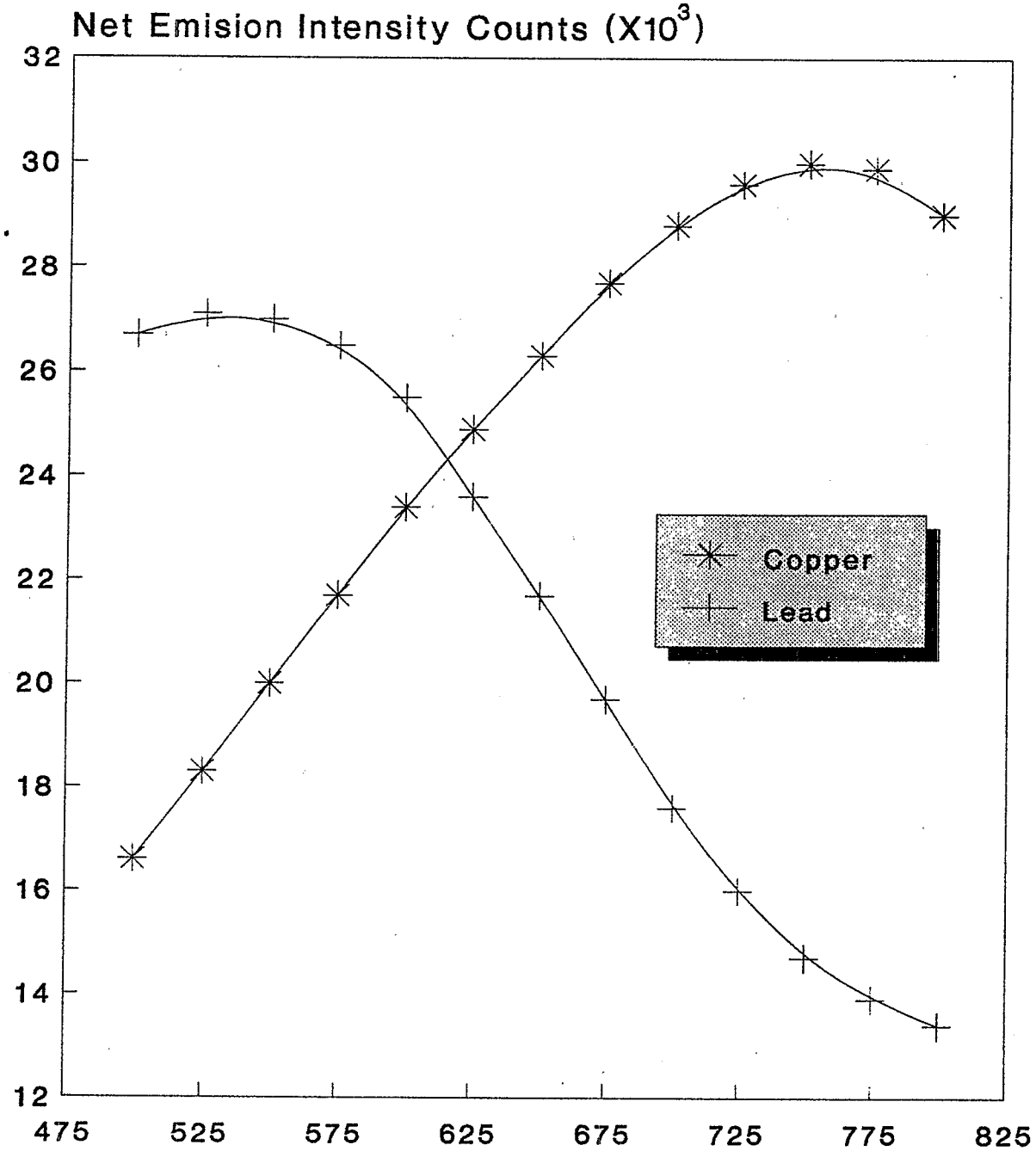

Figure 1

METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

Revision 5.4
EMMC Version

S.E. Long (Technology Applications Inc.), T.D. Martin, and E.R. Martin - Method 200.8, Revisions 4.2 and 4.3 (1990)

S.E. Long (Technology Applications Inc.) and T.D. Martin - Method 200.8, Revision 4.4 (1991)

J.T. Creed, C.A. Brockhoff, and T.D. Martin - Method 200.8, Revision 5.4 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and soils samples. This method is applicable to the following elements:

Analyte		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
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

Estimated instrument detection limits (IDLs) for these elements are listed in Table 1. These are intended as a guide to instrumental limits typical of a system optimized for multielement determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual method detection limits (MDLs) and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions. Given in Table 7 are typical MDLs for both total recoverable determinations by "direct analysis" and where sample digestion is employed.

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 elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v) (Sect. 4.1.4).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the samples have been properly preserved with acid and have turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis".

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample (Sect. 11.2.2).

1.6 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, for "direct analysis" of drinking water (turbidity < 1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided gold is added to both samples and standards alike to eliminate memory interference effects.

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. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains < 0.1 mg/L silver. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

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 should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended.

1.10 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 aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous 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 aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The method describes the multi-element determination of trace elements by ICP-MS.[1-3] Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system. Interferences relating to the technique (Sect. 4) must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards.

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 (Sect. 7.6.1).

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 (Sect. 7.4).

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 (Sect. 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 (Sect 8.5).

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 selected analytical mass(es). (Table 1).

3.6 **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 (Sects. 7.5 & 9.4.5).

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 & 9.3.2).

3.9 **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 (Sect. 9.4).

3.10 **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 (Sects. 7.6.2 & 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 **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 (Sect. 9.2.4 and Table 7).

3.13 **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. 7.8 & 9.2.3).

3.14 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.15 **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. 7.3).

3.16 **Total Recoverable Analyte** - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU (Sect. 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 11.2 & 11.3).

3.17 **Tuning Solution** - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses (Sect. 7.7).

3.18 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

4.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 4), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric

elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

4.1.2 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.1.3 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified[3], and these are listed in Table 2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common ^{82}Kr interference that affects the determination of both arsenic and selenium, can be greatly reduced with the use of high purity krypton free argon.

4.1.4 Physical interferences - Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the

extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended[3] to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects.[4] Internal standards ideally should have similar analytical behavior to the elements being determined.

4.1.5 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, 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. 7.6.3). 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 should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for 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 ten of the method detection limit, should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period. In the determination of mercury, which suffers from severe memory effects, the addition of 100 µg/L gold will effectively rinse 5 µg/L mercury in approximately 2 minutes. Higher concentrations will require a longer rinse time.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents 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.[5,8] A reference file of material data handling sheets should also be 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 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV 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 mass spectrometer:

6.1.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

NOTE: If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result.

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 (Sect. 4.1.3).

6.1.4 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

6.1.5 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., from polyatomic oxide species).

6.1.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high

concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

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

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

6.4 (optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted digestion tubes.

6.5 (optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.6 A gravity convection drying oven with thermostatic control capable of maintaining 105°C ± 5°C.

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

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 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 must 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, (2) depleting element concentrations through adsorption processes. 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 soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 20% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with reagent grade water and storing clean.

NOTE: Chromic acid must not be used for cleaning glassware.

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

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250-mL with 50-mm watch glasses.

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

6.10.5 (optional) PTFE and/or quartz beakers, 250-mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

6.10.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with ETFE (ethylene tetrafluorethylene) screw closure, 125-mL to 250-mL capacities.

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

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (Table 2), however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

7.1.2 Nitric acid (1+1) - Add 500 mL conc. nitric acid to 400 mL of regent grade water and dilute to 1 L.

7.1.3 Nitric acid (1+9) - Add 100 mL conc. nitric acid to 400 mL of reagent grade water and dilute to 1 L.

7.1.4 Hydrochloric acid, concentrated (sp.gr. 1.19).

7.1.5 Hydrochloric acid (1+1) - Add 500 mL conc. hydrochloric acid to 400 mL of reagent grade water and dilute to 1 L.

7.1.6 Hydrochloric acid (1+4) - Add 200 mL conc. hydrochloric acid to 400 mL of reagent grade water and dilute to 1 L.

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

7.1.8 Tartaric acid (CASRN 87-69-4).

7.2 Reagent water - All references to reagent grade water in this method refer to ASTM type I water (ASTM D1193).[9] Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 Standard Stock Solutions - Stock standards may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99 - 99.999% pure). All salts should be dried for 1 h at 105°C, unless otherwise specified. Stock solutions should be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of the multielement stock standards can not be verified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

The following procedures may be used for preparing standard stock solutions:

NOTE: Some metals, particularly those which form surface oxides require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Aluminum solution, stock 1 mL = 1000 μg Al: Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heating to effect solution. Continue heating until volume is reduced to 4 mL. Cool and add 4 mL reagent grade water. Heat until the volume is reduced to 2 mL. Cool and dilute to 100 mL with reagent grade water.

7.3.2 Antimony solution, stock 1 mL = 1000 μg Sb: Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL conc. hydrochloric acid, heating to effect solution. Cool, add 20 mL reagent grade water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with reagent grade water.

7.3.3 Arsenic solution, stock 1 mL = 1000 μg As: Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL reagent grade water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify the solution with 2 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.4 Barium solution, stock 1 mL = 1000 μg Ba: Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL reagent grade water and 2 mL conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100 mL with reagent grade water.

7.3.5 Beryllium solution, stock 1 mL = 1000 μg Be: Dissolve 1.965 g $BeSO_4.4H_2O$ (DO NOT DRY) in 50 mL reagent grade water. Add 1 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.6 Bismuth solution, stock 1 mL = 1000 μg Bi: Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.7 Cadmium solution, stock 1 mL = 1000 μg Cd: Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.8 Chromium solution, stock 1 mL = 1000 μg Cr: Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL reagent grade water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.9 Cobalt solution, stock 1 mL = 1000 μg Co: Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.10 Copper solution, stock 1 mL = 1000 μg Cu: Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.11 Gold solution, stock 1 mL = 1000 μg Au: Dissolve 0.100 g high purity (99.9999%) Au shot in 10 mL of hot conc. nitric acid by dropwise addition of 5 mL conc. HCl and then reflux to expel oxides of nitrogen and chlorine. Cool and dilute to 100 mL with reagent grade water.

7.3.12 Indium solution, stock 1 mL = 1000 μg In: Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.13 Lead solution, stock 1 mL = 1000 μg Pb: Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent grade water.

7.3.14 Magnesium solution, stock 1 mL = 1000 μg Mg: Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.15 Manganese solution, stock 1 mL = 1000 μg Mn: Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.16 Mercury solution, stock, 1 mL = 1000 µg Hg: DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 0.1354 g $HgCl_2$ in reagent water. Add 5.0 mL concentrated HNO_3 and dilute to 100 mL with reagent water.

7.3.17 Molybdenum solution, stock 1 mL = 1000 µg Mo: Dissolve 0.1500 g MoO_3 in a solution mixture of 10 mL reagent grade water and 1 mL conc. ammonium hydroxide., heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.18 Nickel solution, stock 1 mL = 1000 µg Ni: Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.19 Scandium solution, stock 1 mL = 1000 µg Sc: Dissolve 0.1534 g Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.20 Selenium solution, stock 1 mL = 1000 µg Se: Dissolve 0.1405 g SeO_2 in 20 mL ASTM type I water. Dilute to 100 mL with reagent grade water.

7.3.21 Silver solution, stock 1 mL = 1000 µg Ag: Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water. Store in dark container.

7.3.22 Terbium solution, stock 1 mL = 1000 µg Tb: Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.23 Thallium solution, stock 1 mL = 1000 µg Tl: Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL reagent grade water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.24 Thorium solution, stock 1 mL = 1000 µg Th: Dissolve 0.2380 g $Th(NO_3)_4.4H_2O$ (DO NOT DRY) in 20 mL reagent grade water. Dilute to 100 mL with reagent grade water.

7.3.25 Uranium solution, stock 1 mL = 1000 µg U: Dissolve 0.2110 g $UO_2(NO_3)_2.6H_2O$ (DO NOT DRY) in 20 mL reagent grade water and dilute to 100 mL with reagent grade water.

7.3.26 Vanadium solution, stock 1 mL = 1000 µg V: Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.27 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.28 Zinc solution, stock 1 mL = 1000 μg Zn: Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.4 Multielement Stock Standard Solutions - Care must be taken in the preparation of multielement stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, not previously used FEP fluorocarbon bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

Standard Solution A		Standard Solution B
Aluminum	Mercury	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	
Manganese		

Except for selenium and mercury, multielement stock standard solutions A and B (1 mL = 10 μg) may be prepared by diluting 1.0 mL of each single element stock standard in the combination list to 100 mL with reagent water containing 1% (v/v) nitric acid. For mercury and selenium in solution A, aliquots of 0.05 mL and 5.0 mL of the respective stock standards should be diluted to the specified 100 mL (1 ml = 0.5 μg Hg and 50 μg Se). Replace the multielement stock standards when succeeding dilutions for preparation of the calibration standards cannot be verified with the quality control sample.

7.4.1 Preparation of calibration standards - fresh multielement calibration standards should be prepared every two weeks or as needed. Dilute each of the stock multielement standard solutions A and B to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. Depending on the sensitivity of the instrument, concentrations ranging from 10 μg/L to 200 μg/L are suggested, except mercury, which should be limited to $\leq$ 5 μg/L. It should be noted the selenium concentration is always a factor of 5 > the other analytes. If the direct addition procedure is being used (Method A, Sect. 10.3), add internal standards (Sect. 7.5) to the calibration standards and store in FEP bottles. Calibration standards

should be verified initially using a quality control sample (Sect. 7.8).

7.5 Internal Standards Stock Solution - 1 mL = 100 μg. Dilute 10 mL of scandium, yttrium, indium, terbium and bismuth stock standards (Sect. 7.3) to 100 mL with reagent water, and store in a FEP bottle. Use this solution concentrate for addition to blanks, calibration standards and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (Method B, Sect. 10.3).

NOTE: If mercury is to be determined by the "direct analysis" procedure, add an aliquot of the gold stock standard (Sect. 7.3.11) to the internal standard solution sufficient to provide a concentration of 100 μg/L in final the dilution of all blanks, calibration standards, and samples.

7.6 Blanks - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.6.1 Calibration blank - Consists of 1% (v/v) nitric acid in reagent grade water. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards.

7.6.2 Laboratory reagent blank (LRB) - Must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including digestion, when applicable. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards to the solution after preparation is complete.

7.6.3 Rinse blank - Consists of 2% (v/v) nitric acid in reagent grade water.

NOTE: If mercury is to be determined by the "direct analysis" procedure, add gold (Sect. 7.3.11) to the rinse blank to a concentration of 100 μg/L.

7.7 Tuning Solution - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (Sect. 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 μg/L of each element. Internal standards are not added to this solution. (Depending on the sensitivity of the instrument, this solution may need to be diluted 10 fold.)

7.8 Quality Control Sample (QCS) - The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution

analyzed will depend on the sensitivity of the instrument. To prepare the QCS dilute an appropriate aliquot of analytes to a concentration ≤ 100 µg/L in 1% (v/v) nitric acid. Because of lower sensitivity, selenium may be diluted to a concentration of < 500 µg/L, however, in all cases, mercury should be limited to a concentration of ≤ 5 µg/L. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards after dilution, mix and store in a FEP bottle. The QCS should be analyzed as needed to meet data-quality needs and a fresh solution should be prepared quarterly or more frequently as needed.

7.9 Laboratory Fortified Blank (LFB) - To an aliquot of LRB, add aliquots from multielement stock standards A and B (Sect. 7.4) to prepared the LFB. Depending on the sensitivity of the instrument, the fortified concentration used should range from 40 µg/L to 100 µg/L for each analyte, except selenium and mercury. For selenium the concentration should range from 200 µg/L to 500 µg/L, while the concentration range mercury should be limited to 2 µg/L to 5 µg/L. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards to this solution after preparation has been completed.

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 processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months before analysis.

8.2 For the determination of 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. Use a portion of the 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 sixteen 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 sixteen hours until verified to be pH < 2. See Section 8.1.

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

8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, 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 calibration 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 calibration 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 calibration ranges - Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. 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 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 or as required to meet data-

quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Sect. 7.8). To verify the calibration standards the determined mean concentration from 3 analyses of the QCS must be within ± 10% of the stated QCS value. If the QCS is used for determining acceptable on-going instrument performance, analysis of the QCS prepared to a concentration of 100 µg/L must be within ± 10% of the stated value or within the acceptance limits listed in Table 8, whichever is the greater. (If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance.) If the calibration standards and/or acceptable instrument performance cannot be verified, 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 limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit.[7] 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 inappropriately 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 (Sect. 9.4) can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 7.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Sect.

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 (Sect. 7.6.2) with each batch of 20 or fewer of samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. 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 (Sect. 7.9) 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% (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 required control limits of 85-115%. 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 - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration run the calibration blank and calibration standards as surrogate samples immediately following each calibration routine, after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of all analytes within the standard solutions must be within ± 10% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. (The instrument responses from the calibration check may be used for recalibration purposes, however, it must be verified before continuing sample analysis.) If the continuing calibration check is not confirmed within ± 15%, the previous ten samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous ten samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

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 (Sect 9.4.2) is required.

9.4.2 The laboratory must add a known amount of 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. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Sect. 7.9). For solid samples, the concentration added should be 100 mg/kg equivalent (200 µg/L in the analysis solution) except silver which should be limited to 50 mg/kg (Sect 1.8). Over time, samples from all routine sample sources should be fortified.

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 of the analyte added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, 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 recovery of any analyte falls outside the designated range and 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. 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 an uncorrected matrix effect.

9.4.5 Internal standards responses - The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze. If after flushing the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Operating conditions - Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided.

The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions which were used to generate precision and recovery data for this method (Sect. 13) are included in Table 6.

10.2 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument until such time it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.

10.2.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 min for the instrument to warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24,25,26. Resolution at high mass is indicated by lead isotopes 206,207,208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.2.2 Instrument stability must be demonstrated by running the tuning solution (Sect. 7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

10.3 Internal Standardization - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 3. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of five internal standards; scandium, yttrium, indium, terbium and bismuth. These were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution (Method A, Sect. 10.3), or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil (Method B, Sect. 10.3). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 20 µg/L to 200 µg/L of each internal standard is recommended.

Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

10.4 Calibration - Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated using one of the internal standard routines (Method A or B) described in Section 10.3. The instrument must be calibrated for the analytes to be determined using the calibration blank (Sect. 7.6.1) and calibration standards A and B (Sect. 7.4.1) prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

10.5 The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample (Sect. 4.1.5). Solutions should be aspirated for 30 sec prior to the acquisition of data to allow equilibrium to be established.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot ($\geq$ 20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards, cap the tube and mix. The sample is now ready for analysis (Sect. 1.2). Allowance for sample dilution should be made in the 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. For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis follow the procedure given in Sections 11.2.2 through 11.2.8.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with < 1 NTU turbidity), transfer a 100-mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (Sects. 1.2, 1.3, 1.7, & 1.8). (When necessary, smaller sample aliquot volumes may be used.)

NOTE: If the sample contains undissolved solids > 1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 thru 11.3.7.

11.2.3 Add 2 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 2 h for a 100 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 $HCl-H_2O$ azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask or 50-mL class A stoppered graduated cylinder, 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 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.)

11.2.8 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 50-mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards and mix. 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 Solid Sample Preparation - Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (> 20 g) to tared weighing dish, weigh the sample and record the wet weight (WW). (For samples with < 35% moisture a 20 g portion is sufficient. For samples with moisture > 35% a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight (DW) for calculation of percent solids (Sect. 12.6). (The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction.

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

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.) Also, a block digester capable of maintaining a temperature of 95°C

and equipped with 250-mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 min. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the $HCl-H_2O$ azeotrope. Some solution evaporation will occur (3 to 4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.)

11.3.7 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 100-mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are > 0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. If the direct addition procedure (Method A, Sect. 10.3) is being used, add internal standards and mix. The sample extract 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.

NOTE: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

11.4 Sample Analysis

11.4.1 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen the sample for elements at high concentration. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of the analytical data.

11.4.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (Sect. 10.0).

11.4.3 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for data reporting.

11.4.4 All masses which might affect data quality must be monitored during the analytical run. As a minimum, those masses prescribed in Table 4 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

11.4.5 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.6 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute (Sect. 4.1.5). Samples should be aspirated for 30 sec prior to the collection of data.

11.4.7 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Elemental equations recommended for sample data calculations are listed in Table 5. Sample data should be reported in units of μg/L for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL.

12.2 For 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.

12.3 For aqueous samples prepared by total recoverable procedure (Sect. 11.2), multiply solution concentrations by the dilution factor 1.25. If additional dilutions were made to any samples or an aqueous sample

was prepared using the acid-mixture procedure described in Section 11.3, the appropriate factor should be applied to the calculated sample concentrations.

12.4 For total recoverable analytes in solid samples (Sect. 11.3), round the solution analyte concentrations (μg/L in the analysis solution) as instructed in Section 12.2. Multiply the μ/L concentrations in the analysis solution by the factor 0.005 to calculate the mg/L analyte concentration in the 100-mL extract solution. (If additional dilutions were made to any samples, the appropriate factor should be applied to calculate analyte concentrations in the extract solution.) Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

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

where: C = Concentration in the extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1L)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.5 To report percent solids in solid samples (Sect. 11.3) calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 11.3 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

12.6 Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, as the chloride ion is a common constituent of environmental samples.

12.7 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to

both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

12.8 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 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 6. Total recoverable digestion and "direct analysis" MDLs determined using the procedure described in Sect. 9.2.4, are listed in Table 7.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 9 for five water samples representing drinking water, surface water, ground water and waste effluent. Samples were prepared using the procedure described in Sect. 11.2. For each matrix, five replicates were analyzed and the average of the replicates used for determining the sample background concentration for each element. Two further pairs of duplicates were fortified at different concentration levels. For each method element, 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 8.

13.3 Data obtained from single laboratory testing of the method are summarized in Table 10 for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil and EPA Electroplating Sludge. Samples were prepared using the procedure described in Sect. 11.3. For each method element, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples were determined as for Sect. 13.2.

13.4 Data obtained from single laboratory testing of the method for drinking water analysis using the "direct analysis" procedure (Sect. 11.2.1) are given in Table 11. Three drinking water samples of varying hardness collected from Regions 4, 6, and 10 were fortified to contain 1 µg/L of all metal primary contaminants, except selenium, which was added to a concentration of 20 µg/L. For each matrix, four replicate aliquots were analyzed to determine the sample background concentration of each analyte and four fortified aliquots were analyzed to determine mean percent recovery in each matrix. Listed in the Table 11 are the average mean percent recovery of each analyte in the three matrices and the standard deviation of the mean percent recoveries.

13.5 Listed in Table 12 are the regression equations for precision and bias developed from the joint USEPA/Association of Official Analytical Chemists (AOAC) multilaboratory validation study conducted on this

method. These equations were developed from data received from 13 laboratories on reagent water, drinking water and ground water. Listed in Tables 13 and 14, respectively, are the precision and recovery data from a wastewater digestate supplied to all laboratories and from a wastewater of the participant's choice. For a complete review of the study see reference 11. Section 16.0 of this method.

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. 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: ESTIMATED INSTRUMENT DETECTION LIMITS

ELEMENT	RECOMMENDED ANALYTICAL MASS	ESTIMATED IDLs (µg/L) SCANNING MODE[1]	ESTIMATED IDLs (µg/L) SELECTIVE ION MONITORING MODE[2,3]
Aluminum	27	0.05	0.02
Antimony	123	0.08	0.008
Arsenic[3]	75	0.9	0.02
Barium	137	0.5	0.03
Beryllium	9	0.1	0.02
Cadmium	111	0.1	0.02
Chromium	52	0.07	0.04
Cobalt	59	0.03	0.002
Copper	63	0.03	0.004
Lead	206.207,208	0.08	0.015
Manganese	55	0.1	0.007
Mercury	202	n.a.	0.2
Molybdenum	98	0.1	0.005
Nickel	60	0.2	0.07
Selenium[3]	82	5	1.3
Silver	107	0.05	0.004
Thallium	205	0.09	0.014
Thorium	232	0.03	0.005
Uranium	238	0.02	0.005
Vanadium	51	0.02	0.006
Zinc	66	0.2	0.07

Instrument detection limits (3σ) estimated from seven replicate integrations of the blank (1% v/v nitric acid) following calibration of the instrument with three replicate integrations of a multi-element standard.

1 Instrument operating conditions and data acquisition mode are given in Table 6.

2 IDLs determined using state-of-the-art instrumentation (1994). Data for ^{75}As, ^{77}Se, and ^{82}Se were acquired using a dwell time of 4.096 sec with 1500 area count per sec ^{83}Kr present in argon supply. All other data were acquired using a dwell time of 1.024 sec per AMU monitored.

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS		
Molecular Ion	Mass	Element Interference[a]
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se

[a] method elements or internal standards affected by the molecular ions.

TABLE 2 (Continued).

MATRIX MOLECULAR IONS		
BROMIDE[12]		
Molecular Ion	**Mass**	**Element Interference**
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	98	Mo
$Ar^{81}Br^+$	121	Sb
CHLORIDE		
Molecular Ion	**Mass**	**Element Interference**
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
SULPHATE		
Molecular Ion	**Mass**	**Element Interference**
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V,Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	
PHOSPHATE		
Molecular Ion	**Mass**	**Element Interference**
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	
GROUP I, II METALS		
Molecular Ion	**Mass**	**Element Interference**
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	

TABLE 2 (Continued).

MATRIX MOLECULAR IONS

MATRIX OXIDES*

Molecular Ion	Masses	Element Interference
TiO	62-66	Ni,Cu,Zn
ZrO	106-112	Ag,Cd
MoO	108-116	Cd

* Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes are monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 3: INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^{+} (105 amu) and YOH^{+} (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Internal standards recommended for use with this method are shown in bold face. Preparation procedures for these are included in Section 7.3.

TABLE 4: RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121,123	Antimony
75	Arsenic
135,137	Barium
9	Beryllium
106,108,111,114	Cadmium
52,53	Chromium
59	Cobalt
63,65	Copper
206,207,208	Lead
55	Manganese
95,97,98	Molybdenum
60,62	Nickel
77,82	Selenium
107,109	Silver
203,205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66,67,68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

NOTE: Isotopes recommended for analytical determination are underlined.

TABLE 5: RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Al	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{123}C)$	
As	$(1.000)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)]$	(1)
Ba	$(1.000)(^{137}C)$	
Be	$(1.000)(^{9}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(2)
Cr	$(1.000)(^{52}C)$	(3)
Co	$(1.000)(^{59}C)$	
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(4)
Mn	$(1.000)(^{55}C)$	
Mo	$(1.000)(^{98}C)-(0.146)(^{99}C)$	(5)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(6)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Th	$(1.000)(^{232}C)$	
U	$(1.000)(^{238}C)$	
V	$(1.000)(^{51}C)-(3.127)[(^{53}C)-(0.113)(^{52}C)]$	(7)
Zn	$(1.000)(^{66}C)$	

TABLE 5 (Continued)

INTERNAL STANDARDS

Element	Elemental Equation	Note
Bi	(1.000)(^{209}C)	
In	(1.000)(^{115}C)-(0.016)(^{118}C)	(8)
Sc	(1.000)(^{45}C)	
Tb	(1.000)(^{159}C)	
Y	(1.000)(^{89}C)	

C - calibration blank subtracted counts at specified mass.
(1) - correction for chloride interference with adjustment for ^{77}Se. ArCl 75/77 ratio may be determined from the reagent blank. Isobaric mass 82 must be from Se only and not BrH^+.
(2) - correction for MoO interference. Isobaric mass 106 must be from Cd only not ZrO^+. An additional isobaric elemental correction should be made if palladium is present.
(3) - in 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank. Isobaric mass must be from Cr only not ArC^+.
(4) - allowance for isotopic variability of lead isotopes.
(5) - isobaric elemental correction for ruthenium.
(6) - some argon supplies contain krypton as an impurity. Selenium is corrected for ^{82}Kr by background subtraction.
(7) - correction for chloride interference with adjustment for ^{53}Cr. ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only not ArC^+.
(8) - isobaric elemental correction for tin.

TABLE 6: INSTRUMENT OPERATING CONDITIONS FOR PRECISION AND RECOVERY DATA[1]

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15°C
Data Acquisition	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 μs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 minutes per sample

1 The described instrument and operating conditions were used to determine the scanning mode MDL data listed in Table 7 and the precision and recovery data given in Tables 9 and 10.

TABLE 7: METHOD DETECTION LIMITS

AMU ELEMENT	SCANNING MODE[1] TOTAL RECOVERABLE AQUEOUS µg/L	SCANNING MODE[1] SOLIDS mg/kg	SELECTIVE ION MONITORING MODE[2] TOTAL RECOVERABLE AQUEOUS µg/L	SELECTIVE ION MONITORING MODE[2] DIRECT ANALYSIS[3] AQUEOUS µg/L
27 Al	1.0	0.4	1.7	0.04
123 Sb	0.4	0.2	0.04	0.02
75 As	1.4	0.6	0.4	0.1
137 Ba	0.8	0.4	0.04	0.04
9 Be	0.3	0.1	0.02	0.03
111 Cd	0.5	0.2	0.03	0.03
52 Cr	0.9	0.4	0.08	0.08
59 Co	0.09	0.04	0.004	0.003
63 Cu	0.5	0.2	0.02	0.01
206,207,208 Pb	0.6	0.3	0.05	0.02
55 Mn	0.1	0.05	0.02	0.04
202 Hg	n.a.	n.a.	n.a.	0.2
98 Mo	0.3	0.1	0.01	0.01
60 Ni	0.5	0.2	0.06	0.03
82 Se	7.9	3.2	2.1	0.5
107 Ag	0.1	0.05	0.005	0.005
205 Tl	0.3	0.1	0.02	0.01
232 Th	0.1	0.05	0.02	0.01
238 U	0.1	0.05	0.01	0.01
51 V	2.5	1.0	0.9	0.05
66 Zn	1.8	0.7	0.1	0.2

1 Data acquisition mode given in Table 6. Total recoverable MDL concentrations are computed for original matrix with allowance for sample dilution during preparation. Listed MDLs for solids calculated from determined aqueous MDLs.

2 MDLs determined using state-of-the-art instrumentation (1994). Data for ^{75}As, ^{77}Se, and ^{82}Se were acquired using a dwell time of 4.096 sec with 1500 area count per sec ^{83}Kr present in argon supply. All other data were acquired using a dwell time of 1.024 sec per AMU monitored.

3 MDLs were determined from analysis of 7 undigested aqueous sample aliquots.

n.a.- not applicable. Total recoverable digestion not suitable for organo-mercury compounds.

TABLE 8: ACCEPTANCE LIMITS FOR QC CHECK SAMPLE

ELEMENT	QC Check Sample Conc.	METHOD PERFORMANCE (µg/L)[1] Average Recovery	Standard Deviation[2] (S_r)	Acceptance Limits[3] µg/L
Aluminum	100	100.4	5.49	84-117
Antimony	100	99.9	2.40	93-107
Arsenic	100	101.6	3.66	91-113
Barium	100	99.7	2.64	92-108
Beryllium	100	105.9	4.13	88-112[4]
Cadmium	100	100.8	2.32	94-108
Chromium	100	102.3	3.91	91-114
Cobalt	100	97.7	2.66	90-106
Copper	100	100.3	2.11	94-107
Lead	100	104.0	3.42	94-114
Manganese	100	98.3	2.71	90-106
Molybdenum	100	101.0	2.21	94-108
Nickel	100	100.1	2.10	94-106
Selenium	100	103.5	5.67	86-121
Silver	100	101.1	3.29	91-111[5]
Thallium	100	98.5	2.79	90-107
Thorium	100	101.4	2.60	94-109
Uranium	100	102.6	2.82	94-111
Vanadium	100	100.3	3.26	90-110
Zinc	100	105.1	4.57	91-119

1 Method performance characteristics calculated using regression equations from collaborative study, reference 11.
2 Single-analyst standard deviation, S_r.
3 Acceptance limits calculated as average recovery ± 3 standard deviations.
4 Acceptance limits centered at 100% recovery.
5 Statistics estimated from summary statistics at 48 and 64 µg/L.

TABLE 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

DRINKING WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	175	50	115.8	5.9	0.4	200	102.7	1.6	1.1
Sb	<0.4	10	99.1	0.7	2.0	100	100.8	0.7	2.0
As	<1.4	50	99.7	0.8	2.2	200	102.5	1.1	2.9
Ba	43.8	50	94.8	3.9	5.8	200	95.6	0.8	1.7
Be	<0.3	10	113.5	0.4	0.9	100	111.0	0.7	1.8
Cd	<0.5	10	97.0	2.8	8.3	100	101.5	0.4	1.0
Cr	<0.9	10	111.0	3.5	9.0	100	99.5	0.1	0.2
Co	0.11	10	94.4	0.4	1.1	100	93.6	0.5	1.4
Cu	3.6	10	101.8	8.8	17.4	100	91.6	0.3	0.3
Pb	0.87	10	97.8	2.0	2.8	100	99.0	0.8	2.2
Mn	0.96	10	96.9	1.8	4.7	100	95.8	0.6	1.8
Mo	1.9	10	99.4	1.6	3.4	100	98.6	0.4	1.0
Ni	1.9	10	100.2	5.7	13.5	100	95.2	0.5	1.3
Se	<7.9	50	99.0	1.8	5.3	200	93.5	3.5	10.7
Ag	<0.1	50	100.7	1.5	4.2	200	99.0	0.4	1.0
Tl	<0.3	10	97.5	0.4	1.0	100	98.5	1.7	4.9
Th	<0.1	10	109.0	0.7	1.8	100	106.0	1.4	3.8
U	0.23	10	110.7	1.4	3.5	100	107.8	0.7	1.9
V	<2.5	50	101.4	0.1	0.4	200	97.5	0.7	2.1
Zn	5.2	50	103.4	3.3	7.7	200	96.4	0.5	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 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

WELL WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	34.3	50	100.1	3.9	0.8	200	102.6	1.1	1.3
Sb	0.46	10	98.4	0.9	1.9	100	102.5	0.7	1.9
As	<1.4	50	110.0	6.4	16.4	200	101.3	0.2	0.5
Ba	106	50	95.4	3.9	3.3	200	104.9	1.0	1.6
Be	<0.3	10	104.5	0.4	1.0	100	101.4	1.2	3.3
Cd	1.6	10	88.6	1.7	3.8	100	98.6	0.6	1.6
Cr	<0.9	10	111.0	0.0	0.0	100	103.5	0.4	1.0
Co	2.4	10	100.6	1.0	1.6	100	104.1	0.4	0.9
Cu	37.4	10	104.3	5.1	1.5	100	100.6	0.8	1.5
Pb	3.5	10	95.2	2.5	1.5	100	99.5	1.4	3.9
Mn	2770	10	*	*	1.8	100	*	*	0.7
Mo	2.1	10	103.8	1.1	1.6	100	102.9	0.7	1.9
Ni	11.4	10	116.5	6.3	6.5	100	99.6	0.3	0.0
Se	<7.9	50	127.3	8.4	18.7	200	101.3	0.2	0.5
Ag	<0.1	50	99.2	0.4	1.0	200	101.5	1.4	3.9
Tl	<0.3	10	93.9	0.1	0.0	100	100.4	1.8	5.0
Th	<0.1	10	103.0	0.7	1.9	100	104.5	1.8	4.8
U	1.8	10	106.0	1.1	1.6	100	109.7	2.5	6.3
V	<2.5	50	105.3	0.8	2.1	200	105.8	0.2	0.5
Zn	554	50	*	*	1.2	200	102.1	5.5	3.2

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

POND WATER

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	610	50	*	*	1.7	200	78.2	9.2	5.5
Sb	<0.4	10	101.1	1.1	2.9	100	101.5	3.0	8.4
As	<1.4	50	100.8	2.0	5.6	200	96.8	0.9	2.6
Ba	28.7	50	102.1	1.8	2.4	200	102.9	3.7	9.0
Be	<0.3	10	109.1	0.4	0.9	100	114.4	3.9	9.6
Cd	<0.5	10	106.6	3.2	8.3	100	105.8	2.8	7.6
Cr	2.0	10	107.0	1.0	1.6	100	100.0	1.4	3.9
Co	0.79	10	101.6	1.1	2.7	100	101.7	1.8	4.9
Cu	5.4	10	107.5	1.4	1.9	100	98.1	2.5	6.8
Pb	1.9	10	108.4	1.5	3.2	100	106.1	0.0	0.0
Mn	617	10	*	*	1.1	100	139.0	11.1	4.0
Mo	0.98	10	104.2	1.4	3.5	100	104.0	2.1	5.7
Ni	2.5	10	102.0	2.3	4.7	100	102.5	2.1	5.7
Se	<7.9	50	102.7	5.6	15.4	200	105.5	1.4	3.8
Ag	0.12	50	102.5	0.8	2.1	200	105.2	2.7	7.1
Tl	<0.3	10	108.5	3.2	8.3	100	105.0	2.8	7.6
Th	0.19	10	93.1	3.5	10.5	100	93.9	1.6	4.8
U	0.30	10	107.0	2.8	7.3	100	107.2	1.8	4.7
V	3.5	50	96.1	5.2	14.2	200	101.5	0.2	0.5
Zn	6.8	50	99.8	1.7	3.7	200	100.1	2.8	7.7

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

SEWAGE TREATMENT PRIMARY EFFLUENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	1150	50	*	*	3.5	200	100.0	13.8	1.5
Sb	1.5	10	95.7	0.4	0.9	100	104.5	0.7	1.9
As	<1.4	50	104.2	4.5	12.3	200	101.5	0.7	2.0
Ba	202	50	79.2	9.9	2.5	200	108.6	4.6	5.5
Be	<0.3	10	110.5	1.8	4.5	100	106.4	0.4	0.9
Cd	9.2	10	101.2	1.3	0.0	100	102.3	0.4	0.9
Cr	128	10	*	*	1.5	100	102.1	1.7	0.4
Co	13.4	10	95.1	2.7	2.2	100	99.1	1.1	2.7
Cu	171	10	*	*	2.4	100	105.2	7.1	0.7
Pb	17.8	10	95.7	3.8	1.1	100	102.7	1.1	2.5
Mn	199	10	*	*	1.5	100	103.4	2.1	0.7
Mo	136	10	*	*	1.4	100	105.7	2.4	2.1
Ni	84.0	10	88.4	16.3	4.1	100	98.0	0.9	0.0
Se	<7.9	50	112.0	10.9	27.5	200	108.8	3.0	7.8
Ag	10.9	50	97.1	0.7	1.5	200	102.6	1.4	3.7
Tl	<0.3	10	97.5	0.4	1.0	100	102.0	0.0	0.0
Th	0.11	10	15.4	1.8	30.3	100	29.3	0.8	8.2
U	0.71	10	109.4	1.8	4.3	100	109.3	0.7	1.8
V	<2.5	50	90.9	0.9	0.6	200	99.4	2.1	6.0
Zn	163	50	85.8	3.3	0.5	200	102.0	1.5	1.9

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 9 : PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont).

INDUSTRIAL EFFLUENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	44.7	50	98.8	8.7	5.7	200	90.4	2.1	2.2
Sb	2990	10	*	*	0.3	100	*	*	0.0
As	<1.4	50	75.1	1.8	6.7	200	75.0	0.0	0.0
Ba	100	50	96.7	5.5	3.4	200	102.9	1.1	0.7
Be	<0.3	10	103.5	1.8	4.8	100	100.0	0.0	0.0
Cd	10.1	10	106.5	4.4	2.4	100	97.4	1.1	2.8
Cr	171	10	*	*	0.0	100	127.7	2.4	1.7
Co	1.3	10	90.5	3.2	8.7	100	90.5	0.4	1.3
Cu	101	10	*	*	0.9	100	92.5	2.0	1.6
Pb	294	10	*	*	2.6	100	108.4	2.1	0.0
Mn	154	10	*	*	2.8	100	103.6	3.7	1.6
Mo	1370	10	*	*	1.4	100	*	*	0.7
Ni	17.3	10	107.4	7.4	5.0	100	88.2	0.7	1.0
Se	15.0	50	129.5	9.3	15.1	200	118.3	1.9	3.6
Ag	<0.1	50	91.8	0.6	1.7	200	87.0	4.9	16.1
Tl	<0.3	10	90.5	1.8	5.5	100	98.3	1.0	2.8
Th	0.29	10	109.6	1.2	2.7	100	108.7	0.0	0.0
U	0.17	10	104.8	2.5	6.6	100	109.3	0.4	0.9
V	<2.5	50	74.9	0.1	0.3	200	72.0	0.0	0.0
Zn	43.4	50	85.0	4.0	0.6	200	97.6	1.0	0.4

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 10 : PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5170	20	*	*	-	100	*	*	-
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	102.5	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	151.7	25.7	23.7
Mn	370	20	*	*	12.7	100	85.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	95.2	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	102.3	0.8	0.8
Se	<3.2	20	79.5	7.4	26.4	100	100.7	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	94.8	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	97.9	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	76.0	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	102.9	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	106.7	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100	113.4	12.9	14.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 10 : PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont).

NBS 1645 RIVER SEDIMENT

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5060	20	*	*	-	100	*	*	-
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	-	100	*	*	-
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	-	100	-	-	-
Mn	717	20	*	*	-	100	-	-	-
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	<3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 10 : PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont).

EPA ELECTROPLATING SLUDGE #286

Element	Sample Concn. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S(R)	RPD
Al	5110	20	*	*	-	100	*	*	-
Sb	8.4	20	55.4	1.5	4.1	100	61.0	0.2	0.9
As	41.8	20	91.0	2.3	1.7	100	94.2	0.8	1.5
Ba	27.3	20	1.8	7.1	8.3	100	0	1.5	10.0
Be	0.25	20	92.0	0.9	2.7	100	93.4	0.3	0.9
Cd	112	20	85.0	5.2	1.6	100	88.5	0.8	0.5
Cr	7980	20	*	*	-	100	*	*	-
Co	4.1	20	89.2	1.8	4.6	100	88.7	1.5	4.6
Cu	740	20	*	*	6.0	100	61.7	20.4	5.4
Pb	1480	20	*	*	-	100	*	*	-
Mn	295	20	*	*	-	100	-	-	-
Mo	13.3	20	82.9	1.2	1.3	100	89.2	0.4	1.0
Ni	450	20	*	*	6.8	100	83.0	10.0	4.5
Se	3.5	20	89.7	3.7	4.2	100	91.0	6.0	18.0
Ag	5.9	20	89.8	2.1	4.6	100	85.1	0.4	1.1
Tl	1.9	20	96.9	0.9	2.4	100	98.9	0.9	2.4
Th	3.6	20	91.5	1.3	3.2	100	97.4	0.7	2.0
U	2.4	20	107.7	2.0	4.6	100	109.6	0.7	1.8
V	21.1	20	105.6	1.8	2.1	100	97.4	1.1	2.5
Zn	13300	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 11 : PRIMARY DRINKING WATER CONTAMINANTS
PRECISION AND RECOVERY DATA

ANALYTE	REGIONAL SAMPLE BACKGROUND CONCENTRATION, µg/L (IV)	(VI)	(X)	AVERAGE MEAN[1] % RECOVERY	S(R)
Antimony	0.16	0.07	0.03	114%	1.9
Arsenic	< MDL	2.4	1.0	93	8.5
Barium	4.6	280	14.3	(*)	-
Beryllium	< MDL	< MDL	< MDL	100%	8.2
Cadmium	0.05	0.05	0.03	81	4.0
Chromium	0.71	5.1	0.10	94	2.5
Copper	208	130	14.3	(*)	-
Lead	1.2	1.2	2.5	91	2.6
Mercury	< MDL	0.23	< MDL	86	11.4
Nickel	1.7	3.6	0.52	101%	11.5
Selenium	< MDL	4.3	< MDL	98	8.4
Thallium	< MDL	0.01	< MDL	100	1.4

1 The three regional waters were fortified with 1.0 µg/L of all analytes listed, except selenium, which was fortified to 20 µg/L.

(*) Recovery of barium and copper was not calculated because the analyte addition was < 20% the sample background concentration in all waters. (Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration. Sect.9.4.3)

S(R) Standard deviation of the mean percent recoveries.

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Aluminum	8.00	10.01	2.33	1.74	$\bar{X} = 0.992C + 1.19$	11.18	9.02	6.34	$\bar{X} = 0.954C + 2.38$	9.86	7.10	2.70	$\bar{X} = 0.946C + 2.20$
	12.00	10.98	5.16		$S_R = 0.056\bar{X} + 2.59$[c]	11.02	3.02		$S_R = 7.70$[d]	13.40	10.27		$S_R = 0.169\bar{X} + 6.22$[c]
	56.00	59.13	5.55	4.19	$S_r = 0.042\bar{X} + 1.27$	56.97	7.14	6.18	$S_r = 0.013\bar{X} + 6.17$	51.75	10.78	16.92	$S_r = 0.172\bar{X} + 0.75$[c]
	80.00	82.59	4.92			82.73	8.01			82.83	33.37		
	160.00	158.95	11.82	8.90		159.89	11.94	10.59		155.40	15.39	19.27	
	200.00	200.89	8.61			189.98	12.97			189.64	31.46		
Antimony	2.80	2.75	0.27	0.27	$\bar{X} = 0.999C + 0.04$	2.73	0.29	0.17	$\bar{X} = 0.983C + 0.03$	2.82	0.19	0.22	$\bar{X} = 1.003C + 0.01$
	4.00	4.22	0.46		$S_R = 0.013\bar{X} + 0.61$[c]	4.10	0.47		$S_R = 0.049\bar{X} + 0.19$	4.02	0.35		$S_R = 0.059\bar{X} + 0.04$
	20.00	19.76	1.09	0.85	$S_r = 0.022\bar{X} + 0.20$	19.17	1.37	0.66	$S_r = 0.026\bar{X} + 0.08$	20.12	0.82	0.97	$S_r = 0.058\bar{X} + 0.02$
	28.00	27.48	1.38			26.48	1.72			27.77	1.38		
	80.00	82.52	2.24	1.76		83.43	2.05	2.46		80.34	9.14	6.80	
	100.00	98.06	1.34			97.19	5.31			101.09	2.89		
Arsenic	8.00	8.64	3.01	3.02	$\bar{X} = 1.013C + 0.50$	9.00	3.13	1.96	$\bar{X} = 0.993C + 0.57$	10.40	5.17	4.90	$\bar{X} = 0.949C + 0.91$
	12.00	12.58	3.18		$S_R = 0.031\bar{X} + 2.74$	11.37	1.77		$S_R = 0.018\bar{X} + 2.55$	7.85	4.62		$S_R = 0.048\bar{X} + 4.52$
	56.00	55.44	4.64	3.51	$S_r = 0.007\bar{X} + 2.95$	53.77	4.12	4.07	$S_r = 0.031\bar{X} + 1.65$	53.25	3.49	7.88	$S_r = 0.059\bar{X} + 4.29$
	80.00	85.15	2.54			87.72	4.14			83.60	12.46		
	160.00	161.80	11.15	3.96		157.56	4.83	6.30		159.86	11.67	14.94	
	200.00	201.52	10.81			197.99	10.66			194.41	18.24		
Barium	8.01	7.58	0.50	0.48	$\bar{X} = 1.001C - 0.36$	8.21	1.21	1.11	$\bar{X} = 0.995C + 0.37$	8.04	2.60	2.24	$\bar{X} = 1.055C - 0.21$
	12.00	11.81	1.05		$S_R = 0.039\bar{X} + 0.31$	12.56	1.79		$S_R = 0.045\bar{X} + 0.97$[c]	12.85	1.45		$S_R = 0.020\bar{X} + 2.05$
	48.00	47.32	1.60	1.82	$S_r = 0.024\bar{X} + 0.25$	49.13	3.72	3.77	$S_r = 0.040\bar{X} + 0.72$[c]	50.12	2.98	2.19	$S_r = 0.014\bar{X} + 2.08$
	64.00	65.52	2.90			65.30	4.16			69.53	2.66		
	160.00	157.09	6.53	4.07		155.25	7.82	5.67		164.44	8.81	6.61	
	200.00	198.53	8.28			196.52	5.70			208.32	9.22		
Beryllium	2.80	3.31	0.81	0.26	$\bar{X} = 1.056C + 0.32$	3.15	0.47	0.31	$\bar{X} = 1.055C + 0.20$	3.02	0.46	0.22	$\bar{X} = 1.049C + 0.08$
	4.00	4.45	0.73		$S_R = 0.067\bar{X} + 0.55$	4.45	0.51		$S_R = 0.057\bar{X} + 0.28$	4.27	0.44		$S_R = 0.084\bar{X} + 0.16$
	20.00	22.38	2.76	1.00	$S_r = 0.038\bar{X} + 0.11$	21.27	1.23	0.63	$S_r = 0.016\bar{X} + 0.25$	21.55	1.72	1.10	$S_r = 0.043\bar{X} + 0.06$
	28.00	30.02	2.86			29.57	1.67			29.24	2.09		
	80.00	84.18	4.79	4.02		87.59	6.89	1.88		84.23	9.05	4.32	
	100.00	102.88	5.90			102.64	6.27			103.39	10.17		
Cadmium	4.00	4.01	0.34	0.20	$\bar{X} = 1.007C + 0.07$	4.11	0.88	0.71	$\bar{X} = 0.985C + 0.10$	3.98	0.48	0.14	$\bar{X} = 0.944C + 0.11$
	6.00	6.32	0.49		$S_R = 0.041\bar{X} + 0.19$	5.87	0.58		$S_R = 0.031\bar{X} + 0.65$	5.62	0.73		$S_R = 0.017\bar{X} + 1.09$[c]
	20.00	19.81	1.12	0.86	$S_r = 0.022\bar{X} + 0.10$[c]	19.57	1.45	1.26	$S_r = 0.021\bar{X} + 0.61$	18.15	1.73	0.88	$S_r = 0.029\bar{X} + 0.01$
	28.00	28.33	0.94			27.68	1.27			26.86	2.59		
	80.00	81.28	4.91	1.33		80.62	4.45	2.02		77.83	3.05	1.88	
	100.00	100.11	3.24			98.15	3.60			95.31	2.04		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Chromium	8.00	8.27	0.32	1.54	$\bar{X} = 1.017\underline{C} + 0.62$	9.46	2.34	2.08	$\bar{X} = 0.990\underline{C} + 1.45$	8.98	1.47	0.37	$\bar{X} = 1.026\underline{C} + 0.89$
	12.00	13.88	3.10		$S_R = 0.066\bar{X} + 0.48$	13.10	2.39		$S_R = 0.015\bar{X} + 2.19$	13.42	1.13		$S_R = 0.067\bar{X}$ 0.68
	56.00	57.86	4.03	2.68	$S_r = 0.026\bar{X} + 1.25$	56.04	2.24	1.29	$S_r = 2.18$[d]	59.35	5.99	5.42	$S_r = 0.068\bar{X} - 0.37$
	80.00	84.73	2.65			84.38	3.18			83.90	5.70		
	160.00	157.66	13.62	6.97		158.24	5.12	3.16		164.58	14.11	9.80	
	200.00	197.43	9.47			196.72	7.47			199.88	11.19		
Cobalt	0.80	0.88	0.10	0.05	$\bar{X} = 0.977\underline{C} + 0.01$	0.92	0.45	0.31	$\bar{X} = 0.964\underline{C} + 0.06$	0.85	0.13	0.09	$\bar{X} = 0.989\underline{C} - 0.01$
	1.21	0.98	0.04		$S_R = 0.028\bar{X} + 0.06$	1.02	0.10		$S_R = 0.019\bar{X} + 0.32$	1.04	0.18		$S_R = 0.057\bar{X} + 0.09$
	20.10	20.77	0.74	0.67	$S_r = 0.027\bar{X} + 0.02$	20.45	0.91	0.53	$S_r = 0.014\bar{X} + 0.30$	20.81	1.11	1.12	$S_r = 0.012\bar{X} + 0.40$[e]
	28.20	27.75	0.96			27.29	1.22			28.07	2.16		
	80.50	78.59	2.29	2.31		78.04	3.72	1.84		79.26	4.66	1.34	
	101.00	98.79	2.94			97.62	4.62			99.41	4.22		
Copper	4.00	3.88	0.73	0.59	$\bar{X} = 1.003\underline{C} - 0.05$	3.33	0.85	0.99	$\bar{X} = 0.976\underline{C} - 0.38$	3.86	1.40	0.71	$\bar{X} = 0.977\underline{C} - 0.01$
	6.00	6.14	1.00		$S_R = 0.037\bar{X} + 0.64$	5.95	1.78		$S_R = 0.063\bar{X} + 0.86$	5.96	0.95		$S_R = 0.073\bar{X} + 0.92$
	20.00	20.07	1.08	0.92	$S_r = 0.016\bar{X} + 0.51$	18.90	1.64	1.51	$S_r = 0.029\bar{X} + 0.86$	18.97	1.68	2.32	$S_r = 0.077\bar{X} + 0.35$
	28.00	27.97	1.94			27.21	2.76			27.44	2.58		
	80.00	79.80	3.22	1.91		76.64	5.30	3.42		79.30	9.05	6.54	
	100.00	99.57	4.42			96.17	5.64			97.54	11.16		
Lead	4.00	4.00	1.57	1.62	$\bar{X} = 1.043\underline{C} - 0.31$	3.44	1.15	1.18	$\bar{X} = 1.032\underline{C} - 0.30$	4.20	1.13	1.76	$\bar{X} = 1.012\underline{C} + 0.15$
	6.00	5.56	2.00		$S_R = 0.064\bar{X} + 1.43$[c]	6.84	1.10		$S_R = 0.015\bar{X} + 1.06$	6.27	2.38		$S_R = 0.048\bar{X} + 1.27$
	20.00	20.54	2.91	4.36	$S_r = 3.42$[d]	20.18	1.20	1.44	$S_r = 0.011\bar{X} + 1.13$	19.57	2.72	0.88	$S_r = 1.78$[d]
	28.00	30.90	4.58			28.08	1.57			28.55	1.73		
	80.00	80.57	3.13	4.29		80.92	2.30	2.07		82.47	4.38	2.69	
	100.00	102.93	6.62			101.60	3.23			102.47	3.58		
Manganese	0.80	0.86	0.15	0.09	$\bar{X} = 0.983\underline{C} + 0.02$	0.96	0.32	0.42	$\bar{X} = 0.989\underline{C} + 0.10$	0.64	0.22	0.17	$\bar{X} = 0.954\underline{C} - 0.16$
	1.20	1.09	0.12		$S_R = 0.026\bar{X} + 0.11$	1.13	0.38		$S_R = 0.047\bar{X} + 0.29$	0.90	0.21		$S_R = 0.103\bar{X} + 0.14$
	20.00	20.43	0.89	0.72	$S_r = 0.027\bar{X} + 0.06$	21.06	1.32	0.96	$S_r = 0.021\bar{X} + 0.40$	19.61	2.60	2.62	$S_r = 0.025\bar{X} + 0.09$[e]
	28.00	27.53	0.41			27.60	1.47			25.65	4.10		
	80.00	79.00	3.16	2.38		79.57	4.18	2.01		77.38	6.13	2.90	
	100.00	97.60	2.51			97.97	4.10			95.86	6.74		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Molybdenum	2.80	2.63	0.32	0.16	$\bar{X} = 1.012\underline{C} - 0.20$	2.80	0.20	0.32	$\bar{X} = 1.013\underline{C} - 0.07$	3.00	0.47	0.42	$\bar{X} = 1.032\underline{C} - 0.09$
	4.00	3.85	0.31		$S_R = 0.032\underline{X} + 0.22$	3.95	0.47		$S_R = 0.037\underline{X} + 0.17$	3.60	0.90		$S_R = 0.55\underline{X} + 0.43$
	20.00	19.75	0.64	0.64	$S_r = 0.021\bar{X} + 0.09$	19.78	0.60	1.16	$S_r = 0.035\bar{X} + 0.20$	20.69	1.37	1.11	$S_r = 0.042\bar{X} + 0.27$
	28.00	27.87	1.07			27.87	1.51			28.80	2.01		
	80.00	83.07	3.07	1.78		85.65	3.50	3.07		84.26	4.13	4.81	
	100.00	100.08	4.32			99.06	2.89			103.57	6.10		
Nickel	4.00	4.02	0.41	0.50	$\bar{X} = 1.000\underline{C} + 0.12$	3.66	0.53	1.03	$\bar{X} = 0.953\underline{C} - 0.19$	4.81	2.06	2.82	$\bar{X} = 1.022\underline{C} + 0.66$
	6.00	6.36	0.91		$S_R = 0.051\bar{X} + 0.31$	5.44	1.32		$S_R = 0.046\bar{X} + 0.56$	6.67	3.66		$S_R = 0.091\bar{X} + 2.03$
	20.00	19.93	1.30	0.63	$S_r = 0.017\bar{X} + 0.40$	18.42	0.87	1.11	$S_r = 0.023\bar{X} + 0.91$	20.58	3.71	2.37	$S_r = 0.008\bar{X} + 2.75$[c]
	28.00	28.02	1.25			27.09	1.68			30.73	3.75		
	80.00	79.29	2.95	2.55		75.84	4.40	3.94		82.71	9.49	5.42	
	100.00	100.87	7.20			95.83	4.41			101.00	9.89		
Selenium	32.00	33.54	4.63	1.57	$\bar{X} = 1.036\underline{C} - 0.06$	32.57	4.37	3.65	$\bar{X} = 1.022\underline{C} + 0.14$	32.46	4.95	3.24	$\bar{X} = 1.045\underline{C} - 0.83$
	40.00	41.03	6.04		$S_R = 0.051\bar{X} + 3.24$	42.18	3.71		$S_R = 0.056\bar{X} + 2.10$	41.46	3.30		$S_R = 0.037\bar{X} + 2.97$
	80.00	81.40	5.86	5.44	$S_r = 0.061\bar{X} - 0.64$	79.97	6.66	5.28	$S_r = 0.040\bar{X} + 2.15$	81.63	6.94	5.65	$S_r = 0.058\bar{X} + 1.02$
	96.10	98.34	8.57			94.94	7.90			98.92	4.39		
	160.00	163.58	15.69	9.86		163.48	9.17	10.06		167.54	8.69	12.98	
	200.00	214.30	10.57			212.19	16.49			209.21	14.65		
Silver	0.80	0.93	0.09	0.14	$\bar{X} = 0.917\underline{C} + 0.26$	0.70	0.34	0.34	$\bar{X} = 0.888\underline{C} + 0.09$	0.70	0.26	0.10	$\bar{X} = 0.858\underline{C} - 0.00$
	1.20	1.51	0.23		$S_R = 0.196\bar{X} - 0.09$	1.37	0.33		$S_R = 0.186\bar{X} + 0.17$	0.98	0.28		$S_R = 0.169\bar{X} + 0.14$
	48.00	49.39	3.25	1.81	$S_r = 0.053\bar{X} + 0.08$	45.43	6.78	5.15	$S_r = 0.164\bar{X} + 0.18$	45.59	4.27	2.70	$S_r = 0.120\bar{X} - 0.01$
	64.00	63.54	2.75			60.35	2.22			59.71	6.58		
	160.00	136.42	48.31	12.19		119.06	55.28	36.34		121.43	42.55	28.19	
	200.00	153.74	57.34			172.15	31.92			160.69	27.15		
Thallium	2.80	2.89	0.23	0.22	$\bar{X} = 0.984\underline{X} + 0.08$	2.88	0.40	0.16	$\bar{X} = 1.010\underline{C} + 0.01$	2.88	0.14	0.12	$\bar{X} = 1.023\underline{C} - 0.06$
	4.00	3.92	0.15		$S_R = 0.035\bar{X} + 0.09$	3.96	0.21		$S_R = 0.040\bar{X} + 0.21$	3.88	0.37		$S_R = 0.056\bar{X} + 0.04$
	20.00	19.27	0.99	0.67	$S_r = 0.027\bar{X} + 0.13$	19.77	1.13	0.83	$S_r = 0.039\bar{X} + 0.02$	20.22	1.05	0.65	$S_r = 0.049\bar{X} - 0.06$
	28.00	28.08	0.83			27.61	1.24			28.65	1.50		
	80.00	81.29	3.65	2.86		85.32	4.08	4.05		83.97	6.10	6.05	
	100.00	96.69	2.86			100.07	4.33			101.09	4.15		
Thorium	0.80	0.93	0.16	0.09	$\bar{X} = 1.013\underline{C} + 0.08$	0.78	0.13	0.07	$\bar{X} = 1.019\underline{C} - 0.06$	0.87	0.17	0.07	$\bar{X} = 1.069\underline{C} - 0.03$
	1.20	1.22	0.19		$S_R = 0.036\bar{X} + 0.13$	1.09	0.19		$S_R = 0.035\bar{X} + 0.12$	1.15	0.17		$S_R = 0.041\bar{X} + 0.13$
	20.00	20.88	0.90	0.71	$S_r = 0.025\bar{X} + 0.07$	21.66	0.94	0.54	$S_r = 0.024\bar{X} + 0.05$	21.78	0.90	0.94	$S_r = 0.027\bar{X} + 0.04$
	28.00	27.97	1.11			28.09	0.83			29.86	1.65		
	80.10	81.14	2.99	2.14		79.99	2.03	2.60		86.00	3.43	1.95	
	100.00	102.64	3.39			100.50	4.56			107.35	4.72		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Uranium	0.80	0.86	0.05	0.08	$\bar{X} = 1.026\underline{C} - 0.02$	0.85	0.15	0.09	$\bar{X} = 1.026\underline{C} - 0.04$	0.84	0.23	0.19	$\bar{X} = 1.058\underline{C} - 0.06$
	1.20	1.10	0.11		$S_R = 0.048\underline{X} + 0.02$	1.05	0.13		$S_R = 0.044\underline{X} + 0.11$	1.10	0.14		$S_R = 0.039\underline{X} + 0.17$
	20.10	21.38	0.99	0.82	$S_r = 0.027\bar{X} + 0.05$	22.30	1.40	0.46	$S_r = 0.022\bar{X} + 0.07$	21.56	1.11	1.08	$S_r = 0.028\bar{X} + 0.16$
	28.10	28.36	1.10			28.89	1.47			29.86	1.83		
	80.30	82.47	4.03	2.16		80.31	2.00	2.71		85.01	3.76	2.00	
	100.00	103.49	5.24			100.70	5.30			106.47	3.74		
Vanadium	32.00	31.02	2.68	2.19	$\bar{X} = 1.025C - 2.21$	33.15	2.51	2.28	$\bar{X} = 1.022\underline{C} - 0.30$	33.25	3.83	1.87	$\bar{X} = 1.076\underline{C} - 1.87$
	40.00	38.54	2.94		$S_R = 3.79$[d]	40.20	1.88		$S_R = 0.023\underline{X} + 1.45$	40.34	3.08		$S_R = 0.033\underline{X} + 2.25$
	80.00	79.14	4.94	4.29	$S_r = 3.26$[d]	77.83	4.18	2.75	$S_r = 0.023\bar{X} + 1.38$	84.42	3.97	2.93	$S_r = 0.049\bar{X} - 0.09$
	96.00	93.47	3.85			96.32	1.34			98.70	5.03		
	160.00	162.43	5.67	3.30		161.89	7.63	6.56		170.94	9.09	11.55	
	200.00	208.20	2.65			214.91	5.89			217.90	11.36		
Zinc	8.00	8.33	2.56	1.78	$\bar{X} = 1.042\underline{C} + 0.87$	11.60	6.18	5.72	$\bar{X} = 0.943\underline{C} + 2.54$	7.29	1.12	2.20	$\bar{X} = 0.962\underline{C} + 0.07$
	12.00	15.49	4.18		$S_R = 0.041\underline{X} + 2.60$	10.21	4.96		$S_R = 0.048\underline{X} + 5.27$	12.66	3.24		$S_R = 0.093\underline{X} + 0.92$
	56.00	56.07	2.91	2.47	$S_r = 0.030\bar{X} + 1.42$	56.83	7.66	4.56	$S_r = 0.004\bar{X} + 5.66$[c]	54.86	5.12	7.24	$S_r = 0.069\bar{X} + 1.55$
	80.00	85.53	5.81			82.88	8.34			78.62	8.56		
	160.00	165.17	7.78	9.87		156.69	17.01	9.48		150.12	12.52	10.84	
	200.00	207.27	14.61			191.59	17.21			184.37	16.59		

[a] True Value for the concentration added ($\mu g/L$)
[b] Mean Recovery ($\mu g/L$)
[c] $COD_w < 0.5$ - Use of regression equation outside study concentration range not recommended.
[d] $COD_w < 0$ - Mean precision is reported.
[e] $COD_w < 0$ - Unweighted linear regression equation presented.

TABLE 13: BACKGROUND AND SPIKE MEASUREMENTS IN WASTEWATER DIGESTATE[a]

	Background		Concentrate 1					Concentrate 2					
	Conc. µg/L	Std Dev µg/L	Spike µg/L	Found µg/L	Std Dev µg/L	%Rec %	RSD %	Spike µg/L	Found µg/L	Std Dev µg/L	%Rec %	RSD %	RSD_r %
Be	0.0	0.0	100	94.5	11.8	94.5	12.5	125	118.1	14.7	94.5	12.4	3.5
Al	78.2	12.4	200	260.9	41.2	91.4	15.8	250	309.1	48.5	92.4	15.7	2.7
Cr	19.5	8.1	200	222.2	23.3	101.4	10.5	250	274.3	26.6	101.9	9.7	2.0
V	1.9	2.8	250	271.8	36.5	108.0	13.4	200	219.3	30.1	108.7	13.7	2.6
Mn	296.6	24.7	125	419.0	35.7	97.9	8.5	100	397.4	34.8	100.8	8.8	1.0
Co	2.5	0.4	125	124.7	12.3	97.8	9.9	101	100.7	9.4	97.2	9.3	2.8
Ni	47.3	5.0	125	161.7	4.9	91.5	3.0	100	142.7	5.6	95.4	3.9	2.1
Cu	77.4	13.2	125	194.5	29.5	93.7	15.2	100	172.3	26.6	94.9	15.4	2.2
Zn	77.4	4.9	200	257.4	16.3	90.0	6.3	250	302.5	21.1	90.0	7.0	1.8
As	0.8	1.1	200	194.9	8.0	97.1	4.1	250	244.7	12.8	97.6	5.2	3.4
Se	4.5	6.2	250	236.8	14.2	92.9	6.0	200	194.3	9.3	94.9	4.8	3.8
Mo	166.1	9.4	100	269.8	19.0	103.7	7.0	125	302.0	18.0	108.7	6.0	1.5
Ag	0.6	0.7	200	176.0	14.6	87.7	8.3	250	214.6	17.8	85.6	8.3	2.3
Cd	2.7	1.1	125	117.0	4.8	91.4	4.1	100	96.6	3.2	93.9	3.3	2.9
Sb	3.3	0.2	100	100.2	4.8	96.9	4.8	125	125.9	4.3	98.1	3.4	1.8
Ba	68.6	3.3	250	321.0	19.4	101.0	6.0	200	279.3	17.2	105.4	6.2	2.5
Tl	0.1	0.1	100	103.3	8.0	103.2	7.7	125	129.2	8.9	103.3	6.9	2.1
Pb	6.9	0.5	125	135.1	7.8	102.6	5.8	100	110.3	6.3	103.4	5.7	1.8
Th	0.1	0.1	125	140.2	19.5	112.1	13.9	100	113.3	15.4	113.2	13.6	2.7
U	0.4	0.2	125	141.2	19.3	112.6	13.7	100	113.6	16.0	113.2	14.1	2.5

[a] Results from 10 participating laboratories. Wastewater digestate supplied with the study materials. Mean background concentrations determined by the participants.

TABLE 14: SPIKE MEASUREMENTS IN PARTICIPANT'S WASTEWATER[a]

	Concentrate 1					Concentrate 2					
	Spike	Found	Std Dev	%Rec	RSD	Spike	Found	Std Dev	%Rec	RSD	RSD_r
	µg/L	µg/L	µg/L	%	%	µg/L	µg/L	µg/L	%	%	%
Be	101	103.4	12.0	103.4	11.6	125	128.2	13.6	102.6	10.6	2.4
Al	200	198.7	23.9	99.4	12.0	250	252.4	15.5	101.0	6.1	2.9
Cr	200	205.4	12.3	102.7	6.0	250	253.4	15.4	101.4	6.1	1.1
V	250	246.5	4.4	98.6	1.8	200	196.8	2.8	98.4	1.4	2.0
Mn	125	119.0	5.4	95.2	4.5	100	95.5	4.3	95.5	4.5	0.8
Co	125	125.8	7.0	100.6	5.6	101	99.5	5.3	98.5	5.3	1.8
Ni	125	127.4	9.7	101.9	7.6	100	101.0	7.5	101.0	7.4	1.7
Cu	125	126.8	5.3	101.4	4.2	100	105.3	3.6	105.3	3.4	2.8
Zn	200	201.4	36.7	100.7	18.2	250	246.4	29.7	98.6	12.1	2.6
As	200	207.3	11.9	103.7	5.7	250	263.0	2.6	105.2	1.0	3.2
Se	250	256.8	26.4	102.7	10.3	200	214.	18.7	107.3	8.7	3.6
Mo	100	98.6	4.6	98.6	4.7	125	123.2	6.7	98.6	5.4	2.2
Ag	200	200.7	48.9	100.4	24.4	250	231.2	63.5	92.5	27.5	8.2
Cd	125	123.2	11.5	98.6	9.3	100	95.8	2.9	95.8	3.0	5.8
Sb	100	92.2	4.4	92.2	4.8	125	119.0	1.0	95.2	0.8	2.8
Ba	250	245.2	12.8	98.1	5.2	200	204.7	12.1	102.4	5.9	2.1
Tl	100	100.0	0.9	100.0	0.9	125	128.0	6.0	102.4	4.7	3.5
Pb	125	125.8	5.1	100.6	4.1	100	100.8	2.7	100.8	2.7	2.2
Th	125	124.2	7.6	99.4	6.1	100	99.8	5.7	99.8	5.7	3.2
U	125	130.4	10.3	104.3	7.9	100	106.4	6.8	106.4	6.4	2.3

[a]Results from 5 participating laboratories. Mean concentrations before spiking are not listed because they varied considerably among the different wastewaters.

METHOD 200.9

DETERMINATION OF TRACE ELEMENTS BY STABILIZED TEMPERATURE GRAPHITE FURNACE ATOMIC ABSORPTION

Revision 2.2
EMMC Version

J.T. Creed, T.D. Martin, L.B. Lobring, and J.W. O'Dell - Method 200.9, Revision 1.2 (1991)

J.T. Creed, T.D. Martin, and J.W. O'Dell - Method 200.9, Revision 2.2 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 200.9

DETERMINATION OF TRACE ELEMENTS BY STABILIZED TEMPERATURE GRAPHITE FURNACE ATOMIC ABSORPTION

1.0 SCOPE AND APPLICATION

1.1 This method[1] provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption (GFAA) in ground water, surface water, drinking water, storm runoff, industrial and domestic wastewater. This method is also applicable to the determination of total recoverable elements in sediment, sludges, and soil. This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
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
Manganese	(Mn)	7439-96-5
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5

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 can be determined in aqueous samples after suitable filtration and acid preservation.

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed by direct injection into the furnace without acid digestion if the sample has been properly

preserved with acid, has turbidity of < 1 NTU at the time of analysis, and is analyzed using the appropriate method matrix modifiers. This total recoverable determination procedure is referred to as "direct analysis". However, in the determination of some primary drinking water metal contaminants, such as arsenic and thallium preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sect. 10.5).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample.

1.6 Silver is only slightly soluble is the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater 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. The extraction of solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

1.7 Method detection limits and instrument operating conditions for the applicable elements are listed in Table 2. These are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

1.8 The sensitivity and limited linear dynamic range (LDR) of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution as well as the cleanliness of the labware used to perform the dilution can dramatically influence the quality of the analytical results. Therefore, samples types requiring large dilutions (>50:1) should be analyzed by an another approved test procedure which has a larger LDR or which is inherently less sensitive than GFAA.

1.9 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 aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous 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 aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analytes listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipetted onto the platform or a device which provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is pretreated in a char or ashing step which is designed to minimize the interference effects caused by the concomitant sample matrix. After the char step the furnace is allowed to cool prior to atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature where the metal (analyte) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high purity argon.) The resulting atomic cloud absorbs the element specific atomic emission produced by a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL). Following analysis the furnace is subjected to a cleanout period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is required to subtract from the total signal the component which is nonspecific to the analyte. In the absence of interferences, the background corrected absorbance is directly related to the concentration of the analyte. Interferences relating to STPGFAA (Section 4.0) must be recognized and corrected. Suppressions or enhancements of instrument response caused by the sample matrix must be corrected by the method of standard addition (Section 11.5).

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 auto-zero the AA instrument (Sect. 7.10.1).

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 (Sect. 7.9).

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 (Sect. 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 (Sect 8.5).

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

3.6 **Instrument Performance Check (IPC) Solution** - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sects. 7.11 & 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. 7.10.3 & 9.3.2).

3.9 **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 (Sect. 9.4).

3.10 **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 (Sects. 7.10.2 & 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 **Matrix Modifier** - A substance added to the graphite furnace along with the sample in order to minimize the interference effects by selective volatilization of either analyte or matrix components.

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 (Sect. 9.2.4 and Table 2).

3.14 **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. 7.12 & 9.2.3).

3.15 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.16 **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. 9.5.1 & 11.5).

3.17 **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. 7.8).

3.18 **Total Recoverable Analyte** - The concentration of analyte determined to be in either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 11.2 & 11.3).

3.19 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 Several interference sources may cause inaccuracies in the determination of trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

4.2 Spectral interferences are caused by the resulting absorbance of light by a molecule or atom which is not the analyte of interest or emission from black body radiation.

4.2.1 Spectral interferences caused by an element only occur if

there is a spectral overlap between the wavelength of the interfering element and the analyte of interest. Fortunately, this type of interference is relatively uncommon in STPGFAA because of the narrow atomic line widths associated with STPGFAA. In addition, the use of appropriate furnace temperature programs and high spectral purity lamps as light sources can minimize the possibility of this type of interference. However, molecular absorbances can span several hundred nanometers producing broadband spectral interferences. This type of interference is far more common in STPGFAA. The use of matrix modifiers, selective volatilization, and background correctors are all attempts to eliminate unwanted nonspecific absorbance. The nonspecific component of the total absorbance can vary considerably from sample type to sample type. Therefore, the effectiveness of a particular background correction device may vary depending on the actual analyte wavelength used as well as the nature and magnitude of the interference. The background correction device to be used with this method is not specified, however, it must provide an analytical condition that is not subject to the occurring interelement spectral interferences of palladium on copper, iron on selenium, and aluminum on arsenic.

4.2.2 Spectral interferences are also caused by the emissions from black body radiation produced during the atomization furnace cycle. This black body emission reaches the photomultiplier tube, producing erroneous results. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which adequately volatilize the analyte of interest without producing unnecessary black body radiation can help reduce unwanted background emission during analysis.

4.3 Matrix interferences are caused by sample components which inhibit the formation of free atomic analyte atoms during the atomization cycle.

4.3.1 Matrix interferences can be of a chemical or physical nature. In this method the use of a delayed atomization device which provides stabilized temperatures is required. These devices provide an environment which is more conducive to the formation of free analyte atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the analyte. If the determined concentration of the analyte addition is outside a designated range, a possible matrix effect should be suspected (Sect. 9.4.3).

4.3.2 The use of nitric acid is preferred for GFAA analyses in order to minimize vapor state anionic chemical interferences, however, in this method hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, the chloride ion

vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate and a hydrogen(5%)-argon(95%) gas mixture is used for this purpose. The effects and benefits of using this modifier are discussed in detail in reference 2. of Section 16.0. Listed in Section 4.4 are some typical observed effects when using this modifier.

4.4 Specific Element Interferences

Antimony: Antimony suffers from an interference produced by K_2SO_4.[3] In the absence of hydrogen in the char cycle (1300°C), K_2SO_4 produces a relatively high (1.2 abs) background absorbance which can produce a false signal, even with Zeeman background correction. However, this background level can be dramatically reduced (0.1 abs) by the use of a hydrogen/argon gas mixture in the char step. This reduction in background is strongly influenced by the temperature of the char step.

NOTE: The actual furnace temperature may vary from instrument to instrument. Therefore, the actual furnace temperataure should be determined on an individual basis.

Aluminum: The palladium matrix modifier may have elevated levels of Al which will cause elevated blank absorbances.

Arsenic: The HCl present from the digestion procedure can influence the sensitivity for As. 20 µL of a 1% HCl solution with Pd used as a modifier results in a 20% loss in sensitivity relative to the analyte in a 1% HNO_3 solution. Unfortunately, the use of $Pd/Mg/H_2$ as a modifier does <u>not</u> significantly reduce this suppression, and therefore, it is imperative that each sample and calibration standard alike contain the same HCl concentration.[2]

Cadmium: The HCl present from the digestion procedure can influence the sensitivity for Cd. 20 µL of a 1% HCl solution with Pd used as a modifier results in a 80% loss in sensitivity relative to the analyte in a 1% HNO_3 solution. The use of $Pd/Mg/H_2$ as a matrix modifier reduces this suppression to less than 10%.[2]

Lead: The HCl present from the digestion procedure can influence the sensitivity for Pb. 20 µL of a 1% HCl solution with Pd used as a modifier results in a 75% loss in sensitivity relative to the analyte response in a 1% HNO_3 solution. The use of $Pd/Mg/H_2$ as a matrix modifier reduces this suppression to less than 10%.[2]

Selenium: Iron has been shown to suppress Se response with continuum background correction.[3] In addition, the use of hydrogen as a purge gas during the dry and char steps can cause a suppression in Se response if not purged from the

furnace prior to atomization.

Silver: The palladium used in the modifier preparation may have elevated levels of Ag which will cause elevated blank absorbances.

Thallium: The HCl present from the digestion procedure can influence the sensitivity for Tl. 20 μL of a 1% HCl solution with Pd used as a modifier results in a 90% loss in sensitivity relative to the analyte in a 1% HNO_3 solution. The use of $Pd/Mg/H_2$ as a matrix modifier reduces this suppression to less than 10%.[2]

4.5 Memory interferences result from analyzing a sample containing a high concentration of an element (typically a high atomization temperature element) which cannot be removed quantitatively in one complete set of furnace steps. The analyte which remains in the furnace can produce false positive signals on subsequent sample(s). Therefore, the analyst should establish the analyte concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. If this concentration is exceeded, the sample should be diluted and a blank analyzed to assure the memory effect has been eliminated before reanalyzing the diluted sample.

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.[4-7] 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 graphite tube during atomization emits intense UV radiation. Suitable precautions should be taken to protect personnel from such a hazard.

5.5 The use of the argon/hydrogen gas mixture during the dry and char steps may evolve a considerable amount of HCl gas. Therefore, adequate ventilation is required.

5.6 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 Graphite Furnace Atomic Absorbance Spectrophotometer

6.1.1 The GFAA spectrometer must be capable of programmed heating of the graphite tube and the associated delayed atomization device. The instrument must be equipped with an adequate background correction device capable of removing undesirable non-specific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of interelement spectral overlap interferences. The furnace device must be capable of utilizing an alternate gas supply during specified cycles of the analysis. The capability to record relatively fast (< 1 s) transient signals and evaluate data on a peak area basis is preferred. In addition, a recirculating refrigeration bath is recommended for improved reproducibility of furnace temperatures.

6.1.2 Single element hollow cathode lamps or single element electrodeless discharge lamps along with the associated power supplies.

6.1.3 Argon gas supply (high-purity grade, 99.99%) for use during the atomization of selenium, for sheathing the furnace tube when in operation, and during furnace cleanout.

6.1.4 Alternate gas mixture (hydrogen 5% - argon 95%) for use as a continuous gas flow environment during the dry and char furnace cycles.

6.1.5 Autosampler capable of adding matrix modifier solutions to the furnace, a single addition of analyte, and completing methods of standard additions when required.

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

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

6.4 (optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted digestion tubes.

6.5 (optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

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

6.7 (optional) An air displacement pipetter capable of delivering volumes ranging from 100 to 2500 µL with an assortment of high quality disposable pipet tips.

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 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 dilute HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean.[1] Ideally, ground glass surfaces should be avoided to eliminate a potential source of random contamination. When this is impractical, particular attention should be given to all ground glass surfaces during cleaning. Chromic acid cleaning solutions must be avoided because chromium is an analyte.

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

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers, 250-mL with 50-mm watch glasses.

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

6.10.5 (optional) PTFE and/or quartz Griffin beakers, 250-mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

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

6.10.8 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[8] 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+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

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+5) - Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.3 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.[9]

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

7.6 Tartaric acid, ACS reagent grade.

7.7 Matrix Modifier, dissolve 300 mg palladium (Pd) powder in conc. HNO_3 (1 mL of HNO_3, adding 0.1 mL of concentrated HCl if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in ASTM Type I water. Pour the two solutions together and dilute to 100 mL with ASTM Type I water.

NOTE: It is recommended that the matrix modifier be analyzed separately in order to assess the contribution of the modifier to the absorbance of calibration and reagent blank solutions.

7.8 Standard stock solutions 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 FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

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 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,

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

where:

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

7.8.1 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 HNO_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.

7.8.2 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.

7.8.3 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 the 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.

7.8.4 Beryllium solution, stock, 1 mL = 1000 µg Be: DO NOT DRY. Dissolve 19.66 g $BeSO_4 \cdot 4H_2O$ (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.

7.8.5 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.

7.8.6 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.

7.8.7 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.

7.8.8 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.

7.8.9 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.

7.8.10 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.

7.8.11 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.

7.8.12 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.

7.8.13 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.

7.8.14 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.

7.8.15 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.

7.8.16 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1-L volumetric flask with reagent water.

7.9 Preparation of Calibration Standards - Fresh calibration standards (CAL Solution) should be prepared every two weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). The element concentrations in each CAL solution should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. The instrument calibration should be initially verified using a quality control sample (Sections 7.12 & 9.2.3).

NOTE: The appropriate acid diluent for the determination of dissolved elements in water and for the "direct analysis" of drinking water with turbidity < 1 NTU is 1% HNO_3. For total recoverable elements in waters, the appropriate acid diluent is 2% HNO_3 and 1% HCl, and the appropriate acid diluent for total recoverable elements in solid samples is 2% HNO_3 and 2% HCl. The reason for these different diluents is to match the types of acids and the acid concentrations of the samples with the acid present in the standards and blanks.

7.10 Blanks - Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank (LRB) is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the laboratory fortified blank is used to assess routine laboratory performance, and a rinse blank is used to flush the instrument autosampler uptake system. All diluent acids should be made from concentrated acids (Sects. 7.2 & 7.3) and ASTM Type I water.

7.10.1 The calibration blank consists of the appropriate acid diluent (Sect. 7.9 note) (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

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

7.10.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to provide a final concentration which will produce an absorbance of approximately 0.1 for each analyte. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.4 The rinse blank is prepared as needed by adding 1.0 mL of conc. HNO_3 and 1.0 mL conc. HCl to 1 liter of ASTM Type I water and stored in a convenient manner.

7.11 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards (Sect. 7.9 note) by combining method analytes at appropriate concentrations to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in a FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 Quality Control Sample (QCS) - For initial and periodic verification of calibration standards and instrument performance, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards (Sect.7.9 note). The concentration of the analytes in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

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 processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 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.) 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 sixteen 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 sixteen 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 Solid samples usually require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, 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 samples being analyzed by this method.

9.2.2 Linear dynamic range (LDR) - The upper limit of the LDR must be established for the wavelength utilized for each analyte by determining the signal responses from a minimum of six different concentration standards across the range, two of

which are close to the upper limit of the LDR. Determined LDRs must be documented and kept on file. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from the four lower standards. The LDRs should be verified 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.

NOTE: Multiple cleanout furnace cycles may be necessary in order to fully define or utilize the LDR for certain elements such as chromium. For this reason the upper limit of the linear calibration range may not correspond to the upper LDR limit.

Determined sample analyte concentrations that exceed the upper limit of the linear calibration range must either be diluted and reanalyzed with concern for memory effects (Sect. 4.4) or analyzed by another approved method.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Sect. 7.12). If the determined concentrations are not within ± 10% of the stated values, 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 analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[10] 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 = 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 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 inappropriately 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 (Sect. 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 2.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Sect. 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 (Sect. 7.10.2) 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 (Sect. 7.10.3) 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% (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:

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

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent twenty to thirty 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 (Sect. 7.11) and a calibration blank immediately following each calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the IDL, but > a negative signal in concentration units equal to the IDL. 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 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 the calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift 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.

9.4 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 these effects. Unless otherwise specified by the data user, laboratory or

program, the following laboratory fortified matrix (LFM) procedure (Sect. 9.4.2) is required. Also, the analyte addition test (Sect. 9.5.1) can indicate if matrix and other interference effects are operative in selected samples. However, all samples must demonstrate a background absorbance < 1.0 before the test results obtained can be considered reliable.

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. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Sect. 9.3.2). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a 1 g aliquot by multiplying the added analyte concentration (μg/L) in solution by the conversion factor 0.1 (0.001 x μg/L x 0.1L/0.001kg = 0.1, Sect. 12.4). Over time, samples from all routine sample sources should be fortified.

9.4.3 Calculate the percent recovery for each analyte, corrected for 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 25% of the unfortified sample concentration. Percent recovery may be calculated in units appropriate to the matrix, 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 (but is still within the range of calibration) and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related. If the analyte recovery in the LFM is < 70% and the background absorbance is < 1.0, complete the analyte addition test (Sect. 9.5.1) on an undiluted portion of the unfortified sample aliquot. The test results should be evaluated as follows:

1. If recovery of the analyte addition test (< 85%) confirms the a low recovery for the LFM, a suppressive matrix interference is indicated and the unfortified sample aliquot

must be analyzed by method of standard additions (Sect. 11.5).

2. If the recovery of the analyte addition test is between 85% to 115%, a low recovery of the analyte in the LFM (< 70%) may be related to the heterogeneous nature of the sample, the result of precipitation loss during sample preparation, or an incorrect addition prior to preparation. Report analyte data determined from the analysis of the unfortified sample aliquot.

9.4.5 If laboratory performance is shown to be in control (Sect. 9.3), but analyte recovery in the LFM is either > 130% or above the upper calibration limit and the background absorbance is < 1.0, complete the analyte addition test (Sect. 9.5.1) on a portion of the unfortified sample aliquot. (If the determined LFM concentration is above the upper calibration limit, dilute a portion of the unfortified aliquot accordingly with acidified reagent water before completing the analyte addition test.) Evaluate the test results as follows:

1. If the percent recovery of the analyte addition test is > 115%, an enhancing matrix interference (albeit rare) is indicated and the unfortified sample aliquot or its appropriate dilution must be analyzed by method of standard additions (Sect 11.5).

2. If the percent recovery of the analyte addition test is between 85% to 115%, high recovery in the LFM may have been caused by random sample contamination, an incorrect addition of the analyte prior to sample preparation, or sample heterogeneity. Report analyte data determined from the analysis of the unfortified sample aliquot or its appropriate dilution.

3. If the percent recovery of the analyte addition test is < 85%, either a case of both random contamination and an operative matrix interference in the LFM is indicated or a more plausible answer is a heterogenous sample with an suppressive matrix interference. Reported data should be flagged accordingly.

9.4.6 If laboratory performance is shown to be in control (Sect. 9.3), but the magnitude of the sample (LFM or unfortified aliquot) background absorbance is > 1.0, a non-specific spectral interference should be suspected. A portion of the unfortified aliquot should be diluted (1+3) with acidified reagent water and reanalyzed. (Dilution may dramatically reduce a molecular background to an acceptable level. Ideally, the background absorbance in the unfortified aliquot diluted (1+3) should be < 1.0. However, additional dilution may be necessary.) If dilution reduces the background absorbance to acceptable level (< 1.0), complete the analyte addition test (Sect. 9.5.1) on a portion of the diluted unfortified aliquot.

Evaluate the test results as follows:

1. If the recovery of the analyte addition test is between 85% to 115%, report analyte data determined on the dilution of the unfortified aliquot.

2. If the recovery of the analyte addition test is outside the range of 85% to 115%, complete the sample analysis by analyzing the dilution of the unfortified aliquot by method of standard additions (Sect. 11.5).

9.4.7 If either the analysis of a LFM sample(s) or application of the analyte addition test routine indicate an operative interference, all other samples in the batch which are typical and have similar matrix to the LFMs or the samples tested must be analyzed in the same manner. Also, the data user must be informed when a matrix interference is so severe that it prevents the successful analysis of the analyte or when the heterogeneous nature of the sample precludes the use of duplicate analyses.

9.4.8 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.

9.5 The following test can be used to assess possible matrix interference effects and the need to complete the sample analysis by method of standard additions (MSA). Results of this test should <u>not</u> be considered conclusive unless the determined sample background absorbance is < 1.0. Directions for MSA are given in Section 11.5.

9.5.1 Analyte addition test: An analyte standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte addition may be added directly to sample in the furnace and should produce a minimum level absorbance of 0.1. The concentration of the analyte addition plus that in the sample should not exceed the linear calibration range of the analyte. If the analyte is not recovered within the specified limits, a matrix effect should be suspected and the sample must be analyzed by MSA (Sect. 11.5).

10.0 CALIBRATION AND STANDARDIZATION

10.1 Specific wavelengths and instrument operating conditions are listed in Table 2. However, because of differences among makes and models of spectrophotometers and electrothermal furnace devices, the actual instrument conditions selected may vary from those listed.

10.2 Prior to the use of this method the instrument operating conditions must be optimized. The analyst should follow the instructions provided by the manufacturer while using the conditions listed in Table 2 as a guide. Of particular importance is the determination of

the charring temperature limit for each analyte. This limit is the furnace temperature setting where a loss in analyte will occur prior to atomization. This limit should be determined by conducting char temperature profiles for each analyte and when necessary, in the matrix of question. The charring temperature selected should minimize background absorbance while providing some furnace temperature variation without loss of analyte. For routine analytical operation the charring temperature is usually set at least 100°C below this limit. The optimum conditions selected should provide the lowest reliable MDLs and be similar to those listed in Table 2. Once the optimum operating conditions are determined, they should be recorded and available for daily reference.

10.3 Prior to an initial calibration the linear dynamic range of the analyte must be determined (Sect. 9.2.2) using the optimized instrument operating conditions (Sect. 10.2). For all determinations allow an instrument and hollow cathode lamp warm up period of not less than 15 min. If an EDL is to be used, allow 30 min for warm up.

10.4 Before using the procedure (Sect. 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure are described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Sect. 11.4) to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.5 In order to meet or achieve lower MDLs than those listed in Table 2 for "direct analysis" of drinking water with turbidity < 1 NTU preconcentration of the analyte is required. This may be accomplished prior to sample introduction into the GFAA or with the use of multiple aliquot depositions on the GFAA platform or associated delayed atomization device. When using multiple depositions, the same number of equal volume aliquots alike of either the calibration standards or acid preserved samples must be deposited prior to atomization. Following each deposition the drying cycle is completed before the next subsequent deposition. The matrix modifier is added along with each deposition and the total volume of each deposition must not exceed the instrument manufactures recommended capacity of the delayed atomization device. To reduce analysis time the minimum number of depositions required to achieve the desired analytical result should be used. Use of this procedural technique for the "direct analysis" of drinking water must be completed using determined optimized instrument operating conditions for multiple depositions (Sect.10.2) and comply with the method requirements described in Sections 10.3 and 10.4. (See Table 3 for information and data on the determination of arsenic by this procedure.)

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥ 20 mL) of the filtered,

acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Sect. 1.3). Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 thru 11.2.7 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 (Sects. 1.2 & 1.4). For the determination of total recoverable analytes in all other aqueous 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), transfer a 100-mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (Sects. 1.2, & 1.6). (When necessary, smaller sample aliquot volumes may be used.)

NOTE: If the sample contains undissolved solids > 1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 thru 11.3.6.

11.2.3 Add 2 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 2 h for a 100 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 $HCl-H_2O$ azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask, 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 or affect the sample introduction system, 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 Solid Sample Preparation - Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (> 20 g) to tared weighing dish, weigh the sample and record the wet weight (WW). (For samples with < 35% moisture a 20 g portion is sufficient. For samples with moisture > 35% a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight (DW) for calculation of percent solids (Sect. 12.6). (The sample is dried at 60°C to prevent the possible loss of volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction (Sect. 1.6).

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the

beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

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.) Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 min. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the $HCl-H_2O$ azeotrope. Some solution evaporation will occur (3 to 4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog or affect the sample introduction system, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract 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.

11.4 Sample Analysis

11.4.1 Prior to daily calibration of the instrument inspect the graphite furnace, the sample uptake system and autosampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or on a daily basis.

11.4.2 Before beginning daily calibration the instrument system should be reconfigured to the selected optimized operating conditions as determined in Sections 10.1 and 10.2 or 10.5 for the "direct analysis" drinking water with turbidity < 1 NTU. Initiate data system and allow a period of not less than 15 min for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 min for warm up.

11.4.3 After the warm up period but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration 20 times the IDL a minimum of five times. The resulting relative standard deviation (RSD) of absorbance signals must be < 5%. If the RSD is > 5%, determine and correct the cause before calibrating the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Sect. 7.10.1) and calibration standards (Sect. 7.9) prepared at three or more concentrations within the usable linear dynamic range of the analyte (Sects. 4.4 & 9.2.2).

11.4.5 An autosampler must be used to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and cleanout period as programmed. Analyte signals must be integrated and collected as peak area measurements. Background absorbances, background corrected analyte signals, and determined analyte concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for documentation to be kept on file. Flush the autosampler solution uptake system with the rinse blank (Sect. 7.10.4) between each solution injected.

11.4.6 After completion of the initial requirements of this method (Sects. 10.4), samples should be analyzed in the same operational manner used in the calibration routine.

11.4.7 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of < 1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.8 For every new or unusual matrix, when practical, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentration. Information gained from this may be used to prevent potential damage to the instrument and to better estimate which elements may require analysis by graphite furnace.

11.4.9 Determined sample analyte concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects (Sect. 4.4), or determined by another approved test procedure that is less sensitive. Samples with a background absorbance > 1.0 must be appropriately diluted with acidified reagent water and reanalyzed (Sect. 9.4.6). If the method of standard additions is required, follow the instructions described in Section 11.5.

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

11.4.11 Report data as directed in Section 12.

11.5 Standard Additions - If the method of standard addition is required, the following procedure is recommended:

11.5.1 The standard addition technique[11] involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration C_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where, S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus C_s is much greater than C_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.

2. The chemical form of the analyte added must respond in the same manner as the analyte in the sample.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data should be reported in units of µg/L for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Sect. 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

12.3 For total recoverable aqueous analytes (Sect. 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, round the data to the tenths place and report the data in µg/L up to three significant figures. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding the upper limit of the calibration curve. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.4 For total recoverable analytes in solid samples (Sect. 11.3), round the solution analyte concentrations (µg/L) to the tenths place. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

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

where: C = Concentration in extract (µg x 0.001/L)
V = Volume of extract (L, 100 mL = 0.1L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.5 To report percent solids in solid samples (Sect. 11.3) calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where: DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

NOTE: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in Section 11.3 using a separate portion (> 20 g) of the sample and dry to constant weight at 103-105°C.

12.6 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 Instrument operating conditions used for single laboratory testing of the method and MDLs are listed in Table 2.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 1A-C for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil, and EPA Electroplating Sludge. Samples were prepared using the procedure described in Section 11.3. For each matrix, five replicates were analyzed, and an average of the replicates was used for determining the sample background concentration. Two other pairs of duplicates were fortified at different concentration levels. The sample background concentration, mean spike percent recovery, the standard deviation of the average percent recovery, and the relative percent difference between the duplicate-fortified determinations are listed in Table 1A-C. In addition, Table 1D-F contains single-laboratory test data for the method in aqueous media including drinking water, pond water, and well water. Samples were prepared using the procedure described in Section 11.2. For each aqueous matrix five replicates were analyzed, and an average of the replicates was used for determining the sample background concentration. Four samples were fortified at the levels reported in Table 1D-1F. A percent relative standard deviation is reported in Table 1D-1F for the fortified samples. An average percent recovery is also reported in Tables 1D-F.

NOTE: Antimony and aluminum manifest relatively low percent recoveries (see Table 1A, NBS River Sediment 1645).

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. 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 rule 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 15.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1A. PRECISION AND RECOVERY DATA FOR NBS RIVER SEDIMENT 1645

Solid Sample	Certified Value+	Average Sed Conc (mg/kg)	% RSD	Average Percent Recovery (20 mg/kg)[x]	S(r)	RPD	Average Percent Recovery (100 mg/kg)[x]	S(r)	RPD
Aluminum	22600	6810	4.6	*	--	--	*	--	--
Antimony	(51)	25.8	8.2	74.9	8.3	9.5	99.0	1.5	2.7
Arsenic	(66)	69.2	3.4	69.8	19.0	12.0	89.2	4.3	7.3
Cadmium	10.2	10.8	3.7	115.3	2.6	4.0	110.7	0.7	1.7
Chromium	29600	32800	1.6	*	--	--	*	--	--
Copper	109	132	4.8	99.1	14.2	0	111.5	3.6	2.6
Manganese	785	893	5.1	*	--	--	103.2	26.4	4.7
Selenium	1.5	0.7	20.4	96.0	15.9	45.2	105.4	4.0	10.7
Silver	--	1.7	3.1	101.8	3.8	9.7	93.5	1.9	5.6
Tin	--	439	4.4	--	--	--	--	--	--

% RSD Percent Relative Standard Deviation (n = 5)
S(r) Standard Deviation of Average Percent Recovery
RPD Relative Percent Difference Between Duplicate Recovery Determinations
* Fortified concentration <10% of sample concentration
-- Not determined
+ Values in parenthesis are noncertified
x Fortified concentration

TABLE 1B. PRECISION AND RECOVERY DATA FOR EPA HAZARDOUS SOIL 884

Solid Sample	Average Sed Conc (mg/kg)	% RSD	Average Percent Recovery (20 mg/kg)[x]	S(r)	RPD	Average Percent Recovery (100 mg/kg)[x]	S(r)	RPD
Aluminum	6410	3.3	*	--	--	*	--	--
Antimony	4.6	14.7	61.4	2.7	7.4	60.9	1.7	7.1
Arsenic	8.7	4.6	109.8	2.1	3.5	103.7	1.5	3.6
Cadmium	1.8	10.3	115.4	0.8	1.4	99.0	4.3	12.1
Chromium	84.0	4.2	95.5	33.8	17.9	120.8	6.6	8.9
Copper	127	4.3	108.0	15.2	2.6	117.7	5.4	5.7
Manganese	453	6.0	*	--	--	99.2	13.9	1.6
Selenium	0.6	7.5	95.0	8.4	24.1	96.9	3.3	9.7
Silver	0.9	18.5	100.1	3.8	10.2	93.5	1.3	3.8
Tin	18.4	3.7	--	--	--	--	--	--

% RSD Percent Relative Standard Deviation (n = 5)
S(r) Standard Deviation of Average Percent Recovery
RPD Relative Percent Difference Between Duplicate Recovery Determinations
* Fortified concentration <10% of sample concentration
-- Not determined
x Fortified concentration

TABLE 1C. PRECISION AND RECOVERY DATA FOR EPA ELECTROPLATING SLUDGE 286

Solid Sample	Average Sed Conc (mg/kg)	% RSD	Average Percent Recovery (20 mg/kg)[x]	S(r)	RPD	Average Percent Recovery (100 mg/kg)[x]	S(r)	RPD
Aluminum	6590	2.7	*	--	--	*	--	--
Antimony	7.7	3.9	68.6	2.3	5.7	60.7	3.1	12.8
Arsenic	33.7	2.7	87.6	2.6	1.7	100.2	1.5	3.1
Cadmium	119	1.3	81.9	7.9	3.0	112.5	3.9	4.7
Chromium	8070	4.5	*	--	--	*	--	--
Copper	887	1.6	*	--	--	99.5	21.9	6.0
Manganese	320	1.6	*	--	--	101.0	6.4	4.0
Selenium	0.8	6.7	99.4	0.8	2.3	96.8	0.7	1.9
Silver	6.5	2.3	102.8	2.5	5.3	92.3	1.9	5.4
Tin	21.8	3.2	--	--	--	--	--	--

% RSD Percent Relative Standard Deviation (n = 5)
S(r) Standard Deviation of Average Percent Recovery
RPD Relative Percent Difference Between Duplicate Recovery Determinations
* Fortified concentration <10% of sample concentration
-- Not determined
x Fortified concentration

TABLE 1D. PRECISION AND RECOVERY DATE FOR POND WATER

Element	Average Conc. µg/L	% RSD	Fortified Conc. µg/L[1]	% RSD at Fortified Conc.[2]	Average Percent Recovery
Ag	<0.5	*	1.25	3.7	107.5
Al	550	1.2	--	--	--
As[3]	3.2	4.1	10	0.8	100.5
Be	0.05	36.4	2.5	14.0	90.0
Cd	<0.05	*	0.5	4.5	99.1
Co	<0.7	*	10	2.8	97.3
Cr	0.75	8.7	2.5	1.8	98.5
Cu	2.98	11.2	10	2.9	101.9
Fe	773	5.7	--	--	--
Mn	751	2.2	--	--	--
Ni	2.11	6.8	20	1.6	105.6
Pb	1.22	20.5	25	1.8	101.6
Sb[3]	4	*	25	0.4	115.2
Se[3]	<0.8	*	25	1.6	97.8
Sn[3]	<0.6	*	50	3.3	117.5
Tl	<1.7	75.0	50	5.2	101.0
	<0.7				

< Sample concentration less than the established method detection limit.

* Not determined on sample concentrations less than the method detection limit.

[1] Fortified sample concentration based on 100-mL sample volumes.

[2] RSD are reported on 50-mL sample volumes.

[3] Electrodeless discharge lamps were used.

TABLE 1E. PRECISION AND RECOVERY DATE FOR DRINKING WATER

Element	Average Conc. µg/L	% RSD	Fortified Conc. µg/L[1]	% RSD at Fortified Conc.[2]	Average Percent Recovery
Ag	<0.5	*	1.25	5.6	94.6
Al	163.6	2.5	150	6.4	111.7
As[3]	0.5	10.5	10	0.6	88.4
Be	<0.02	*	2.5	9.4	106.0
Cd	<0.05	*	0.5	6.3	105.2
Co	<0.7	*	10	3.9	88.5
Cr	<0.1	*	2.5	3.1	105.7
Cu	2.6	7.3	10	1.2	111.5
Fe	9.1	17.6	150	5.9	107.8
Mn	0.9	1.3	2.5	0.7	96.7
Ni	0.8	32.7	20	4.3	103.8
Pb	<0.7	*	10	4.0	101.8
Sb[3]	<0.8	*	15	14.7	101.4
Se[3]	<0.6	*	25	1.5	88.9
Sn[3]	<1.7	*	50	0.4	100.7
Tl	<0.7	*	20	2.8	95.4

< Sample concentration less than the established method detection limit.

* Not determined on sample concentrations less than the method detection limit.

[1] Fortified sample concentration based on 100-mL sample volumes.

[2] RSD are reported on 50-mL sample volumes.

[3] Electrodeless discharge lamps were used.

TABLE 1F. PRECISION AND RECOVERY DATE FOR WELL WATER

Element	Average Conc. µg/L	% RSD	Fortified Conc. µg/L[1]	% RSD at Fortified Conc.[2]	Average Percent Recovery
Ag	<0.5	*	1.25	3.6	108.3
Al	14.4	26.7	150	1.5	97.1
As[3]	0.9	14.2	10	2.1	101.6
Be	<0.02	*	2.5	3.4	103.7
Cd	1.8	11.9	0.5	4.6	109.3
Co	4.0	2.9	10	1.0	95.8
Cr	<0.1	*	2.5	4.0	102.6
Cu	35.9	1.2	10	0.6	90.2
Fe	441	6.6	--	--	--
Mn	3580	2.7	--	--	--
Ni	11.8	3.2	20	4.0	105.7
Pb	<0.7	*	25	0.7	102.2
Sb[3]	<0.8	*	25	1.2	114.3
Se[3]	<0.6	*	25	1.2	95.9
Sn[3]	<1.7	*	50	3.0	106.1
Tl	<0.7	*	50	1.4	98.0

< Sample concentration less than the established method detection limit.

* Not determined on sample concentrations less than the method detection limit.

[1] Fortified sample concentration based on 100-mL sample volumes.

[2] RSD are reported on 50-mL sample volumes.

[3] Electrodeless discharge lamps were used.

TABLE 2. RECOMMENDED GRAPHITE FURNACE OPERATING CONDITIONS AND RECOMMENDED MATRIX MODIFIER[1-3]

Element	Wavelength	Slit	Temperature Char	(C)[5] Atom	MDL[4] (µg/L)
Ag	328.1	0.7	1000	1800	0.5[9]
Al	309.3	0.7	1700	2600	7.8[9]
As[7]	193.7	0.7	1300	2200	0.5
Be	234.9	0.7	1200	2500	0.02
Cd	228.8	0.7	800	1600	0.05
Co	242.5	0.2	1400	2500	0.7
Cr	357.9	0.7	1650	2600[6]	0.1
Cu	324.8	0.7	1300	2600[6]	0.7
Fe	248.3	0.2	1400	2400	-
Mn	279.5	0.2	1400	2200	0.3
Ni	232.0	0.2	1400	2500	0.6
Pb	283.3	0.7	1250	2000	0.7
Sb[7]	217.6	0.7	1100	2000	0.8
Se[7]	196.0	2.0	1000	2000	0.6
Sn[7]	286.3	0.7	1400[8]	2300	1.7
Tl	276.8	0.7	1000	1600	0.7

1 Matrix Modifier = 0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$.

2 A 5% H_2 in Ar gas mix is used during the dry and char steps at 300 mL/min for all elements.

3 A cool down step between the char and atomization is recommended.

4 Obtained using a 20-µL sample size and stop flow atomization.

5 Actual char and atomization temperatures may vary from instrument to instrument and are best determined on an individual basis. The actual drying temperature may vary depending on the temperature of the water used to cool the furnace.

6 A 7-s atomization is necessary to quantitatively remove the analyte from the graphite furnace.

7 An electrodeless discharge lamp was used for this element.

8 An additional low temperature (approximately 200°C) per char is recommended.

9 Pd modifier was determined to have trace level contamination of this element.

TABLE 3. MULTIPLE DEPOSITION - ARSENIC PRECISION AND RECOVERY DATA[1,2]

Drinking Water Source	Average Conc. µg/L	%RSD	Fortified Conc. µg/L	%RSD	Percent Recovery
Cinti. Ohio	0.3	41%	3.8	3.9%	88%
Home Cistern	0.2	15%	4.1	1.7%	98%
Region I	0.7	7.3%	5.0	1.9%	108%
Region VI	2.6	3.4%	6.7	4.3%	103%
Region X	1.1	4.8%	5.0	1.7%	97%
NIST 1643c*	3.9	7.1%	--	--	95%

[1] The recommended instrument conditions given in Table 2 were used in this procedure except for using diluted (1+2) matrix modifier and six - 36 µL depositions (30 µL sample + 1 µL reagent water + 5 µL matrix modifier) for each determination (Sect. 10.5). The amount of matrix modifier deposited on the platform with each determination (6 x 5 µL) = 0.030 mg Pd + 0.02 mg $Mg(NO_3)_2$. The determined arsenic MDL using this procedure is 0.1 µg/L.

[2] Sample data and fortified sample data were calculated from four and five replicate determinations, respectively. All drinking waters were fortified with 4.0 µg/L arsenic. The instrument was calibrated using a blank and four standard solutions (1.0, 2.5, 5.0, and 7.5 µg/L).

* The NIST 1643c reference material Trace Elements in Water was diluted (1+19) for analysis. The calculated diluted arsenic concentration is 4.1 µg/L. The listed precision and recovery data are from 13 replicate determinations collected over a period of four days.

METHOD 200.15

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

Revision 1.2
EMMC Version

T.D. Martin, C.A. Brockhoff, and J.T. Creed - Method 200.15, Revision 1.2 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 200.15

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 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
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)	7439-93-2
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
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5

(continues on next page)

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

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

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) (Sect. 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% to 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, & Na) range from 10 mg/L to 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 (Sect. 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 (Sect. 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 (Sect. 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 (Sect 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 ten 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 (Sects. 7.12 & 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 (Sect. 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 (Sects. 7.11.3 & 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 (Sect. 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 (Sects. 7.11.2 & 9.3.1).

3.12 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Sect. 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 (Sect. 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 (Sects. 7.16 & 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 (Sects. 7.13 & 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 (Sects. 7.14, 7.15 & 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. 9.5.1 & 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 (Sect. 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 (Sect. 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sects. 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 (Sect. 9.2.2). See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are <u>not</u> used, either on-going SIC solutions (Sect. 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, > the analyte IDL, or false negative analyte concentration, < 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 (Sect. 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 ten 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 sec 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 to 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 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 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 (Sect. 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 HNO_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 $BeSO_4 \cdot 4H_2O$ (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 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 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 $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (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 (Sect. 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, Sects. 1.10 & 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 $\leq$ 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 (Sects. 1.10 & 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 $\leq$ 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, Sect. 9.2.2.)

NOTE: If wavelengths other than those recommended in Table 1 are used, other solutions different from those above (a thru 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 5 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., $\geq$ 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 $\geq$ 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 (Sect. 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 6 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 sixteen 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 sixteen 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 (Sect. 7.13). 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.

9.2.4 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 = 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 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 inappropriately 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 (Sect. 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 (Sect. 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 (Sect. 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 (Sect. 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% (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 required control limits of 85-115%. 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 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 (Sect. 7.12) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the analyte IDL, but > 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 (Sect 9.4.2) is required. Also, other tests such as the analyte addition test (Sect. 9.5.1) and sample dilution test (Sect. 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 (Sect. 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 $\leq$ 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 (Sect. 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) (Sect. 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% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is < 20% of the sample analyte concentration, the following dilution 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 to 1500 watts forward power, 12-to 16-mm viewing height, 12 to 19 liters/min argon coolant flow, 0.5 to 1 L/min argon aerosol flow, 1.5 to 2.5 mL/min sample pumping rate with a 1-min 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 (Sect. 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 to 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 (Sect. 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 to 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 (Sect. 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 (Sect 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 (Sect. 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 (Sect. 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%, Sect. 1.4), transfer a 100-mL (± 1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker (Sects. 1.2, 1.3, 1.6, 1.7, 1.8, & 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 1 h 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-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 (Sect.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 (Sect. 7.10) and the calibration blank (Sect. 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 sec 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 (Sect. 7.11.4) for a minimum of 60 seconds (Sect. 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 (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, 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 Sect.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 (Sect. 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.

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 hundredth place and report analyte concentrations up to three significant figures.

12.3 For dissolved analytes (Sect. 11.1) and total recoverable analyses of drinking water with turbidity < 1NTU (Sect. 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 (Sects. 11.2.2 - 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 > 2 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 (Sects. 11.2.2 -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., Sect. 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.

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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 Sect. 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	0.005	0.03
K	0.09	0.05
Mg	0.005	0.01
Na	0.04	0.05
SiO_2	0.002	0.03

(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 (Sect. 1.10)

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

ICP SPECTROMETER	
Incident rf power	1400 watts
Reflected rf power	< 5 watts
Viewing height above 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.)

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	109	0.2	0.4
Al	98.3	40.0	108	5.1	1.0	400	111	0.7	0.7
As	<3	30.0	110	1.5	2.7	300	114	0.7	1.2
B	26.8	20.0	104	2.6	0.2	200	99	0.4	0.6
Ba	30.2	20.0	105	1.4	1.0	200	104	0.4	0.6
Be	<0.05	4.0	110	0.1	0.3	40	108	0.5	0.9
Cd	<0.4	4.0	106	2.3	4.3	40	106	0.6	1.2
Ce	<5	50.0	108	4.7	8.7	500	106	0.4	0.7
Co	<0.6	20.0	108	0.5	1.0	200	107	0.5	1.0
Cr	<2	20.0	105	0.2	0.5	200	108	0.2	0.4
Cu	3.9	20.0	92	0.8	0.9	200	104	0.2	0.4
Fe	7.3	20.0	98	0.7	0.0	200	108	0.6	1.1
Hg	<3	30.0	103	4.3	8.4	300	104	0.0	0.1
Li	4.4	20.0	108	1.5	0.3	200	106	0.4	0.6
Mn	0.26	10.0	108	0.3	0.1	100	107	0.5	0.8
Mo	<2	20.0	107	0.8	1.4	200	105	0.7	1.3
Ni	1.0	10.0	108	4.6	5.6	100	106	0.3	0.1
Pb	<4	15.0	98	5.7	11.6	400	112	0.3	0.6
Sb	<3	30.0	117	1.7	2.8	300	114	0.5	0.8
Se	<5	50.0	101	6.4	12.7	500	114	0.4	0.7
Sn	<5	40.0	119	1.1	1.9	400	114	0.7	1.3
Ti	0.23	20.0	109	0.1	0.0	200	108	0.5	0.8
Tl	<6	40.0	108	2.9	5.3	400	110	1.0	1.7
V	<2	20.0	105	3.0	5.7	200	105	1.5	2.9
Zn	4.5	20.0	111	0.8	0.2	200	113	0.1	0.2

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.)

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	2.5
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 <10% of sample background concentration.

TABLE 6. PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont.)

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.)

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

(1) Mean sample concentration and relative standard deviation were determined from 5 replicate aliquots of each sample.

METHOD 218.6

DETERMINATION OF DISSOLVED HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER, AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY

Revision 3.3
EMMC Version

E.J. Arar, S.E. Long (Technology Applications, Inc.), and J.D. Pfaff - Method 218.6, Revision 3.2 (1991)

E.J. Arar, J.D. Pfaff, and T.D. Martin - Method 218.6, Revision 3.3 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 218.6

DETERMINATION OF DISSOLVED HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER, AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for determination of dissolved hexavalent chromium (as CrO_4^{2-}) in drinking water, groundwater, and industrial wastewater effluents.

Analyte	Chemical Abstracts Service Registry Number (CASRN)
Hexavalent Chromium (as CrO_4^{2-})	11104-59-9

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 The method detection limits (MDL) obtained by a single laboratory for hexavalent chromium (Cr(VI)) in the above matrices are listed in Table 1. The MDL obtained by an individual laboratory for a specific matrix may differ from those listed depending on the nature of the sample and the instrumentation used. A multilaboratory method detection limit (MMDL) in reagent water was determined to be 0.4 µg/L. The IMDL was based upon the within-laboratory standard deviation (s_r) of thirteen paired analyses of samples by thirteen laboratories at an average analyte concentration of 1.4 µg/L.

1.4 Samples containing high levels of anionic species such as sulphate and chloride may cause column overload. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). Samples must be stored at 4°C and analyzed within 24 h of collection.

1.5 This method should be used by analysts experienced in the use of ion chromatography.

2.0 SUMMARY OF METHOD

2.1 An aqueous sample is filtered through a 0.45-μm filter and the filtrate is adjusted to a pH of 9 to 9.5 with a concentrated buffer solution. A measured volume of the sample (50-250 μL) is introduced into the ion chromatograph. A guard column removes organics from the sample before the Cr(VI), as CrO_4^{2-}, is separated on a high capacity anion exchange separator column. Post-column derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex at 530 nm.

3.0 DEFINITIONS

3.1 **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 (Sect. 7.9).

3.2 **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.

3.3 **Instrument Performance Check (IPC) Solution** - A solution of the method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.4 **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.

3.5 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.6 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which a known quantity of the method analyte is 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 concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured value in the LFM corrected for background concentration.

3.7 **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 the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

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

3.9 **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.10 **Quality Control Sample (QCS)** - A solution of the method analyte of known concentration which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

3.11 **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.

4.0 INTERFERENCES

4.1 Interferences which affect the accurate determination of Cr(VI) may come from several sources.

4.1.1 Contamination - A trace amount of Cr is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess for potential Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact of caustic or acidic reagents or samples with stainless steel or pigmented material.

4.1.2 Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. At pH 6.5 or greater, however, CrO_4^{2-} which is less reactive than $HCrO_4^-$ is the predominant species

4.1.3 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulphate, will cause a loss of Cr(VI). The column specified in this method can handle samples containing up to 5% sodium sulphate or 2% sodium chloride[2]. Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

5.0 SAFETY

5.1 Hexavalent chromium is toxic and a suspected carcinogen and should be handled with appropriate precautions. Extreme care should be exercised when weighing the salt for preparation of the stock standard. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of chemicals specified in this method. A reference file of material

safety data sheets should also be available to all personnel involved in the chemical analysis.[3,4]

6.0 EQUIPMENT AND SUPPLIES

6.1 Ion Chromatograph

6.1.1 Instrument equipped with a pump capable of withstanding a minimum backpressure of 2000 psi and of delivering a constant flow in the range of 1-5 mL/min and containing no metal parts in the sample, eluent or reagent flow path.

6.1.2 Helium gas supply (High purity, 99.995%).

6.1.3 Pressurized eluent container, plastic, 1- or 2-L size.

6.1.4 Sample loops of various sizes (50-250μL).

6.1.5 A pressurized reagent delivery module with a mixing tee and beaded mixing coil.

6.1.6 Guard Column - A column placed before the separator column and containing a sorbent capable of removing strongly absorbing organics and particles that would otherwise damage the separator column (Dionex IonPac NG1 or equivalent).

6.1.7 Separator Column - A column packed with a high capacity anion exchange resin capable of separating CrO_4^{2-} from other sample constituents (Dionex IonPac AS7 or equivalent).

6.1.8 A low-volume flow-through cell, visible lamp detector containing no metal parts in contact with the eluent flow path. Detection wavelength is at 530 nm.

6.1.9 Recorder, integrator or computer for receiving analog or digital signals for recording detector response (peak height or area) as a function of time.

6.2 Labware - All reusable labware (glass, quartz, polyethylene, Teflon, etc.), including the sample containers, should be soaked overnight in laboratory grade detergent and water, rinsed with water, and soaked for 4 h in a mixture of dilute nitric and hydrochloric acid (1+2+9) followed by rinsing with tap water and ASTM type I water.

NOTE: Chromic acid must not be used for cleaning glassware.

6.2.1 Glassware - Class A volumetric flasks and a graduated cylinder.

6.2.2 Assorted Class A calibrated pipettes.

6.2.3 10-mL male luer-lock disposable syringes.

6.2.4 0.45-μm syringe filters.

6.2.5 Storage bottle - High density polypropylene, 1-L capacity.

6.3 Sample Processing Equipment

6.3.1 Liquid sample transport containers - High density polypropylene, 125-mL capacity.

6.3.2 Supply of dry ice or refrigerant packing and styrofoam shipment boxes.

6.3.3 pH meter - To read pH range 0-14 with accuracy $\pm$ 0.03 pH units.

6.3.4 0.45-μm filter discs, 7.3-cm diameter (Gelman Acro 50A, Mfr. No. 4262 or equivalent).

6.3.5 Plastic syringe filtration unit (Baxter Scientific, Cat. No. 1240 IN or equivalent).

7.0 REAGENTS AND STANDARDS

7.1 Reagents - All chemicals are ACS grade unless otherwise indicated.

7.1.1 Ammonium hydroxide, NH_4OH, (sp.gr. 0.902), (CASRN 1336-21-6).

7.1.2 Ammonium sulphate, $(NH_4)_2SO_4$, (CASRN 7783-20-2).

7.1.3 1,5-Diphenylcarbazide, (CASRN 140-22-7).

7.1.4 Methanol, HPLC grade.

7.1.5 Sulfuric acid, concentrated (sp.gr. 1.84).

7.2 Reagent Water - For all sample preparations and dilutions, ASTM Type I water (ASTM D1193) is required. Suitable water may be obtained by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 Cr(VI) Stock Standard Solution - To prepare a 1000 mg/L solution, dissolve 4.501 g of $Na_2CrO_4 \cdot 4H_2O$ in ASTM Type I water and dilute to 1 L. Transfer to a polypropylene storage container.

7.4 Laboratory Reagent Blank (LRB) - Aqueous LRBs can be prepared by adjusting the pH of ASTM Type I water to 9-9.5 with the same volume of buffer as is used for samples.

7.5 Laboratory Fortified Blank (LFB) - To an aliquot of LRB add an aliquot of stock standard (Sect. 7.3) to produce a final concentration of 100

μg/L of Cr(VI). The LFB must be carried through the entire sample preparation and analysis scheme.

7.6 Quality Control Sample (QCS) - A quality control sample must be obtained from an outside laboratory. Dilute an aliquot according to instructions and analyze with samples. A recommended minimum concentration for the QCS is 10 μg/L.

7.7 Eluent - Dissolve 33 g of ammonium sulphate in 500 mL of ASTM type I water and add 6.5 mL of ammonium hydroxide. Dilute to 1 L with ASTM type I water.

7.8 Post-Column Reagent - Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL of HPLC grade methanol. Add to about 500 mL of ASTM type I water containing 28 mL of 98% sulfuric acid while stirring. Dilute with ASTM type I water to 1 L in a volumetric flask. Reagent is stable for four or five days but should be prepared only as needed.

7.9 Buffer Solution - Dissolve 33 g of ammonium sulphate in 75 mL of ASTM type I water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with ASTM type I water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration and pH adjustment should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For determination of dissolved Cr(VI), the sample should be filtered through a 0.45-μm filter. Use a portion of the sample to rinse the syringe filtration unit and filter and then collect the required volume of filtrate. Adjust the pH of the sample to 9-9.5 by adding dropwise a solution of the buffer, periodically checking the pH with the pH meter. Approximately 10 mL of sample are sufficient for three IC analyses.

8.3 Ship and store the samples at 4°C. Bring to ambient temperature prior to analysis. Samples must be analyzed within 24 h of 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 analysis of laboratory reagent blanks, and fortified blanks and samples 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 (MDLs and linear dynamic range) and laboratory performance prior to sample analyses.

9.2.2 Method detection limit (MDL) -- A MDL should be established using reagent water fortified at a concentration of two-five times the estimated detection limit. To determine the MDL value, 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 n-1 degrees of freedom at the 99% confidence level; t = 3.143 for six degrees of freedom.

s = standard deviation of the replicate analyses.

The MDL must be sufficient to detect Cr (VI) at the required level according to compliance monitoring regulation (Sect. 1.2). The MDL should be determined annually, when a new operator begins work or whenever there is a change in instrument analytical hardware or operating conditions.

9.2.3 Linear dynamic range (LDR) -- The LDR should be determined by analyzing a minimum of 7 calibration standards ranging in concentration from 1 µg/L to 5,000 µg/L across all sensitivity settings of the spectrophotometer. Normalize responses by dividing the response by the sensitivity setting multiplier. Perform the linear regression of normalized response vs. concentration and obtain the constants m and b, where m is the slope of the line and b is the y-intercept. Incrementally analyze standards of higher concentration until the measured absorbance response, R, of a standard no longer yields a calculated concentration, C_c, that is $\pm$ 10% of the known concentration, C, where $C_c = (R - b)/m$. That concentration defines the upper limit of the LDR for your instrument and analytical operating conditions. Samples having a concentration that is $\geq$ 90% of the upper limit of the LDR must be diluted to fall within the bounds of the current calibration curve concentration range and reanalyzed.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 The laboratory must analyze at least one LRB (Sect. 7.4) with each set of samples. Reagent blank data are used to assess contamination from a laboratory environment. If the

Cr(VI) value in the reagent blank exceeds the determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

9.3.2 The laboratory must analyze at least one LFB (Sect. 7.5) with each set of samples. Calculate accuracy as percent recovery (Sect. 9.4.2). If the recovery of Cr(VI) falls outside the control limits (Sect. 9.3.3), then the procedure is judged out of control, and the source of the problem should be identified and resolved before continuing the analysis.

9.3.3 Until sufficient data become available (usually a minimum of 20 to 30 analyses), assess laboratory performance against recovery limits of 90-110%. When sufficient internal performance data becomes available, develop control limits from the percent mean recovery (x) and the standard deviation (s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = x + 3s$$
$$\text{LOWER CONTROL LIMIT} = x - 3s$$

9.3.4 To verify that the instrument is properly calibrated on a continuing basis, run a LRB and a IPC (Sect. 3.3) after every ten analyses. The results of analyses of standards will indicate whether the calibration remains valid. If the measured concentration of the IPC (a midpoint calibration standard) deviates from the true concentration by more than $\pm$5%, perform another analysis of the LPC. If the discrepancy is still $\pm$5% of the known concentration then the instrument must be recalibrated and the previous ten samples reanalyzed. The instrument response from the calibration check may be used for recalibration purposes.

9.3.5 Quality control sample (QCS) - Each quarter, the laboratory should analyze one or more QCS. If criteria provided with the QCS are not within $\pm$10% of the stated value, corrective action must be taken and documented.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 The laboratory must add a known amount of Cr(VI) to a minimum of 10% of samples. The concentration level can be the same as that of the laboratory fortified blank (Sect. 7.5).

9.4.2 Calculate the percent recovery for Cr(VI) corrected for background concentration measured in the unfortified sample, and compare this value to the control limits established in Sect. 9.3.3 for the analysis of LFBs. Fortified recovery

calculations are not required if the concentration of Cr(VI) added is less than 2X the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_F - C}{F} \times 100$$

where:

R = percent recovery
C_F= fortified sample concentration
C = sample background concentration
F = concentration equivalent of Cr(VI) added to sample

9.4.3 If the recovery of Cr(VI) falls outside control limits established in Section 9.3.3 and the recovery obtained for the LFB was 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. The result for Cr(VI) in the unfortified sample must be labelled 'suspect matrix'.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish IC operating conditions as indicated in Table 2. The flow rate of the eluent pump is set at 1.5 mL/min and the pressure of the reagent delivery module adjusted so that the final flow rate of the post column reagent (Sect. 7.8) from the detector is 2.0 mL/min. This requires manual adjustment and measurement of the final flow rate using a graduated cylinder and a stop watch. A warm up period of approximately 30 min after the flow rate has been adjusted is recommended and the flow rate should be checked prior to calibration and sample analysis.

10.2 Injection sample loop size should be chosen based on anticipated sample concentrations and the selected sensitivity setting of the spectrophotometer. A 250-μL loop was used to establish the method detection limits in Table 1. A 50-μL loop is normally sufficient for higher concentrations. The sample volume used to load the sample loop should be at least 10 times the loop size so that all tubing in contact with sample is thoroughly flushed with new sample to minimize cross-contamination.

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 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 The recommended calibration routine is given in Section 11.3.

11.0 PROCEDURE

11.1 Filtered, pH adjusted samples at 4°C should be brought to ambient temperature prior to analysis.

11.2 Initiate instrument operating configuration described in Section 10 and Table 2.

11.3 Calibration - Before samples are analyzed a calibration should be performed using a minimum of three calibration solutions that bracket the anticipated concentration range of the samples. Calibration standards should be prepared from the stock standard (Sect. 7.3) by appropriate dilution with ASTM type I water (Sect. 7.2) in volumetric flasks. The solution should be adjusted to pH 9-9.5 with the buffer solution (Sect. 7.9) prior to final dilution.

11.4 Construct a calibration curve of analyte response (peak height or area) versus analyte concentration over a concentration range of one or two orders of magnitude. The calibration range should bracket the anticipated concentration range of samples. The coefficient of correlation (r) for the curve should be 0.999 or greater.

11.5 Draw into a new, unused syringe (Sect. 6.2.3) approximately 3 mL of sample. Inject 10X the volume of the sample loop into the injection valve of the IC. Sample concentrations that exceed the calibration range must be diluted and reanalyzed.

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

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The sample concentration can be calculated from the calibration curve. Report values in µg/L. Sample concentrations must be corrected for any Cr(VI) contamination found in the LRB.

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

13.0 METHOD PERFORMANCE

13.1 Instrumental operating conditions used for single-laboratory testing of the method are summarized in Table 2. MDLs for dissolved Cr(VI) in five matrix waters are listed in Table 1.

13.2 Single-analyst precision and accuracy data for five matrix waters, drinking water, deionized water, groundwater, treated municipal sewage

wastewater, and treated electroplating wastewater are listed in Table 3.

13.3 Pooled Precision and Accuracy: This method was tested by 21 volunteer laboratories in a joint study by the USEPA and the American Society for Testing and Materials (ASTM). Mean recovery and accuracy for Cr(VI) (as CrO_4^{2-}) was determined from the retained data of 13 laboratories in reagent water, drinking water, ground water, and various industrial wastewaters. For reagent water, the mean recovery and the overall, and single-analyst relative standard deviations were 105%, 7.8% and 3.9% respectively. For the other matrices combined, the same values were 96.7%, 11.9% and 6.3%, respectively. Table 4 contains the linear equations that describe the single-analyst standard deviation, overall standard deviation and mean recovery of Cr(VI) in reagent water and matrix water.

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. 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 rule 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 Sect. 14.2.

16.0 REFERENCES

1. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A. and Budde, W.L., "Trace Analyses for Wastewaters", Environ. Sci. and Technol., Vol.15, No.12, 1981, pp.1426-1435.

2. Dionex Technical Note No. 26, May 1990.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986.

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

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1. METHOD DETECTION LIMIT FOR CR(VI)

Matrix Type	Conc. Used to Compute MDL µg/L	MDL µg/L
Reagent Water	1	0.4
Drinking Water	2	0.3
Ground Water	2	0.3
Primary Sewage wastewater	2	0.3
Electroplating wastewater	2	0.3

TABLE 2. ION CHROMATOGRAPHIC CONDITIONS

Columns: Guard Column - Dionex IonPac NG1
Separator Column - Dionex IonPac AS7

Eluent: 250 mM $(NH_4)_2SO_4$
100 mM NH_4OH
Flow rate = 1.5 mL/min

Post-Column Reagent: 2mM Diphenylcarbohydrazide
10% v/v CH_3OH
1 N H_2SO_4
Flow rate = 0.5 mL/min

Detector: Visible 530 nm

Retention Time: 3.8 min

TABLE 3. SINGLE ANALYST PRECISION AND ACCURACY

Sample Type	Cr(VI) (µg/L) (a)	Mean Recovery (%)	RPD (b)
Reagent Water	100	100	0.8
	1000	100	0.0
Drinking Water	100	105	6.7
	1000	98	1.5
Groundwater	100	98	0.0
	1000	96	0.8
Primary sewage wastewater effluent	100	100	0.7
	1000	104	2.7
Electroplating wastewater effluent	100	99	0.4
	1000	101	0.4

(a) Sample fortified at this concentration level.
(b) RPD - relative percent difference between duplicates.

TABLE 4. SINGLE-ANALYST PRECISION, OVERALL PRECISION AND RECOVERY FROM MULTILABORATORY STUDY

	Reagent Water (6-960 µg/L)	Matrix Water (6-960 µg/L)
Mean Recovery	$X = 1.020C + 0.592$	$X = 0.989C - 0.411$
Overall Standard Deviation	$s_R = 0.035X + 0.893$	$s_R = 0.059X + 1.055$
Single-Analyst Standard Deviation	$s_r = 0.021X + 0.375$	$s_r = 0.041X + 0.393$

X Mean concentration, µg/L, exclusive of outliers.
C True value, µg/L.
s_R Overall standard deviation.
s_r Single-analyst standard deviation.

METHOD 245.1

DETERMINATION OF MERCURY IN WATER BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

Revision 3.0
EMMC Version

J.F. Kopp, M.C. Longbottom, and L.B. Lobring - Mercury in Water (Cold Vapor Technique), Revision 1.0, (1972)

J.F. Kopp and L.B. Lobring - Method 245.1, Revision 2.0 (1979)

L.B. Lobring and B.B. Potter - Method 245.1, Revision 2.3 (1991)

J.W. O'Dell, B.B. Potter, L.B. Lobring, and T.D. Martin - Method 245.1, Revision 3.0 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 245.1

DETERMINATION OF MERCURY IN WATER BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This procedure[1] measures total mercury (organic + inorganic) in drinking, surface, ground, sea, brackish waters, industrial and domestic wastewater.

Analyte	Chemical Abstracts Service Registry Number (CASRN)
Mercury	7439-97-6

1.2 The range of the method is 0.2 to 10 μg Hg/L. The range may be extended above or below the normal range by increasing or decreasing sample size. However, the actual method detection limit and linear working range will be dependent on the sample matrix, type of instrumentation configuration, and selected operating conditions.

1.3 Reduced volume or semi-automated versions of this method, that use the same reagents and molar ratios, are acceptable provided they meet the quality control and performance requirements stated in the method (Sect. 9.0).

1.4 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.

2.0 SUMMARY OF METHOD

2.1 A known portion of a water sample is transferred to a BOD bottle, equivalent ground glass stoppered flask or other suitable closed container. It is digested in diluted potassium permanganate-potassium persulfate solutions and oxidized for 2 h at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

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 auto-zero the instrument.

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **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.

3.4 **Instrument Performance Check (IPC) Solution** - A solution of the method analyte, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.5 **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.

3.6 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.7 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 **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 the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

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

3.10 **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.11 **Quality Control Sample (QCS)** - A solution of the method analyte of known concentration which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

3.12 **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.13 **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.

4.0 INTERFERENCES

4.1 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures (Sect. 9) must be strictly followed.

4.2 Volatile materials (e.g. chlorine) which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the digestion vessel (BOD bottle) should be purged before addition of stannous chloride solution.

4.3 Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as total Kjeldahl nitrogen (TKN) or chemical oxygen demand (COD).

5.0 SAFETY

5.1 The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices.[2] Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[3, 4]

5.2 Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

5.3 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.

5.4 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.

6.0 EQUIPMENT AND SUPPLIES

6.1 Atomic Absorption Cold Vapor System

6.1.1 Atomic Absorption Spectrophotometer - Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. The use of background correction is recommended, but is not mandatory.

6.1.2 Mercury Hollow Cathode Lamp - Single element hollow cathode lamp or electrodeless discharge lamp and associated power supply.

6.1.3 Absorption Cell - Standard spectrophotometer cells 10-cm long, having quartz windows may be used. Suitable cells may be constructed from plexiglass tubing, 1-in. O.D. by 4 1/2-in. long. The ends are ground perpendicular to the longitudinal axis and quartz windows (1-in. diameter by 1/16-in. thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4-in. O.D.) are attached approximately 1/2-in. from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

6.1.4 Aeration Tubing - Inert mercury-free tubing is used for passage of mercury vapor from the sample bottle to the absorption cell. In some systems, mercury vapor is recycled. Straight glass tubing terminating in a coarse porous glass aspirator is used for purging mercury released from the water sample in the BOD bottle.

6.1.5 Air Pump - Any pump (pressure or vacuum system) capable of passing air 1 L/min is used. Regulated compressed air can be used in an open one-pass system.

6.1.6 Drying Tube - Tube (6-in. x 3/4-in. OD) containing 20 g of magnesium perchlorate. The filled tube is inserted (in-

line) between the BOD bottle and the absorption tube. In place of the magnesium perchlorate drying tube, a small reading lamp is positioned to radiate heat (about 10°C above ambient) on the absorption cell. Heat from the lamp prevents water condensation in the cell.

6.1.7 Recorder - Any multi-range variable speed recorder or data system that is compatible with the UV detection system is suitable.

Note: Instruments designed specifically for mercury measurement using the cold vapor technique are commercially available and may be substituted for the atomic absorption cold vapor system described above.

6.2 Flowmeter, capable of measuring an air flow of 1 L/min.

6.3 A water bath with a covered top and capacity to maintain a water depth of 2 to 3 inches at 95°C.

6.4 Analytical balance, with capability to measure to 0.1 mg, for use in weighing reagents and preparing standards.

6.5 Labware - All reusable labware should be sufficiently clean for the task objectives. Particular attention should be given to all ground glass surfaces during cleaning. Routinely all items should be soaked in 30% HNO_3 and rinsed three times in reagent water. Digestion containers used in sample preparation that do not rinse clean of the previous sample should be washed with a detergent solution prior to acid cleaning.

6.5.1 Glassware - Volumetric flasks and graduated cylinders.

6.5.2 BOD bottles (or other equivalent suitable closed containers).

6.5.3 Assorted calibrated pipettes.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities which bias analytical results. All reagents should be assayed by the chemical manufacturer for mercury and meet ACS specifications. The assayed mercury level of all solid reagents used in this method should not exceed 0.05 ppm. It is recommended that the laboratory analyst assay all reagents for mercury.

7.2 Reagent Water, ASTM type II[5].

7.3 Nitric Acid (HNO_3), concentrated (sp.gr. 1.41), assayed mercury level is not to exceed 1 µg/L.

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

7.4 Sulfuric Acid (H_2SO_4), concentrated (sp.gr. 1.84), assayed mercury level is not to exceed 1 µg/L.

7.4.1 Sulfuric acid, 0.5 N - Slowly add 14.0 mL of conc. H_2SO_4 to 500 mL of reagent water and dilute to 1 L with reagent water.

7.5 Mercury standard, stock, 1 mL = 100 µg Hg: DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 0.1354 g $HgCl_2$ in 75 mL reagent water. Add 50.0 mL concentrated HNO_3 (Sect. 7.3) and dilute to volume in 1-L volumetric flask with reagent water.

7.6 Mercury calibration standard (CAL) - To each volumetric flask used for serial dilutions, acidify with (0.1 to 0.2% by volume) HNO_3 (Sect. 7.3). Using mercury stock standard (Sect. 7.5), make serial dilutions to obtain a concentration of 0.1 µg Hg/mL.

7.7 Potassium permanganate solution - Dissolve 5 g of $KMnO_4$ in 100 mL of reagent water.

7.8 Potassium persulfate solution - Dissolve 5 g of $K_2S_2O_8$ in 100 mL of reagent water.

7.9 Sodium chloride-hydroxylammonium chloride solution - Dissolve 12 g of NaCl and 12 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 mL reagent water. (Hydroxylamine sulfate $(NH_2OH)_2 \cdot H_2SO_4$ may be used in place of hydroxylamine hydrochloride.)

7.10 Stannous chloride solution - Add 25 g of $SnCl_2 \cdot 2H_2O$ to 250 mL of 0.5 N H_2SO_4 (Sect. 7.4.1). This mixture is a suspension and should be stirred continuously during use.

7.11 Blanks - Three 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, and the laboratory fortified blank is used to assess routine laboratory performance.

7.11.1 The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

7.11.2 The laboratory reagent blank (LRB) is prepared in the manner as the calibration blank except the LRB must be carried through the entire sample preparation scheme.

7.11.3 The laboratory fortified blank (LFB) is prepared by fortifying a sample size volume of laboratory reagent blank solution with mercury to a suitable concentration of > 10X the MDL, but <

the midpoint concentration of the calibration curve. The LFB must be carried through the entire sample preparation scheme.

7.12 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It must contain all reagents in the same concentration as the calibration solutions and mercury at an appropriate concentration to approximate the midpoint of the calibration curve. The IPC solution should be prepared from the same CAL standard (Sect. 7.6) as used to prepare the calibration 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, analysis of a QCS is required. The QCS must be obtained from an outside source different from the standard stock solution, but prepared in the same manner as the calibration solutions. The concentration of the mercury in the QCS solution should be such that the resulting solution will provide an absorbance reading near the midpoint of the calibration curve. The QCS should be analyzed quarterly or more frequently as needed to meet data-quality needs.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

8.2 For the determination of total mercury (inorganic + organic) in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid (Sect. 7.3.1) 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 as soon as possible after 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 withdrawing an aliquot for 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 additional sixteen hours until verified to be pH < 2. The preserved sample should be analyzed within 28 days of collection.

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.

8.3 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 by analysis of laboratory reagent blanks, fortified blanks and samples used for continuing check on method performance. Commercially available water quality control samples are acceptable for routine laboratory use. The laboratory is required to maintain performance records that define the quality of the data 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. It must be determined from a linear calibration prepared from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The LDR should be determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The determined LDR 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 LDR 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 a QCS (Sect. 7.13). To verify the calibration standards, the determined concentration of the QCS must be within ± 10% of the stated value. If the calibration standard cannot 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) - A mercury MDL must be established using an LRB solution fortified at a concentration of two to three times the estimated detection limit.[6] To determine MDL values, take seven replicate aliquots of the fortified LRB 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 = 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%, the concentration used to determine the mercury MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in an LRB solution represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Sect. 9.4) can give confidence to the MDL value determined in LRB solution.

The MDL must be sufficient to detect mercury at the required level according to compliance monitoring regulation (Sect. 1.2). The mercury MDL 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 (Sect. 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 (Sect. 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 mercury added to fortify the LRB solution.

If the recovery of mercury falls outside the required control limits of 85-115%, the analysis 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% (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:

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

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten new recovery measurements, new control limits 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 - For all determinations the laboratory must analyze the IPC solution (Sect. 7.12) and a calibration blank immediately following each calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the MDL. 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 cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or in the case of drift 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.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect mercury 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 (Sect 9.4.2) is required.

9.4.2 The laboratory must add a known amount of mercury to a minimum of 10% of samples or one sample per sample set, whichever is greater. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. Select a sample with a low mercury background that is representative of the type of water samples being analyzed. It is recommended that this sample be analyzed prior to fortification. The concentration of mercury added may vary based on the nature of samples being analyzed. When possible, the concentration should be the same as that added to the LRB, but should not exceed the midpoint concentration of the calibration curve. Over time, samples from all routine sample sources should be fortified.

9.4.3 Calculate the percent recovery, corrected for background concentration measured in the unfortified sample aliquot, and compare these values to the control limits to the designated LFM recovery range of 70-130%. 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 mercury added to water sample.

9.4.4 If mercury recovery falls outside the designated range, and the laboratory performance is shown to be in control (Sect. 9.3),

the recovery problem encountered with the fortified water sample is judged to be matrix related, not system related. The result for mercury in the unfortified sample must be labelled to inform the data user that the results are suspect due to matrix effects.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Conveniently arrange and connect the various components of the instrument system using one of the options shown in Figure 1. If adjustable, the monochromator should be set to 253.65 nm. Prior to the use of this method the air flow should be optimized. (The recommended air flow rate through the system is 1 liter per minute.) For all determinations allow an instrument and hollow cathode lamp warm up period of not less than 15 min. When an instrument designed specifically for the determination of mercury by the cold vapor technique is being utilized, the analyst should follow the instructions provided by the manufacturer.

10.2 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 used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.3 The recommended calibration routine is given in Section 11.2.

11.0 PROCEDURE

11.1 Sample Preparation

11.1.1 Transfer 100 mL of the water sample [or an aliquot diluted with reagent water (Sect. 7.2) to 100 mL] into a sample container.

NOTE: For reduced volume analysis, adjust sample and reagent volumes to maintain the required sample to reagent ratios.

11.1.2 Add 5 mL of H_2SO_4 (Sect. 7.4) and 2.5 mL of HNO_3 (Sect. 7.3) to the container.

11.1.3 To each container add 15 mL $KMnO_4$ solution (Sect. 7.7). For sewage or industry wastewaters, additional $KMnO_4$ may be required. Shake and add additional portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of $K_2S_2O_8$ solution (Sect. 7.8) to each container. Mix thoroughly, cap and cover the top of the sample container (if required) with aluminum foil or other appropriate cover. Heat for 2 h in a water bath at 95°C.

11.1.4 Remove the sample containers from the water bath and cool to room temperature. (During the cool down period proceed with instrument warm up and calibration.)

11.1.5 When the samples are at room temperature, to each container, add 6 mL of NaCl-$(NH_2OH)_2 \cdot H_2SO_4$ solution (Sect. 7.9) to reduce the excess permanganate.

11.2 Sample Analysis

11.2.1 Before beginning daily calibration the instrument should be reconfigured to the optimized conditions. Turn on the instrument and circulating pump. Adjust pump rate to 1 L/min or as required. Allow system to stabilize.

11.2.2 Prepare calibration standards by transferring 0.5, 1.0, 2.0, 5.0 and 10 mL aliquots of the 0.1 µg/mL CAL (Sect. 7.6) to a series of sample containers (Sect. 6.5.2). Dilute the standard aliquots to 100 mL with reagent water (Sect. 7.2) and process as described in Sects. 11.1.2, 11.1.3 (without heating), and 11.1.5. These solutions contain 0.05 to 1.0 µg of Hg. (Other appropriate calibration standards, volumes, and ranges may also be used.)

11.2.3 Treating each standard solution container individually, add 5 mL of $SnCl_2$ solution (Sect. 7.10) and immediately attach the container to the aeration apparatus. The absorbance, as exhibited either on the instrument or recording device, will increase and reach maximum within 30 sec. As soon as the maximum response is obtained, approximately 1 min, open the bypass value (or optionally remove aspirator from the sample container if it is vented under the hood) and continue aeration until the absorbance returns to its minimum value.

11.2.4 Close the by-pass value, remove the aspirator from the standard solution container and continue aeration. Repeat (Sect. 11.2.3) until data from all standards have been collected.

11.2.5 Construct a standard curve by plotting peak height, area or maximum response obtained from each standard solution, versus micrograms of mercury in the container. The standard curve must comply with Sect. 9.2.2. Calibration using computer or calculator based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6 Following calibration the digested samples are analyzed in the same manner as the standard solutions described in Section 11.2.3. However, prior to the addition of the $SnCl_2$ solution, place the aspirator inside the container above the liquid, and purge the head space (20 to 30 sec) to remove possible gaseous interference.

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

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 From the prepared calibration curve (Sect. 11.2.4) compute sample values by comparing response with the standard curve.

12.2 Calculate the mercury concentration in the sample by the formula:

$$\mu g\ Hg/L = \left(\frac{\mu g\ Hg\ in}{aliquot}\right)\left(\frac{1{,}000}{mL\ of\ aliquot}\right)$$

12.3 Report mercury concentrations to the proper significant figures in mg/L, µg/L or ng/L as required.

13.0 METHOD PERFORMANCE

13.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 µg/L Hg and fortified with concentration of 1.0, 3.0, and 4.0 µg/L Hg, the standard deviations were ± 0.14, ± 0.10 and ± 0.08 µg/L Hg, respectively. Standard deviation at the 0.35 µg/L Hg level was ± 0.16 µg/L Hg. Percent recoveries at the three levels were 89%, 87%, and 87%, respectively.

13.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study is found in Table 1.

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. 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 rule 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 Sect. 14.2.

16.0 REFERENCES

1. Kopp, J.F., Longbottom, M.C., and Lobring, L.B., " 'Cold Vapor' Method for Determining Mercury"; J. Am. Water Works Assoc., Vol. 64, No. 1, January 1972.

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

3. "OSHA Safety and Health Standards, General Industry", (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

4. "Proposed OSHA Safety and Health Standards, Laboratories", Occupational Safety and Health Administration, Federal Register, July 24, 1986.

5. "Specification for Reagent Water", D1193, Annual Book of ASTM Standards, Vol. 11.01, 1990.

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

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. INTERLABORATORY PRECISION AND ACCURACY DATA FOR FLAMELESS ATOMIC ABSORPTION

Number of Labs	True Values µg/L	Mean Value µg/L	Standard Deviation µg/L	RSD %	Mean Accuracy as % Bias
76	0.21	0.349	0.276	89	66
80	0.27	0.414	0.279	67	53
82	0.51	0.674	0.541	80	32
77	0.60	0.709	0.390	55	18
82	3.4	3.41	1.49	44	0.34
79	4.1	3.81	1.12	29	-7.1
79	8.8	8.77	3.69	42	-0.4
78	9.6	9.10	3.57	39	-5.2

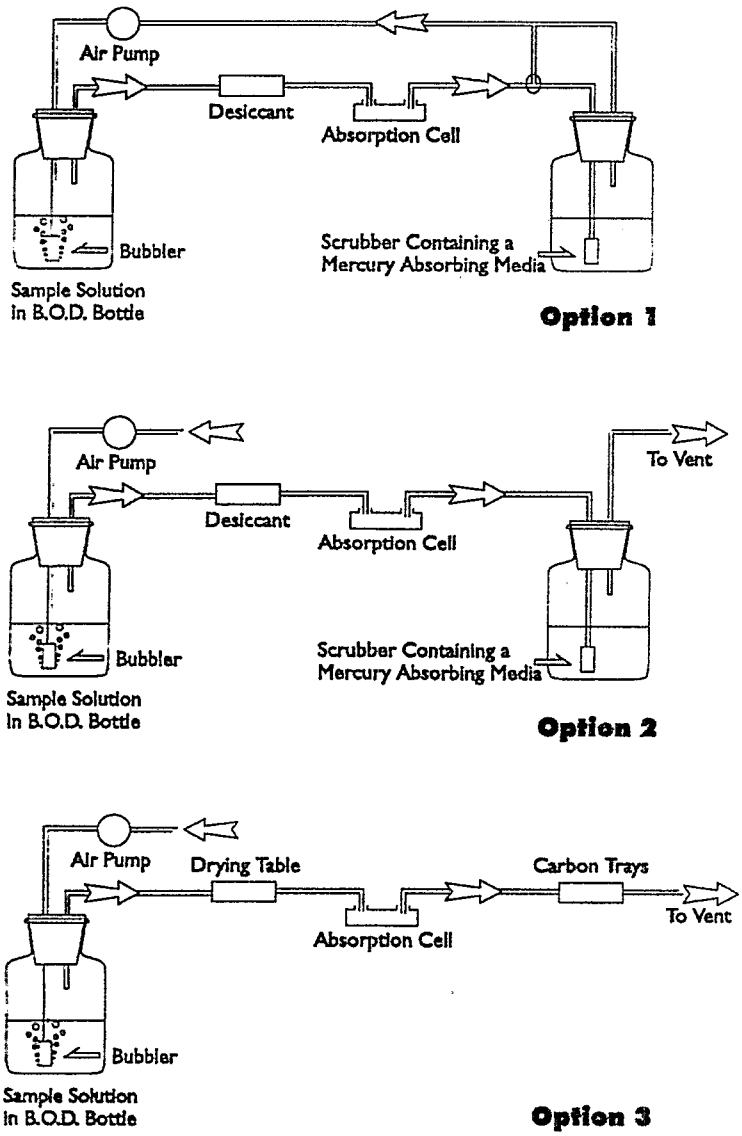

Figure 1. Apparatus for Flameless Mercury Determination

Because of the toxic nature of mercury vapor, inhalation must be avoided. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, P.O. Box 2526, Columbus, OH 43216, Catalog No. 580-13 or 580-22.

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