METHOD 200.9

**DETERMINATION OF TRACE ELEMENTS BY STABILIZED TEMPERATURE
GRAPHITE FURNACE ATOMIC ABSORPTION**

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EMMC Version

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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 Number (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 (Section 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 (Section 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 (Section 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 (Section 11.1).

3.4   **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Section 8.5).

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 (Sections 7.11 and 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 (Sections 7.10.3 and 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 (Section 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 (Sections 7.10.2 and 9.3.1).

3.11 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Section 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 (Section 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 (Sections 7.12 and 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 (Sections 9.5.1 and 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 (Section 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 (Sections 11.2 and 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 (Section 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. Twenty 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 _not_ 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. Twenty 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. Twenty 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. Twenty 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 100-2500 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 four hours 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 (99.99-99.999% pure). All compounds must be dried for one hour at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

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

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

From pure element,

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

From pure compound,

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

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

7.8.1 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 HN0$_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.8.2 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$_2$O$_3$ (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH$_4$OH. 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: <u>DO NOT DRY</u>. 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 and 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 (Sections 7.2 and 7.3) and ASTM Type I water.

7.10.1 The calibration blank consists of the appropriate acid diluent (Section 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 L 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 (Section 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 (Section 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 six months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are

recommended to avoid possible contamination.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

8.3   For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1.

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

8.4   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 (Section 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 (Section 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:

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

where: t = Student's t value for a 99% confidence level and a standard

deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate.   If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inapprop-riately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 2.

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

9.3   Assessing Laboratory Performance (mandatory)

9.3.1   Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Section 7.10.2) 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 (Section 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% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

    UPPER CONTROL LIMIT   = x + 3S
     LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%.   After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to established an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution - For all determinations the laboratory must analyze the IPC solution (Section 7.11) and a calibration blank immediately following each calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be less than the IDL, but greater than 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 (Section 9.4.2) is required. Also, the analyte addition test (Section 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 (Section 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, Section 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 thesample

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 (Section 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 (Section 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 (Section 11.5).

2.   If the recovery of the analyte addition test is between 85-115%, 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 (Section 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 (Section 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 (Section 11.5).

2.   If the percent recovery of the analyte addition test is between 85-115%, 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 (Section 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 (Section 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 85-115%, 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 85-115%, complete the sample analysis by analyzing the dilution of the unfortified aliquot by method of standard additions (Section 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 not 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 85-115% 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 (Section 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 (Section 9.2.2) using the optimized instrument operating conditions (Section 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 minutes for warm up.

10.4   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 are described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Section 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 (Section 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 ($\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). Cap the tube and mix. The sample is now ready for analysis (Section 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 through 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 (Sections 1.2 and 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 (Sections 1.2 and 1.6). (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 through 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 85ºC. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95ºC.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. <u>DO NOT BOIL</u>. This step takes about two hours 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 (Section 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 (Section 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 minutes. 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 (3-4 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 minutes for instrument and hollow cathode lamp warm up. If an EDL is to be used, allow 30 minutes 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 (Section 7.10.1) and calibration standards (Section 7.9) prepared at three or more concentrations within the usable linear dynamic range of the analyte (Sections 4.4 and 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 (Section 7.10.4) between each solution injected.

11.4.6   After completion of the initial requirements of this method (Section 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 (Section 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 (Section 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 12.0.

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. 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 = 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 is made much less than V_X, and thus C_S i much greater than C, 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 $\mu g/L$ for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Section 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 (Section 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 (Section 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:

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

where: C = Concentration in the 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.

12.5   To report percent solids in solid samples (Section 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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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 DATA 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 DATA 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 DATA 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. RECOMMEND 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 (Section 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.