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METHOD 200.9

TRACE ELEMENTS IN WATER, SOLIDS, AND BIOSOLIDS BY STABILIZED TEMPERATURE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

Revision 3.0
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J.T. Creed, T.D. Martin, and J.W. O'Dell - Method 200.9, Revision 2.2 (1994)

Disclaimer

This draft method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. EPA plans further validation of this draft method. The method may be revised following validation to reflect results of the study. This method version contains minor editorial changes to the October 2000 version.

EPA welcomes suggestions for improvement of this method. Suggestions and questions concerning this method or its application should be addressed to:

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Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "must," "shall," and "may not" define procedures required for producing reliable data for producing reliable results. The terms "may" and “should” indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 200.9

Trace Elements in Water, Solids, and Biosolids by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry

1.0 Scope and Application

1.1 This method provides procedures for the determination of dissolved and total recoverable elements by graphite furnace atomic absorption spectrometry (GFAA) in ground water, surface water, drinking water, storm runoff, and industrial and domestic wastewater (Reference 1). This method is also applicable to the determination of total recoverable elements in sediment, biosolids (municipal sewage sludge), 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 To confirm approval of this method 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 11.5.8).

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., soil, biosolids, sediment and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing total suspended solids $\geq$1% (w/v) should be extracted as a solid sample.

1.6 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 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 extract of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner.

1.7 Method detection limits (MDLs; 40 CFR 136, Appendix B) and minimum levels (MLs) when no interferences are present will be determined for this method through a validation study (Table 1). The ML for each analyte can be calculated by multiplying the MDL by 3.18 and rounding to the nearest (2, 5, or 10 X 10^n) where n is an integer.

1.8 The sensitivity and limited linear dynamic range (LDR) of GFAA often requires dilution of a sample prior to analysis. The 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 requiring large dilutions (>50:1) should be analyzed by another approved test procedure having a larger LDR or having less sensitivity 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.

1.10 This method is accompanied by Appendix A: Total Solids in Solid and Semi-Solid Matrices. The procedure in Appendix A should be followed for sludge and solid samples analyzed under Sections 11.3 and 11.4.

1.11 This method will be validated in biosolids for those analytes regulated under 40 CFR Part 503 only. It is believed to be applicable for the analysis of biosolids for all analytes listed in Section 1.1.

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 solid or aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. For total recoverable analysis of a sludge sample, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids and hydrogen peroxide. After cooling, the sample is made up to volume, 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 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, an aliquot of the sample and the matrix modifier are first pipetted onto the instrument platform, a device which permits delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon - 5% hydrogen). The sample is allowed to dry 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 matrix interference effects. 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. (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 or an electrodeless discharge lamp (EDL). Following analysis, the furnace is subjected to a clean out period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, a correction is required to subtract background absorbance from the total signal. In the absence of interferences, 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 11.6).

3.0 Definitions

3.1 Biosolids–A solid, semisolid, or liquid residue (sludge) generated during treatment of domestic sewage in a treatment works.

3.2 Calibration blank–A volume of reagent water acidified with the same acid matrix as the calibration standards. The calibration blank is a zero standard and is used to auto-zero the AA instrument (Section 7.13.1).

3.3 Calibration standard–A solution prepared from the dilution of stock standard solutions (Section 7.11). The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

3.4 Calibration verification (CV) solution–A solution of method analytes, used to evaluate performance of the instrument system with respect to a defined set of method criteria (Sections 7.14 and 9.3).

3.5 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 8.2).

3.6 Field blank–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 field blank is to determine if method analytes or other interferences are present in the field environment (Section 9.5.2).

3.7 Linear dynamic range (LDR)–The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

3.8 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.

3.9 Matrix spike (MS) and matrix spike duplicate (MSD)–Two aliquots of the same environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample, and their purpose is to determine whether the sample matrix contributes bias to the analytical results and to indicate precision associated with laboratory procedures. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations (Section 9.4).

3.10 May–This action, activity, or procedural step is neither required nor prohibited.

3.11 May not–This action, activity, or procedural step is prohibited.

3.12 Method blank–An aliquot of reagent water or other blank matrices that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Sections 7.13.2 and 9.5.1).

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 9.2.1 and Table 1). The MDL is determined according to procedures in 40 CFR Part 136 Appendix B.

3.14 Minimum level (ML)–The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample weights, volumes and cleanup procedures have been employed.

3.15 Must–This action, activity, or procedural step is required.

3.16 Ongoing precision and recovery (OPR) standard–The OPR test is used to ensure that the laboratory meets performance criteria during the period that samples are analyzed. It also separates laboratory performance from method performance on the sample matrix. For aqueous samples, the OPR solution is an aliquot of method blank to which known quantities of the method analytes are added in the laboratory. For solid samples, the use of clean sand, soil or peat moss to which known quantities of the method analytes are added in the laboratory is recommended. The OPR is analyzed in the same manner as samples (Section 9.6).

3.17 Shall–This action, activity or procedural step is required.

3.18 Should–This action, activity, or procedural step is suggested but not required.

3.19 Solid sample–For the purpose of this method, a sample taken from material classified as either soil, sediment or industrial sludge.

3.20 Standard addition–The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to that analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.7 and 11.6).

3.21 Standard stock 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 7.11).

3.22 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, 11.3, and 11.4).

3.23 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: spectral, matrix, and memory.

4.2 Spectral interferences are caused by the resulting absorbance of light from the spectrometer lamp by a molecule or atom which is not the analyte of interest. Spectral interferences also can arise from black body radiation coming from the carbon platform.

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 this technology. In addition, the use of appropriate

furnace temperature programs and high spectral-purity lamps as light sources can minimize this type of interference. However, molecular absorbances can span several hundred nanometers producing broadband spectral interferences. This latter interference is far more common in STPGFAA. Matrix modifiers, selective volatilization, and background correctors can all be used to minimize unwanted nonspecific absorbance. The nonspecific component of total absorbance can vary considerably among sample types. 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, whichever one is chosen must provide an analytical condition that is not subject to the occurring inter-element 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 from the carbon surface of the sample platform. The magnitude of this interference can be minimized by proper furnace tube alignment and monochromator design. In addition, atomization temperatures which are adjusted to adequately volatilize the analyte of interest while minimizing black body radiation can reduce unwanted background emission.

4.3 Matrix interferences are caused by sample components which inhibit the formation of free atomic analyte 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 matrix interferences. 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).

4.3.2 The use of nitric acid is preferred for most 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. The effects and benefits of using this modifier are discussed in detail in Reference 2. Listed in Section 4.4 are some typically observed effects when using this modifier.

4.4 Specific element interferences.

4.4.1 Antimony–Antimony suffers from an interference produced by K_2SO_4 (Reference 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 reduced dramatically (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 optimal furnace temperature should be determined on each instrument.*

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

4.4.3 Arsenic–HCl present from digestion can influence As sensitivity. Twenty micro liters 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 (Reference 2).

4.4.4 Cadmium–HCl present from digestion can influence Cd sensitivity. Twenty micro liters of a 1% HCl solution with Pd used as a modifier results in an 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% (Reference 2).

4.4.5 Lead–HCl present from digestion can influence Pb sensitivity. Twenty micro liters 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% (Reference 2).

4.4.6 Selenium–Iron has been shown to suppress Se response with continuum background correction (Reference 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.

4.4.7 Silver–Palladium used in a modifier preparation may have elevated levels of Ag which will cause elevated blank absorbances.

4.4.8 Thallium–HCl present from digestion can influence Tl sensitivity. Twenty micro liters 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% (Reference 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. Analyte which remains in a furnace can produce false positive signals on subsequent sample(s). Therefore, an 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 analyzing the diluted sample.

5.0 Safety

5.1 The toxicity and 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 (References 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 to laboratory personnel as both 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 as well as 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 agents.

5.4 During atomization, the graphite tube emits intense UV radiation. Suitable eye-safe precautions should be taken to protect laboratory personnel.

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

NOTE: *The mention of trade names or commercial products in this method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus and materials other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.*

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 nonspecific absorbance over the spectral region of interest and provide an analytical condition not subject to the occurrence of inter-element spectral overlap interferences. The furnace device must be capable of using 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. Multi-element lamps may be used if they can be shown to meet the detection limit and quality control requirements in Section 9.2.

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 clean out.

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. This gas mixture must be used for all metals. Care must be taken when the gas mixture is used for selenium (Section 4.4.6).

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, preparing standards, and 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 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 100 - 2500 µL with an assortment of high quality, disposable pipet tips.

6.7 Mortar and pestle, ceramic or nonmetallic material.

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

6.9 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) HNO_3 or a mixture of dilute HNO_3 and HCl (1:2:9), rinsing with reagent water and storing clean (Reference 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.

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

6.9.2 Assorted calibrated pipettes.

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

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

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

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

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

6.9.8 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. Whenever possible, high-purity reagents that conform to the American Chemical Society specifications should be used (Reference 8). 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 (Reference 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 reagent water. Pour the two solutions together and dilute to 100 mL with reagent 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 Hydrogen peroxide, 30%, stabilized certified reagent grade.

7.9 Clean sand or soil–All references to clean sand or soil in this method refer to sand or soil certified to be free of the analytes of interest at or above their MDLs or to contain those analytes at certified levels.

7.10 Peat moss–All references to peat moss in this method refer to sphagnum peat moss certified to be free of arsenic, cadmium, copper, lead, nickel, and selenium at or above their MDLs or to contain those analytes at certified levels.

7.11 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 cannot be verified.

CAUTION: *Many of these chemicals are extremely toxic if inhaled or swallowed. 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.

Equation 1

From a pure element:

$$C = \frac{m}{V}$$

Where:

C = concentration (mg/L)
m = mass (mg)
V = volume (L)

From pure compound:

$$C = \frac{m * g_f}{V}$$

Where:

C = concentration (mg/L)
m = mass (mg)
g_f = gravimetric factor (mass fraction of the analyte in the compound)
V = volume (L)

7.11.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed to at least four significant figures, in 4.0 mL (1:1) HCl and 1.0 mL concentrated HNO_3 in a beaker. Warm the beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL (1:1) HCl and dilute to volume with reagent water.

7.11.2 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.

7.11.3 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.

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

7.11.5 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.

7.11.6 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.

7.11.7 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.

7.11.8 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.

7.11.9 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.

7.11.10 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.

7.11.11 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.

7.11.12 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.

7.11.13 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.

7.11.14 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 a clear bottle completely with aluminum foil to protect solution from light.

7.11.15 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.

7.11.16 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.

7.12 Preparation of calibration standards–Fresh calibration standards 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 calibration 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 7.15 and 9.2.4).

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 sludge and 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.*

7.13 Blanks–Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, a method blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background, 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 reagent water.

7.13.1 The calibration blank consists of the appropriate acid diluent (Section 7.12 note) (HCl/HNO_3) in ASTM Type I water. The calibration blank should be stored in a FEP bottle.

7.13.2 The method blank must contain all reagents in the same volumes as used in processing the samples. The method blank must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.13.3 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. The blank may be stored in a convenient manner.

7.14 Calibration verification (CV) solution–The CV solution is used to periodically verify instrument calibration during analysis. It should be prepared in the same acid mixture as the calibration standards (Section 7.12 note) by combining method analytes at appropriate concentrations to approximate the midpoint of the calibration curve. The CV 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 calibration verification solutions be prepared at specified concentrations in order to meet specific program needs.

7.15 Quality control sample (Reference sample)–The QCS must be obtained from an outside source separate from standard stock solutions, and is prepared in the same acid mixture as the calibration standards (Section 7.12 note). For initial and periodic verification of calibration standards and instrument performance, analysis of a method blank that has been fortified with the QCS is required. Analyte concentrations 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 if instability is noted.

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 aliquots are removed 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 dissolved metals, the sample must be filtered through a 0.45 µm capsule membrane filter at the time of collection or as soon thereafter as is practical. (A glass or metal-free plastic filtering apparatus is 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 to pH <2 with (1:1) HNO_3 immediately following filtration.

8.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1:1) HNO_3 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 immediately prior to withdrawing an aliquot for processing or "direct analysis." If for some reason such as high alkalinity, sample pH is >2, more acid must be added and the sample held for an additional 16 hours until verified to be pH <2.

NOTE: *When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood (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 if required by the data user. Use the same container and acid as used in sample collection.

9.0 Quality Control

9.1 Each laboratory applying this method is required to maintain a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory

capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to demonstrate that results of the analysis meet the performance criteria of the method.

9.1.1 The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, preconcentration, cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in the method for the analytes of interest.

9.1.2.1 Each time the method is modified, the analyst is required to repeat the procedure in Section 9.2. If the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDLs (40 CFR Part 136, Appendix B) are lower than the MDLs for the analytes in this method, or one-third the regulatory compliance level, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument according to Section 10.0.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A listing of metals measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating reason(s) for the modification(s).

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Calibration
(b) Calibration verification
(c) Initial precision and recovery
(d) Analysis of blanks
(e) Accuracy assessment

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include, where possible:

(a) Sample numbers and other identifiers
(b) Digestion/preparation or extraction dates
(c) Analysis dates and times
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Volume before the extraction/concentration step
(g) Volume after each extraction/concentration step
(h) Final volume before analysis
(i) Injection volume
(j) Dilution data, differentiating between dilution of a sample or extract
(k) Instrument and operating conditions (make, model, revision, modifications)
(l) Sample introduction system (ultrasonic nebulizer, flow injection system, etc.)
(m) Preconcentration system
(n) Operating conditions (background corrections, temperature program, flow rates, etc.)
(o) Detector (type, operating conditions, etc.)
(p) Spectra, printer tapes, and other recordings of raw data
(q) Quantitation reports, data system outputs, and other data to link raw data to results reported

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. Section 9.5 describes the required types, procedures, and criteria for analysis of blanks.

9.1.4 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision of the method and to monitor for matrix interferences (Section 9.4). When results of these spikes indicate atypical method performance, alternative extraction or cleanup techniques must be used to bring method performance within acceptable limits. If method performance cannot be brought within the limits given in this method, the results may not be reported for regulatory compliance purposes.

9.1.5 The laboratory must, on an ongoing basis, demonstrate through calibration verification (Section 9.3) and through analysis of the ongoing precision and recovery standard (Section 9.6) that the analytical system is meeting the performance criteria.

9.1.6 The laboratory must maintain records to define the quality of data that are generated. Development of accuracy statements is described in Section 9.4.4.1 and 9.6.7.

9.1.7 All samples must be associated with an acceptable OPR, MS/MSD, IPR, and uncontaminated blanks.

9.2 Initial demonstration of laboratory capability.

9.2.1 Method detection limit—To establish the ability to detect the trace metals of interest, the analyst must determine the MDL for each analyte according to the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Table 1 (to be confirmed during validation study), or one-third the regulatory compliance limit, whichever is greater. MDLs should be determined when a new operator begins work or whenever a change in instrument hardware or operating conditions is made that may affect the MDL. MDLs must be determined for solids with clean sand or soil if solid samples are to be analyzed, peat moss for biosolids and/or for reagent water if aqueous samples are to be analyzed. MDLs also must be determined for biosolids with peat moss if sludge samples are to be analyzed for arsenic, cadmium, copper, lead, nickel, and selenium.

9.2.2 Initial precision and recovery (IPR)–To establish the ability to generate acceptable precision and recovery, the analyst must perform the following operations.

9.2.2.1 Spike four aliquots of reagent water for aqueous samples, clean sand or soil for solid samples, or peat moss for biosolid samples, with the metal(s) of interest at one to five times the ML. Analyze the four aliquots according to the procedures in Section 11.0. All digestion, extraction, and concentration steps, and the containers, labware, and reagents that will be used with samples must be used in this test.

9.2.2.2 Using results of the set of four analyses, compute the average percent recovery (X) for the metal(s) in each aliquot and the standard deviation of the recovery (s) for each metal.

9.2.2.3 For each metal, compare s and X with the corresponding limits for IPR in (Table 2- to be determined in validation study). If s and X for all metal(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that metal. Correct the problem and repeat the test.

9.2.3 Linear dynamic range (LDR)–The upper limit of the LDR must be established for the wavelength used for each analyte by determining the signal responses from a minimum of six different concentration standards across the range, two of which should be 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. Sample analyte concentrations that exceed the upper limit of the linear calibration range must either be diluted and analyzed again with concern for memory effects (Section 4.5) or be

analyzed by another approved method. The LDRs should be verified annually or whenever, in the judgement of the analyst, there is a change in analytical performance.

NOTE: *Multiple clean out 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.*

9.2.4 Quality Control Sample (QCS)–When beginning the use of this method, quarterly, and as required to meet data quality needs, the analyst must verify the calibration standards and acceptable instrument performance by preparing and analyzing three aliquots of a reference sample (Section 7.15). To verify the calibration standards, the determined mean concentration from three analyses of the reference sample must be within ± 5% of the stated reference sample values. If the reference sample results are not within the required limits, an immediate second analysis of the reference sample is recommended to confirm unacceptable performance. If the calibration standards and acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before either proceeding with further sample analyses.

9.3 Calibration verification (CV) solution–A laboratory must analyze a CV solution (Section 7.12) 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.

9.3.1 The calibration blank results must always be less than the analyte ML, or one-third the regulatory compliance level, whichever is greater. The results must also by greater than a negative signal in concentration units equal to the ML.

9.3.2 Analysis of the CV solution immediately following calibration must verify that the instrument is within performance criteria to be determined by the validation study (Table 2 - to be determined by the validation study).

9.3.3 If calibration cannot be verified within the specified limits, reanalyze either or both the CV solution and the calibration blank. If the second analysis of the CV solution or the calibration blank confirms that the calibration is outside acceptable 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 CV solution and calibration blank must be analyzed again. Analysis data of the calibration blank and CV solution must be kept on file with sample analyses data.

9.4 Matrix spike (MS) and matrix spike duplicates (MSD)–To assess the performance of the method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (one sample in ten) of the samples from a given sampling site or, if for compliance monitoring, from a given discharge. Blanks may not be used for MS/MSD analysis.

9.4.1 The concentration of the MS and MSD spike shall be determined as follows:

9.4.1.1 If, as in compliance monitoring, the concentration of analytes in the sample is being checked against a regulatory concentration limit, the

spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater.

9.4.1.2 If the concentration of analytes in a sample is not being checked against a regulatory concentration limit, the spike shall be at 1-5 times the background concentration of the sample.

9.4.1.3 For solid and sludge samples, 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, Section 12.4). (For notes on Ag, see Sections 1.6).

9.4.2 Assessing spike recovery.

9.4.2.1 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established *a priori*.

9.4.2.2 Prepare a standard solution to produce an appropriate concentration in the sample (Section 9.4.1).

NOTE: *The concentration of iron and aluminum in solids can vary greatly and is not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the OPR may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis is recommended. After subtraction of the OPR spike, the calculated sample concentration after dilution should agree within 10% of the original determination of sample concentration. 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 possibly affect the analysis.*

9.4.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A). Calculate the percent recovery (P) in each aliquot (Equation 2).

Equation 2

$$P = 100 * \frac{(A - B)}{T}$$

where:

P = Percent recovery
A = Measured concentration of analyte after spiking
B = Measured concentration of analyte before spiking
T = True concentration of the spike

9.4.3 Compare the percent recovery with the QC acceptance criteria in Table 2 (to be determined in validation study).

9.4.3.1 If P falls outside the designated range for recovery in Table 2, the results have failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard (Section 9.6). If the OPR is within established performance criteria (Table 2), the analytical system is within specification and the problem can be attributed to interference by the sample matrix. 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.

9.4.3.2 If the analyte MS/MSD recovery is <70% and the background absorbance is <1.0, the analyte addition test (Section 9.7) should be performed on an undiluted portion of an unfortified sample aliquot. Test results should be evaluated as follows:

9.4.3.2.1 If recovery of the analyte addition test (<85%) confirms a low recovery for the MS/MSD, a suppressive matrix interference is indicated and an unfortified sample aliquot must be analyzed by the method of standard additions (Section 11.6).

9.4.3.2.2 If recovery of the analyte addition test is between 85 - 115%, a low recovery of the analyte in the MS/MSD (<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 an unfortified sample aliquot.

9.4.3.3 If laboratory performance is shown to be acceptable (Section 9.5.1 and Section 9.6), but analyte recovery in the MS/MSD is either >130% or above the upper calibration limit, and the background absorbance is <1.0, the analyte addition test should be performed (Section 9.7) on an unfortified sample aliquot. (If the MS/MSD concentration is above the upper calibration limit, dilute a portion of an unfortified aliquot with

acidified reagent water before completing the analyte addition test). Evaluate the test results as follows:

9.4.3.3.1 If the percent recovery of an 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 the method of standard additions (Section 11.6).

9.4.3.3.2 If the percent recovery of an analyte addition test is between 85 - 115%, high recovery in the MS/MSD may have been caused by random sample contamination, sample heterogeneity, or incorrect addition of the analyte prior to sample processing. Report analytical data from an unfortified sample aliquot or its appropriate dilution.

9.4.3.3.3 If the percent recovery of an analyte addition test is <85%, a heterogenous sample with a suppressive matrix may be indicated. Other possible causes may be a combination of random contamination and a positive matrix interference. Reported data should be flagged accordingly.

9.4.3.4 If laboratory performance is shown to be acceptable (Section 9.5.1 and Section 9.6), but the background absorbance is >1.0, a nonspecific spectral interference should be suspected. A portion of the unfortified aliquot should be diluted (1:3) with acidified reagent water and analyzed again. (Dilution may dramatically reduce molecular background to an acceptable level. Ideally, background absorbance in the unfortified aliquot diluted (1:3) should be <1.0. However, additional dilution may be necessary). If dilution reduces background absorbance to an acceptable level (<1.0), complete the analyte addition test (Section 9.7) on a dilute unfortified aliquot. Evaluate test results as follows:

9.4.3.4.1 If recovery of the analyte addition test is between 85 - 115%, report the analytical data acquired from the dilute, unfortified aliquot.

9.4.3.4.2 If recovery of the analyte addition test is outside the range of 85 - 115%, complete sample analysis by analyzing a dilute, unfortified aliquot following the method of standard additions (Section 11.6).

9.4.3.5 If either analysis of MS/MSD samples or application of the analyte addition test indicate a positive interference, all other samples in the batch which are typical and have a matrix similar to the MS/MSD or the tested samples 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.

9.4.3.6 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 an analyst's and a laboratory's ability to perform a method acceptably.

9.4.4 Recovery for samples should be assessed and records maintained.

9.4.4.1 After the analysis of five samples of a given matrix type (river water, biosolids, etc.) for which the metal(s) pass the tests in Section 9.4.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (SP) for the metal(s). Express the accuracy assessment as a percent recovery interval from P - 2SP to P + 2SP for each matrix. For example, if P = 90% and SP = 10% for five analyses, the accuracy interval is expressed as 70 - 110%.

9.4.4.2 Update the accuracy assessment for each metal in each matrix on a regular basis (e.g., after each 5 - 10 new measurements).

9.4.5 Precision of matrix spike and matrix spike duplicate.

9.4.5.1 Calculate the relative percent difference (RPD) between the MS and MSD (Equation 3). Use the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.4.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 3

$$RPD = 200 * \frac{\left(\left|D_1 - D_2\right|\right)}{\left(D_1 + D_2\right)}$$

where:

RPD = Relative percent difference
D_1 = Concentration of the analyte in the MS sample.
D_2 = Concentration of the analyte in the MSD sample.

9.4.5.2 The relative percent difference between the matrix spike and the matrix spike duplicate must be less than 20% (RPD acceptance value will be verified in the validation study). If this criterion is not met, the analytical system is out of control. In this case, correct the problem and reanalyze all samples in the sample batch associated with the MS/MSD that failed the RPD test.

9.5 Blanks.

9.5.1 Method blank.

9.5.1.1 Prepare a method blank with each sample batch (samples of the same matrix -reagent water for aqueous samples, clean sand or soil for solid samples, peat moss for biosolid samples) started through the sample preparation process (Section 11.0) on the same 12-hour shift, for a maximum of 20 samples. Analyze the blank immediately after the OPR is analyzed (Section 9.6) to demonstrate freedom from contamination.

9.5.1.2 If the analyte(s) of interest or any potentially interfering substance is found in the method blank at a concentration equal to or greater than the ML (Table 1 to be determined during the validation study) or 1/3 the regulatory compliance level, whichever is greater, sample analysis must be halted, the source of contamination determined, the samples and a new method blank prepared, and the new sample batch and method blank analyzed.

9.5.1.3 Alternatively, if a sufficient number (three minimum) of blanks are analyzed, the average concentration plus two standard deviations must be less than the regulatory compliance level.

9.5.1.4 If the result for a single method blank remains above the ML or if the result for the average concentration plus two standard deviations of three or more blanks exceeds the regulatory compliance level, results for samples associated with those blanks may not be reported for regulatory compliance purposes. Stated another way, results for IPR tests (Section 9.2) and all samples must be associated with an uncontaminated method blank before these results may be reported for regulatory compliance purposes.

9.5.2 Field blank.

9.5.2.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.5.2.2 If the metal of interest or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML, or greater than one-fifth the level in the associated sample(s), whichever is greater, results for the associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.5.2.3 Alternatively, if a sufficient number (three minimum) of field blanks are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample for that analyte, whichever is greater.

9.5.2.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken prior to sampling.

9.5.3 Equipment blanks—Before any sampling equipment is used at a given site, it is recommended that the laboratory or cleaning facility generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are recommended: bottle blanks and sampler check blanks.

9.5.3.1 Bottle blanks—After undergoing appropriate cleaning procedures (Section 6.9), bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to pH < 2 and allowed to stand for a minimum of 24 hours. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

9.5.3.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field.

9.5.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field. For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the sampler into the water and pumping water into a sample container. Whatever precautions and equipment are used in the field should also be used to generate these blanks.

9.5.3.2.2 The sampler check blank should be analyzed using the procedures in this method. If the target analyte(s) or any potentially interfering substance is detected in the blank, the source of

contamination or interference must be identified and the problem corrected. The equipment should be demonstrated to be free from contamination before the equipment is used in the field.

9.5.3.2.3 Sampler check blanks should be run on *all* equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.6 Ongoing precision and recovery.

9.6.1 For aqueous samples, prepare an OPR solution identical to the IPR aliquots (Section 9.2.2). The solution must be analyzed with each preparation batch (samples of the same matrix started through the sample preparation process (Section 11.0) on the same 12-hour shift, to a maximum of 20 samples).

9.6.2 For solid samples, the use of clean sand or soil fortified as in Section 9.6.1 is recommended.

9.6.3 For biosolid samples, the use of peat moss fortified as in Section 9.6.1 is recommended.

9.6.4 Analyze the OPR solution before the method blank and samples are analyzed.

9.6.5 Compute the percent recovery of each metal in the OPR sample.

9.6.6 For each metal, compare the OPR concentration to the limits for ongoing recovery in (Table 2- to be determined in validation study). If all metal(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual recovery falls outside of the range given, the analytical processes are not being performed properly for that metal. Correct the problem, prepare the sample batch again, and repeat the OPR test.

9.6.7 Add results that pass the specifications in Section 9.6.6 to IPR and previous OPR data for each metal in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each metal in each matrix type by calculating average percent recovery (P) and standard deviation of percent recovery (SP). Express accuracy as a recovery interval from P - 2SP to P + 2SP. For example, if P = 95% and SP = 5%, accuracy is 85 - 105%.

9.7 An analyte addition test can be used to assess possible matrix interference effects and the need to complete a sample analysis using the method of standard additions (MSA, Section 11.6). Results of this test should <u>not</u> be considered conclusive unless the determined sample background absorbance is <1.0. An analyte standard, when 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 11.6).

10.0 Calibration and Standardization

10.1 Prior to an initial calibration, the linear dynamic range of the analyte must be determined (Section 9.2.3) using optimized instrument operating conditions (Section 11.5). For all determinations, allow an instrument and hollow cathode lamp warm up period of not less than 15 minutes. If an EDL is to be used, allow 30 minutes for warm up.

10.2 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Section 7.13.1) and calibration standards (Section 7.12) prepared at three or more concentrations within the usable linear dynamic range of the analyte (Section 9.2.3). The lowest calibration point (excluding the calibration blank) must be equal to the ML (Table 1, to be determined during the validation study).

10.2 The calibration line should include at least three non-zero points with the high standard near the upper limit of the linear dynamic range (Section 9.2.3) and the low standard that contains the analyte(s) of interest at the ML (to be determined during the validation study). Replicates of a calibration blank (Section 7.13.1) and the 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 (Reference 12).

10.3 Calculate the slope and intercept of a line using weighted linear regression. Use the inverse of the standard's concentration squared ($1/x^2$) as the weighting factor. The calibration is acceptable if the R^2 is greater than 0.995 and the absolute value of the intercept is less than the MDL for the target analyte. If these conditions are not met, then the laboratory may not report data analyzed under that calibration and must recalibrate the instrument.

10.4 The concentration of samples is determined using Equation 4.

Equation 4

$$y = mx + b$$

where y = *sample concentration*
m = *slope (calculated in Section 10.3)*
x = *instrument response*
b = *intercept (calculated in Section 10.3)*

10.5 Response factor may be calculated as an alternative to weighted linear regression for instrument calibration. Calculate the response factor (RF) of the analytes for each of the standards (Equation 5.)

Equation 5

$$RF = \frac{R_x}{C_x}$$

where:

R_x = *Peak height or area*
C_x = *Concentration of standard x*

10.5.1 Calculate the mean response factor (RF_m), the standard deviation of the RF_m, and the relative standard deviation (RSD) of the mean (Equation 6).

Equation 6

$$RSD = 100 * \frac{SD}{RF_m}$$

where:

RSD = Relative standard deviation of the mean
SD = Standard deviation of the RF_m
RF_m = *the mean response factor*

10.5.2 Performance criteria for the calibration will be calculated after the validation of the method.

11.0 Procedure

11.1 Aqueous sample preparation (Dissolved analytes)–For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥20 mL) of filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1:1) HNO_3 to adjust the acid concentration of the aliquot to approximate a 1% (v/v) HNO_3 solution (e.g., add 0.2 mL (1:1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations (Section 12).

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 "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. Make allowance for sample dilution in the data calculation (Sections 12). For 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 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. (When necessary, smaller sample aliquot volumes may be used).

NOTE: *If the sample is not a biosolids sample and 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 through 11.3.6.*

11.2.3 Add 2 mL (1:1) HNO_3 and 1.0 mL of (1:1) HCl to a 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 to prevent sample contamination from the fume hood environment. Other contamination avoidance steps should be taken as needed.

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 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. Add reagent water to bring the final volume of the sample solution to 50 mL. Stopper the volumetric flask 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 a sample contains suspended solids that would clog or adversely affect an instrument sample introduction system, a portion of the sample may be filtered 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 sample 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 a tared weighing dish. For samples with

<35% moisture, a 20 g portion is sufficient. For samples with moisture >35%, a larger aliquot of 50 - 100 g is required. Dry the sample to a constant weight at 60°C (The sample is dried at 60°C to prevent the loss of volatile metallic compounds).

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve, and grind it with a mortar and pestle. (The sieve, mortar, and pestle should be cleaned between samples). From the dried, ground material, weigh a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer it 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 beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C.

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).*

11.3.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (approximately 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 prior to analysis. However, care should be exercised to avoid 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 completed sample preparation.

11.3.7 Determine the total solids content of the sample using the procedure in Appendix A.

11.4 Sludge sample preparation–Total recoverable analytes.

11.4.1 Determination of total recoverable analytes in sludge samples containing estimated total suspended solids ≥1% (w/v).

11.4.1.1 Mix the sample thoroughly. Transfer a portion (>20 g) of the sample to a 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 of 50 - 100 g is required. Dry the

sample to a constant weight at 60°C (The sample is dried at 60°C to prevent the loss of volatile metallic compounds).

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

11.4.1.3 Add 10 mL of (1:1) HNO_3 to the beaker and cover the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample for 10 minutes. Remove the sample from the hot plate and allow to cool. Add 5 mL of concentrated HNO_3 to the beaker, replace the watch glass, return to the hot plate, and reflux for 30 minutes. Repeat this last step once. Remove the beaker from the hot plate and allow to cool. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. Place the beaker on the hot plate and heat the sample until a gentle effervescence is observed. Once the reaction has subsided, additional 1 mL aliquots of 30% H_2O_2 should be added until no effervescence is observed. The total amount of 30% H_2O_2 added should not exceed 10 mL. Add 2 mL concentrated HCl and 10 mL of reagent water to the sample, cover with a watch glass, and reflux for 15 minutes.

11.4.1.4 Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample may be centrifuged.

11.4.1.5 Determine the total solids content of the sample using the procedure in Appendix A.

11.4.2 Determination of total recoverable analytes in sludge samples containing estimated total suspended solids < 1% (w/v).

11.4.2.1 Transfer 100 mL of well-mixed sample to a 250 mL Griffin beaker.

11.4.2.2 Add 3 mL of concentrated HNO_3 and place the beaker on a hot plate. Heat the sample and cautiously evaporate to a volume of 5 mL. If the sample contains a large amount of dissolved solids, adjust this volume upwards to prevent the sample from going to dryness. Remove the beaker from the hot plate and allow the sample to cool. Add 3 mL of concentrated HNO_3, cover with a watch glass and gently reflux the sample until the sample is completely digested or no further changes in appearance occur, adding additional aliquots of acid, if necessary, to prevent the sample from going to dryness. Remove the watch glass and reduce the sample volume to 3 mL, again adjusting upwards if necessary.

11.4.2.2 Cool the beaker, then add 10 mL of reagent water and 4 mL of (1:1) HCl to the sample and reflux for 15 minutes. Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample volume may be centrifuged.

11.4.2.3 Determine the total solids content of the sample using the procedure in Appendix A.

11.5 Sample analysis.

11.5.1 Inspect the graphite furnace, the sample uptake system, and autosampler injector for any problems that would affect instrument performance. If necessary, clean the system and replace the graphite tube and/or platform.

11.5.2 Configure the instrument.

11.5.2.1 Specific wavelengths and instrument operating conditions are listed in Table 3. However, because of differences among makes and models of spectrophotometers and electrothermal furnace devices, the actual instrument conditions selected may vary from those listed.

11.5.2.2 Prior to the use of this method, instrument operating conditions must be optimized. An analyst should follow the instructions provided by the manufacturer while using the conditions listed in Table 3 as a guide. Of particular importance is the determination of the charring temperature limit for each analyte. This limit is the furnace temperature setting when 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 analyses, the charring temperature is set typically to at least 100°C below this limit. Optimum conditions should provide the lowest reliable MDLs and be similar to those listed in Table 1 (to be confirmed during collaborative validation study). Once optimum operating conditions have been determined, they should be recorded and available for daily reference.

11.5.2.3 Configure the instrument system to optimize operating conditions for the "direct analysis" of drinking water with turbidity <1 NTU. Initiate the 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.

11.5.2.4 After the warm up period, but before calibration, instrument stability must be demonstrated by analyzing a standard solution with a concentration

20 times the ML, 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.

11.5.3 Before using the method to analyze samples, there must be data available documenting initial demonstration of laboratory capability. Required and acceptable data and procedures are described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Sections 10.0 and 11.5.2) subsequently used for sample analysis. These documented data must be kept on file and be available for review by the data user.

11.5.4 An autosampler must be used to introduce all solutions to the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and clean out periods 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 displayed on a CRT for immediate review by the analyst and be available as hard copy for documentation to be kept on file. The autosampler solution uptake system must be flushed with the rinse blank (Section 7.13.3) between injections.

11.5.5 During the analysis of samples, a laboratory must comply with the required quality control described in Sections 9.0. Only during determination of dissolved analytes or "direct analysis" of drinking water with turbidity of <1 NTU is the sample digestion step of the method blank, OPR, MS, and MSD not required.

11.5.6 Matrix interferences.

11.5.6.1 For every new or unusual matrix, it is highly recommended that an inductively coupled plasma atomic emission spectrometer be used to screen for high element concentrations whenever practical. Information gained may reduce potential damage to the atomic absorption instrument and estimate which elements require graphite furnace analysis.

11.5.6.2 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the test described in Section 9.7 is recommended.

11.5.7 Sample analyte concentrations measured at 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and analyzed with concern for memory effects (Section 4.5), or be 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 analyzed again (Section 9.4.3.4). If the method of standard additions is required, follow the instructions described in Section 11.6.

11.5.8 In order to meet or achieve lower MDLs than those listed in Table 1 for "direct analysis" of drinking water with turbidity <1 NTU, analyte preconcentration 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 of either the calibration standards or acid preserved samples must be deposited prior to atomization. Following each deposition, the drying cycle must be completed before beginning the next deposition. Matrix modifier must be added along with each deposition and the total volume of each deposition must not exceed the instrument 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 multiple deposition technique for the "direct analysis" of drinking water must be completed using optimized instrument operating conditions (Section 11.5.2) and must comply with the method requirements described in Section 9.2. (See Table 3 for information and data on the determination of arsenic by this procedure).

11.5.9 Report data as directed in Section 12.0.

11.6 Standard additions–If the method of standard addition (MSA) is required, the following procedure is recommended:

11.6.1 The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution (Reference 11). 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_2, are taken. To the first (aliquot 1) is added a small volume (V_1) of a standard analyte solution of concentration C. To the second (aliquot 2) is added the same volume (V_1) of reagent matrix water. It is best if V_2 is much less than V_1 to avoid excess dilution of the sample matrix. The analytical signals of aliquots 1 and 2 are measured and corrected for non-analyte signals. The unknown sample concentration (C_s) is calculated:

Equation 7

$$C_s = \frac{S_2 * V_1 * C}{\left(S_1 - S_2\right) * V_2}$$

where:
C_s = *Sample concentration (mg/L)*
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 used for MSA (L)*

If a separation or concentration step is required, the additions are made before separation or concentration and carried through the entire procedure. For the results from this technique to be valid, the following limitations apply:

1. The calibration 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.

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

12.0 Data Analysis and Calculations

12.1 Data should be reported in mg/L for aqueous samples and mg/kg dry weight for sludge and solid samples.

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

12.3 For total recoverable analytes in aqueous samples (Section 11.2), multiply solution analyte concentrations by the dilution factor (when a 100 mL aliquot is used to produce the 50 mL final solution, the dilution factor will equal 0.5). Round the data to the tenths place and report the data in mg/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 and sludge samples (Sections 11.3 and 11.4), round the solution analyte concentrations (mg/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 Equation 8. Do not report analyte data below the solids MDL.

Equation 8

$$C_s = \frac{C * V * D}{W}$$

where:

C_s = *Sample concentration (mg/kg, dry-weight basis)*
C = Concentration in the extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1 L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (kg, 1 g = 0.001 kg)

12.5 To report percent solids in solid and sludge samples, use the procedure given in Appendix A.

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 application of the method and resulting MDLs are listed in Table 1.

13.2 Method performance criteria is given in Table 2 (to be determined in validation study).

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. 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, by complying discharge permit requirements 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, Flow Charts, and Validation Data

Table 1: MDLs and MLs of the method (to be determined during collaborative validation study).

Table 2: Performance criteria of the method (to be determined during collaborative validation study).

TABLE 3. 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.

Appendix A: Total Solids in Solid and Semisolid Matrices

1.0 Scope and Application

1.1 This procedure is applicable to the determination of total solids in such solid and semisolid samples as soils, sediments, biosolids (municipal sewage sludge) separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other biosolids dewatering processes.

1.2 This procedure is taken from EPA Method 1684: *Total, Fixed, and Volatile Solids in Solid and Semi-Solid Matrices.*

1.3 Method detection limits (MDLs) and minimum levels (MLs) have not been formally established for this draft procedure. These values will be determined during the validation of Method 1684.

1.4 This procedure is performance based. The laboratory is permitted to omit any step or modify any procedure (e.g. to overcome interferences, to lower the cost of measurement), provided that all performance requirements in this procedure are met. Requirements for establishing equivalency are given in Section 9.1.2 of Method 200.9.

1.5 Each laboratory that uses this procedure must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1 Sample aliquots of 25-50 g are dried at 103°C to 105°C to drive off water in the sample.

2.3 The mass of total solids in the sample is determined by comparing the mass of the sample before and after each drying step.

3.0 Definitions

3.1 Total Solids–The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

3.2 Additional definitions are given in Sections 3.0 of Method 200.9.

4.0 Interferences

4.1 Sampling, subsampling, and pipeting multi-phase samples may introduce serious errors (Reference 13.1). Make and keep such samples homogeneous during transfer. Use special handling to ensure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If visible suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, intensive homogenization is required to ensure accurate results. When dried,

some samples form a crust that prevents evaporation; special handling such as extended drying times are required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

4.2 The temperature and time of residue drying has an important bearing on results (Reference 1). Problems such as weight losses due to volatilization of organic matter, and evolution of gases from heat-induced chemical decomposition, weight gains due to oxidation, and confounding factors like mechanical occlusion of water and water of crystallization depend on temperature and time of heating. It is therefore essential that samples be dried at a uniform temperature, and for no longer than specified. Each sample requires close attention to desiccation after drying. Minimize the time the desiccator is open because moist air may enter and be absorbed by the samples. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.3 Residues dried at 103°C to 105°C may retain some bound water as water of crystallization or as water occluded in the interstices of crystals. They lose CO_2 in the conversion of bicarbonate to carbonate. The residues usually lose only slight amounts of organic matter by volatilization at this temperature. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

4.4 Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

4.5 The determination of total solids is subject to negative error due to loss of ammonium carbonate and volatile organic matter during the drying step at 103°C to 105°C. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem.

5.0 Safety

5.1 Refer to Section 5.0 of Method 200.9 for safety precautions.

6.0 Equipment and Supplies

NOTE: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Evaporating Dishes–Dishes of 100-mL capacity. The dishes may be made of porcelain (90-mm diameter), platinum, or high-silica glass.

6.2 Watch glass–Capable of covering the evaporating dishes (Section 6.1).

6.3 Steam bath.

6.4 Desiccator–Moisture concentration in the desiccator should be monitored by an instrumental indicator or with a color-indicator desiccant.

6.5 Drying oven–Thermostatically-controlled, capable of maintaining a uniform temperature of 103°C to 105°C throughout the drying chamber.

6.6 Analytical balance–Capable of weighing to 0.1 mg for samples having a mass up to 200 g.

6.7 Container handling apparatus–Gloves, tongs, or a suitable holder for moving and handling hot containers after drying.

6.8 Bottles–Glass or plastic bottles of a suitable size for sample collection.

6.9 Rubber gloves (Optional).

6.10 No. 7 Cork borer (Optional).

7.0 Reagents and Standards

7.1 Reagent water–Deionized, distilled, or otherwise purified water.

7.2 Sodium chloride-potassium hydrogen phthalate standard (NaCl-KHP).

7.2.1 Dissolve 0.10 g sodium chloride (NaCl) in 500 mL reagent water. Mix to dissolve.

7.2.2 Add 0.10 g potassium hydrogen phthalate (KHP) to the NaCl solution (Section 7.2.1) and mix. If the KHP does not dissolve readily, warm the solution while mixing. Dilute to 1 L with reagent water. Store at 4°C. Assuming 100% volatility of the acid phthalate ion, this solution contains 200 mg/L total solids, 81.0 mg/L volatile solids, and 119 mg/L fixed solids.

8.0 Sample Collection, Preservation, and Storage

8.1 Use resistant-glass or plastic bottles to collect sample for solids analysis, provided that the material in suspension does not adhere to container walls. Sampling should be done in accordance with Reference 13.2. Begin analysis as soon as possible after collection because of the impracticality of preserving the sample. Refrigerate the sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 hours. Under no circumstances should the sample be held more than seven days. Bring samples to room temperature before analysis.

9.0 Quality Control

9.1 Quality control requirements and requirements for performance-based methods are given in Section 9.1 of Method 200.9.

9.2 Initial demonstration of laboratory capability - The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL) - The method detection limit should be established for the analyte, using diluted NaCl-KHP standard (Section 7.2). To determine MDL values, take seven replicate aliquots of the diluted NaCl-KHP solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

9.2.2 Initial Precision and Recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Prepare four samples by diluting NaCl-KHP standard (Section 7.2) to 1-5 times the MDL. Using the procedures in Section 11, analyze these samples for total solids.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (x) and the standard deviation (s, Equation 1) of the percent recovery for total solids.

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x^2)}{n}}{n-1}}$$

Where:

n = number of samples
x = % recovery in each sample
s = standard deviation

9.2.2.3 Compare s and x with the corresponding limits for initial precision and recovery in Table 2 (to be determined in validation study). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Laboratory blanks

9.3.1 Prepare and analyze a laboratory blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample, and will consist of approximately 25 g of reagent water.

9.3.2 If material is detected in the blank at a concentration greater than the MDL (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.4 Ongoing Precision and Recovery

9.4.1 Prepare an ongoing precision and recovery (OPR) solution identical to the IPR solution described in Section 9.2.2.1.

9.4.2 An aliquot of the OPR solution must be analyzed with each sample batch (samples started through the sample preparation process (Section 11) on the same 12-hour shift, to a maximum of 20 samples).

9.4.3 Compute the percent recovery of total solids in the OPR sample.

9.4.4 Compare the results to the limits for ongoing recovery in Table 2 (to be determined in validation study). If the results meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, the recovery of total solids falls outside of the range given, the analytical processes are not being performed properly. Correct the problem, reprepare the sample batch, and repeat the OPR test. All samples must be associated with an OPR analysis that passes acceptance criteria before the sample results can be reported for regulatory compliance purposes.

9.4.5 results that pass the specifications in Section 9.4.4 to IPR and previous OPR data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from R-2SR to R+2SR. For example, if R=05% and SR=5%, the accuracy is 85-115%.

9.5 Duplicate analyses

9.5.1 Ten percent of samples must be analyzed in duplicate. The duplicate analyses must be performed within the same sample batch (samples whose analysis is started within the same 12-hour period, to a maximum of 20 samples).

9.5.2 The total solids of the duplicate samples must be within 10%.

10.0 Calibration and Standardization

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.

10.2 Calibration shall be within ± 10% (i.e. ±0.2 mg) at 2 mg and ± 0.5% (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 Procedure

11.1 Preparation of evaporating dishes–Heat dishes and watch glasses at 103°C to 105°C for 1 hour in an oven. Cool and store the dried equipment in a desiccator. Weigh each dish and watch glass prior to use (record combined weight as "W_{dish}").

11.2 Preparation of samples

11.2.1 Fluid samples–If the sample contains enough moisture to flow readily, stir to homogenize, place a 25 to 50 g sample aliquot on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Evaporate the samples to dryness on a steam bath. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

NOTE: *Weigh wet samples quickly because wet samples tend to lose weight by evaporation. Samples should be weighed immediately after aliquots are prepared.*

11.2.2 Solid samples–If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place a 25 to 50 g sample aliquot of the pulverized sample on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

11.3 Dry the samples at 103°C to 105°C for a minimum of 12 hours, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Heat the residue again for 1 hour, cool it to balance temperature in a desiccator, and weigh. Repeat this heating, cooling, desiccating, and weighing procedure until the weight change is less than 5% or 50 mg, whichever is less. Record the final weight as "W_{total}."

NOTE: *It is imperative that dried samples weighed quickly since residues often are very hygroscopic and rapidly absorb moisture from the air. Samples must remain in the dessicator until the analyst is ready to weigh them.*

12.0 Data Analysis and Calculations

12.1 Calculate the % solids or the mg solids/kg sludge for total solids (Equation 2).

Equation 2

$$\%\ total\ solids = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 100$$

or

$$\frac{mg\ total\ solids}{kg\ sludge} = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 1{,}000{,}000$$

Where:

W_{dish} = *Weight of dish (mg)*
W_{sample} = *Weight of wet sample and dish (mg)*
W_{total} = *Weight of dried residue and dish (mg)*

12.2 Sample results should be reported as % solids or mg/kg to three significant figures. Report results below the ML as < the ML, or as required by the permitting authority or in the permit.

13.0 Method Performance

13.1 Method performance (MDL and quality control acceptance criteria) will be determined during the multi-lab validation of this method.

13.2 Total solids duplicate determinations must agree within 10% to be reported for permitting purposes. If duplicate samples do not meet this criteria, the problem must be discovered and the sample must be run over.

14.0 Pollution Prevention

14.2 Pollution prevention details are given in Section 14 of Method 200.9.

15.0 Waste Management

15.1 Waste management details are given in Section 15 of Method 200.9.

16.0 References

16.1 "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35: Section 1090 (Safety), 1992.

16.2 U.S. Environmental Protection Agency, 1992. Control of Pathogens and Vector Attraction in Sewage Sludge. Publ 625/R-92/013. Office of Research and Development, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Tables containing method requirements for QA/QC will be added after the validation study has been performed.