METHOD 200.7

TRACE ELEMENTS IN WATER, SOLIDS, AND BIOSOLIDS
BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRY

Revision 5.0

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Acknowledgments

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 "shall," "must," and "may not" define procedures required for producing reliable results. The terms "should" and "may" 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 200.7

Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry

1.0   Scope and Application

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

Analyte		Chemical Abstract Services Registry Number (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Cerium[a]	(Ce)	7440-45-1
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica[b]	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4

Analyte		Chemical Abstract Services Registry Number (CASRN)
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Yttrium	(Y)	7440-65-5
Zinc	(Zn)	7440-66-6

[a]Cerium has been included as a method analyte for correction of potential inter-element spectral interference.
[b]This method is <u>not</u> suitable for the determination of silica in solids.

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

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

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

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

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

> **NOTE:** *When analyzing samples containing high levels of silver as might occur in the photographic manufacturing industries, EPA Method 272.1 can be used for silver determinations. Based on the use of cyanogen iodide (CNI) as a stabilizing agent, Method 272.1 can be used on samples containing up to 4 mg/L of Ag. However, it should be recognized that CNI is an extremely hazardous and environmentally toxic reagent, and should be used with the utmost caution.*

1.8   The extraction of tin from solid or sludge samples should be prepared using aliquots <1 g when determined sample concentrations exceed 1%.

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

1.10   The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided the sample solution is adjusted to contain the

same mixed acid (HNO$_3$ + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.11   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. There may be difficulties in analyzing molybdenum in biosolids with a radial ICP, thus the determination of some analytes in biosolids may require the use of an axial ICP. More information will be provided by the validation study.

1.12   Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. 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. Preliminary MDL values are given in Table 4. 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.

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

2.0   Summary of Method

2.1   An aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are solubilized by gentle refluxing with HNO$_3$ and HCl. For the total recoverable analysis of a sludge sample containing <1% total suspended solids, analytes are solubilized by successive refluxing with HNO$_3$ and HCl. For total recoverable analysis of a sludge sample containing total suspended solids ≥1% (w/v), analytes are solubilized by refluxing with HNO$_3$, background organic materials are oxidized with peroxide, and analytes are further solubilized by refluxing with HCl. After cooling, the sample is made up to volume, mixed and then centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the addition of the appropriate volume of HNO$_3$, and then diluted to a predetermined volume and mixed before analysis.

2.2   The analysis described in this method involves multi-elemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry.

Samples are nebulized and the resulting aerosols are transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. The background must be measured adjacent to an analyte wavelength during analysis. Interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, and 11.0.

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 (Section 7.12.1). The calibration blank is a zero standard and is used to calibrate the ICP instrument.

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

3.4   Calibration verification (CV) solution–A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Section 7.13).

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 (Section 8.5). The field blank is analyzed to determine if method analytes or other interferences are present in the field environment.

3.7   Internal standard–Pure analyte(s) added to a sample, extract, or standard solution in a known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Section 11.6).

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

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 9.5).

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 matrix 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 (Section 7.12.2).

3.13   Method detection limit (MDL)–The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence (Section 9.2.1). The MDL is determined according to procedures described 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 standard (OPR)–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 9.7).

3.17   Plasma solution–A solution that is used to determine the optimum height above the work coil for viewing the plasma (Section 7.16).

3.18   Reference sample–A solution of method analytes of known concentrations which is used to fortify an aliquot of method blank or sample matrix (Section 7.14). The reference sample is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory and/or instrument performance.

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

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

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

3.22   Spectral interference check (SIC) solution–A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria (Sections 7.15 and 9.4).

3.23   Standard addition–The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.5.3.1 and 11.6).

3.24   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 7.10).

3.25   Total recoverable analyte–The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU (Section 11.2.1), or by analysis of the solution extract of a sludge, solid, or unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 through 11.4).

3.26   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 $105°C$.

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

4.0   Interferences

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

     4.1.1   Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (inter-element or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

     4.1.2   Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for inter-element contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables (Reference 8). Users may apply inter-element correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

     4.1.3   When inter-element corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.15. Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary

depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences (References 7 and 8).

4.1.4   The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to use a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must either be free of off-line inter-element spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 9.4 for required spectral interference test criteria.

4.1.5   When inter-element corrections are *not* used, either ongoing SIC solutions (Section 7.15) must be analyzed to verify the absence of inter-element spectral interference, or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration greater than the analyte MDL, or false negative analyte concentration less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the

zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, e.g., 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2   Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3   Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4   Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.12.1). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the

rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be analyzed again after a long rinse period.

5.0   Safety

5.1   The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be 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 9, 10, 11, and 12). A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 and HCl present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

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

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

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

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

6.0   Equipment and Supplies

> **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 EPA. Equivalent performance may be achievable using apparatus and materials other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.*

6.1   Inductively coupled plasma emission spectrometer:

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

   6.1.2   Radio-frequency generator compliant with FCC regulations.

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

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

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

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

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

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

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

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

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

6.8   Mortar and pestle, ceramic or other nonmetallic material.

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

6.10   Labware–Prevention of contamination and loss are of prime consideration for determination of trace levels of elements. Potential contamination sources

include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. One recommended procedure found to provide clean labware includes 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 HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean (References 2 and 3). Chromic acid cleaning solutions must be avoided because chromium is an analyte.

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

6.10.2 Assorted calibrated pipettes.

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

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

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

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

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

7.0   **Reagents and Standards**

7.1   Reagents may contain elemental impurities which might affect analytical data. Only high purity reagents that conform to the American Chemical Society specifications should be used whenever possible (Reference 13). 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 (specific gravity = 1.19).

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

7.2.2 Hydrochloric acid (1+4)–Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

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

7.3 Nitric acid, concentrated (specific gravity = 1.41).

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

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

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

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

7.4 Reagent water–All references to water in this method refer to ASTM Type I grade water (Reference 14).

7.5 Ammonium hydroxide, concentrated (specific gravity = 0.902).

7.6 Tartaric acid–ACS reagent grade.

7.7 Hydrogen peroxide–H_2O_2.

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

7.7.2 Hydrogen peroxide, 30%, stabilized certified reagent grade.

7.8 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.

7.9 Peat moss-All references to peat moss in this method refer to sphagnum peat moss free of arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium and zinc analytes at or above their MDLs (Table 4) or to contain those analytes at certified levels.

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

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

Typical stock solution preparation procedures follow for 1 L quantities (Equations 1 and 2), 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 pure element,

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

where:

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

Equation 2

From pure compound,

$$C = \frac{(m)(g_f)}{V}$$

where:

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

7.10.1 Aluminum solution, stock, 1 mL = 1000 µg Al–Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm beaker slowly to effect solution. When dissolution is

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complete, transfer solution quantitatively to a 1-L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.10.2 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.

7.10.3 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.

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

7.10.5 Beryllium solution, stock, 1 mL = 1000 µg Be–<u>DO NOT DRY</u>. Dissolve 19.66 g $BeSO_4$•$4H_2O$ (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.

7.10.6 Boron solution, stock, 1 mL = 1000 µg B–<u>DO NOT DRY</u>. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

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

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

10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

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

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

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

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

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

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

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

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

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

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

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

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

7.10.21   Phosphorus solution, stock, 1 mL = 1000 µg P–Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

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

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

7.10.24   Silica solution, stock, 1 mL = 1000 µg SiO_2–<u>DO NOT DRY</u>. Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four

significant figures, in 200 mL (1+20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

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

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

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

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

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

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

7.10.31   Vanadium solution, stock, 1 mL = 1000 µg V–Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to

> effect dissolution. Let solution cool and dilute with reagent water to volume in a 1-L volumetric flask.

7.10.32   Yttrium solution, stock 1 mL = 1000 µg Y–Dissolve 1.270 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1-L volumetric flask with reagent water.

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

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

> **NOTE:** *If the addition of silver to the recommended mixed-acid calibration standard results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.5 mg/L.*

7.12   Blanks–Three types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the method blank is used to assess possible contamination from the sample preparation procedure, and a rinse blank is used to flush the sample uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.12.1 The calibration and rinse blanks are prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The blanks should be stored separately in FEP bottles.

7.12.2 The method blank is reagent water that is carried through the same entire preparation scheme as the samples including sample digestion, when applicable. When the method blank is analyzed, it will contain all the reagents in the same volumes as the samples.

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

7.14 Reference sample–Analysis of a reference sample is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The reference sample must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the reference sample solution should be ≥ 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The reference sample solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed. Alternatively, the reference sample may be a standard or certified reference material traceable to the National Institute of Standards and Technology.

7.15 Spectral interference check (SIC) solutions–SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L Al; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) inter-element spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. Multi-element SIC solutions may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution (Reference 3).

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

7.16   Plasma solution–The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 5 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and diluting to 500 mL with reagent water. Store in a FEP bottle.

8.0   Sample Collection, Preservation, and Storage

8.1   Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must** be tested immediately prior to withdrawing an aliquot 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.

> **NOTE:** *Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipette and test the aliquot.*

8.2   For the determination of the dissolved elements, a sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical). Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to pH <2 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 samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior to withdrawing an aliquot for processing or "direct analysis." If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 16 hours until verified to be pH <2.

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

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

8.5   A field blank should be prepared and analyzed as required by the data user. Use the same conditions (i.e., container, filtration and preservation) as used in sample collection.

8.6   If a total solids determination is required, then a separate aliquot should be collected following the procedure given in Section 8.0 of Appendix A.

9.0   Quality Assurance/Quality Control

9.1   Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 24). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with analyte(s) 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 determine that results of the analysis meet the performance characteristics of the method.

   9.1.1   The analyst shall 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 this 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 MDL (40 CFR Part 136, Appendix B) is lower than the MDL for that analyte in this method, or one-third the regulatory compliance level, whichever is higher. If

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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 analytes measured, by name and CAS Registry number.

9.1.2.2.3   A narrative stating the 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)   Method detection limit
(b)   Calibration
(c)   Calibration verification
(d)   Initial precision and recovery
(e)   Ongoing precision and recovery
(f)   Analysis of blanks
(g)   Matrix spike and matrix spike duplicate analyses

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)   Mass 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 9.6 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 9.5). When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits. If method performance cannot be brought within the limits given in this method, the result may not be reported for regulatory compliance purposes.

9.1.5   The laboratory shall, on an ongoing basis, demonstrate through calibration verification (Section 9.3) and through analysis of the OPR standard (Section 9.7) that the analytical system is meeting the performance criteria.

9.1.6   The laboratory shall maintain records to define the quality of data that are generated. Development of accuracy statements is described in Sections 9.5.5.1 and 9.7.7.

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 analyte(s) of interest, the analyst shall 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 specified in Table 4 (to be determined by the validation study) or one-third the regulatory compliance limit, whichever is greater. MDLs must 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 matrix if solid samples are to be run and/or with a reagent water matrix if aqueous samples are to be run. MDLs also must be determined for biosolids with peat moss if sludge samples are to be analyzed for arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc.

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

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

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

  9.2.2.3 For each analyte, compare s and X with the corresponding limits for IPR in (Table 5- to be determined in validation study). If s and X for all analyte(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 analyte. Correct the problem and repeat the test.

9.2.3 Linear dynamic range (LDR)–The upper limit of the LDR must be established for each wavelength used. It must be determined from a linear calibration prepared in the normal manner using the established

analytical operating procedure for the instrument. The LDR should be determined by analyzing successively higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Calculated sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and analyzed again. The LDRs should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they should be redetermined.

9.2.4 Reference sample–When beginning the use of this method, quarterly, and as needed to meet data quality requirements, the analyst must verify the calibration standards and acceptable instrument performance with the preparation and analysis of a reference sample (Section 7.14). 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 value. If the reference sample is not within the required limits, an immediate second analysis of the reference sample is recommended to confirm unacceptable performance. If both the calibration standards and acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Calibration verification–A laboratory must analyze a CV solution (Section 7.13) and a calibration blank (Section 7.12.1) immediately following daily calibration, after every 10th sample (or more frequently, if required), and at the end of the sample run. The analysis data of the calibration blank and CV solution must be kept on file with the sample analyses data.

9.3.1 The result of the calibration blank should be less than the analyte ML or one-third the regulatory compliance level, whichever is greater.

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 5).

9.3.3 If the calibration cannot be verified within the specified limits, both the CV solution and the calibration blank should be analyzed again. If the second analysis of the CV solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected, and/or the instrument recalibrated. All

samples following the last acceptable CV solution must be analyzed again.

9.4   Spectral interference check (SIC) solution–For all determinations the laboratory must periodically verify the inter-element spectral interference correction routine by analyzing SIC solutions (Section 7.15).

9.4.1   For interferences from iron and aluminum, only those correction factors (positive or negative) which, when multiplied by 100, exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis. The lower calibration blank control limit is determined by subtracting the ML, or one-third the regulatory compliance limit, whichever is greater, from zero.

9.4.2   For the other interfering elements, only those correction factors (positive or negative) which, when multiplied by 10 to calculate apparent analyte concentrations that exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis.

9.4.3   If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (Section 7.15, a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If, after subtraction of the analyte ML, or one-third the regulatory compliance, whichever is greater, the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

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

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

all inter-element spectral correction factors must be verified annually and updated if necessary.

9.4.5 All inter-element spectral correction factors must be verified whenever there is a change in instrument operating conditions. Examples of changes requiring rigorous verification of spectral correction factors are: changes in incident power, changes in nebulizer gas flow rate, or installation of a new torch injector with a different orifice.

9.4.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

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

9.5 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 10) 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.

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

9.5.1.1 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. (For notes on Ag, Sn, and Ba see Sections 1.7, 1.8, and 1.9).

9.5.1.2 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.

9.5.1.3 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 in solution (mg/L) by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag, Sn, and Ba see Sections 1.7, 1.8, and 1.9).

9.5.2 Assessing spike recovery.

9.5.2.1 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*.

NOTE: *The concentrations of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids and sludge can vary greatly and are not necessarily predictable. Major constituents should not be spiked to >25 mg/L so that the sample matrix is not altered and the analysis is not affected.*

9.5.2.2 Prepare a standard solution to produce an appropriate concentration in the sample (Section 9.5.1).

9.5.2.3 Spike two additional sample aliquots with the spiking solution and analyze these aliquots as described in Section 11 to determine the concentration after spiking (A).

9.5.2.4 Calculate the percent recovery (P) in each aliquot (Equation 3).

Equation 3

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

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

9.5.3 Compare the percent recovery with the QC acceptance criteria in Table 5 (to be determined in validation study).

9.5.3.1   If P falls outside the designated range for recovery in Table 5, the results have failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard (Section 9.7). If the OPR is within established performance criteria (Table 5), 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, and analysis by method of standard addition or the use of an internal standard(s) (Section 11.6) should be considered.

9.5.3.2   If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and analyze the sample batch again.

9.5.4 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.6.

9.5.4.1   Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should have a recovery of 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum level of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the dilution test described in Section 9.5.4.2 should be used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions or the use of an appropriate internal standard element may provide more accurate data.

9.5.4.2   Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection limit in the original solution but <90% of the linear limit), an analysis of a 1+4 dilution should agree (after correction for the fivefold dilution) within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

9.5.5 Recovery for samples should be assessed and records maintained.

    9.5.5.1   After the analysis of five samples of a given matrix type (river water, biosolids, etc.). For which the analyte(s) pass the tests in Section 9.5.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (SP) for the analyte(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 of river water, the accuracy interval is expressed as 70 - 110%.

    9.5.5.2   Update the accuracy assessment for each metal in each matrix regularly (e.g., after each five to ten new measurements).

9.5.6 Precision of matrix spike and duplicate.

    9.5.6.1   Relative percent difference between duplicates–Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 4 using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.5.2 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 4

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

where:

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

    9.5.6.2   The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 5 (to be determined in validation study). If the criterion is not met, the system is judged to be outside accepted limits of performance. The problem must be identified and corrected, and the analytical batch must be analyzed again.

9.5.6.3   Reference material analysis can provide additional interference data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.6   Blanks.

9.6.1 Method blank.

9.6.1.1   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, to a maximum of 20 samples). Analyze the blank immediately after the OPR is analyzed (Section 9.7) to demonstrate freedom from contamination.

9.6.1.2   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 4, to be determined by the validation study) or 1/3 the regulatory compliance level, whichever is greater, sample analysis must be halted, the source of the contamination determined, the samples must be prepared again with a fresh method blank and OPR and analyzed again.

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

9.6.1.4   If the result for a single 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.

9.6.2 Field blank.

9.6.2.1   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 20 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.6.2.2   If the analyte(s) 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, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.6.2.3   Alternatively, if a sufficient number of field blanks (three minimum) 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, whichever is greater.

9.6.2.4   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 the next sampling event.

9.6.3   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.

9.6.3.1   Bottle blanks–After undergoing appropriate cleaning procedures (Section 6.10), 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.

9.6.3.2 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.

   9.6.3.2.1 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.

   9.6.3.2.2 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.

   9.6.3.2.3 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.

9.7 Ongoing precision and recovery.

   9.7.1 For aqueous samples, prepare an OPR sample (laboratory fortified method blank) identical to the IPR aliquots (Section 9.2.2.1) 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) by spiking an aliquot of reagent water with the analyte(s) of interest.

   9.7.2 For solid samples, the use of clean sand or soil fortified as in Section 9.7.1 is recommended.

9.7.3 For biosolid samples, the use of peat moss fortified as in Section 9.7.1 is recommended.

9.7.4 Analyze the OPR sample immediately before the method blank and samples from the same batch.

9.7.5 Compute the percent recovery of each analyte in the OPR sample.

9.7.6 For each analyte, compare the concentration to the limits for ongoing recovery in (Table 5 - to be determined in validation study). If all analyte(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 analyte. Correct the problem, prepare the sample batch again with fresh OPR and method blank, and reanalyze the QA/QC and samples.

9.7.7 Add results that pass the specifications in Section 9.7.6 to IPR and previous OPR data for each analyte in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte in each matrix type by calculating the average percent recovery (P) and the standard deviation of percent recovery (SP). Express the accuracy as a recovery interval from P - 2SP to P + 2SP. For example, if P = 95% and SP = 5%, the accuracy is 85 - 105%.

10.0 Calibration and Standardization

10.1 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.11).

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 (Section 1.12, Table 4, 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 20).

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 5.

Equation 5

$$y = mx + b$$

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) at each concentration, as follows:

Equation 6

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

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 7).

Equation 7

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

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, drinking and surface waters, pipet an aliquot ($\geq$20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) 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). If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects.

> **NOTE:** *If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 through 11.2.7 prior to analysis.*

11.2 Aqueous Sample Preparation–Total Recoverable Analytes

11.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered, acid preserved sample aliquot using the sample preparation procedure described in Section 11.1 while making allowance for sample dilution in the data calculation (Section 12.0). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis, follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples of >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 contains <u>undissolved</u> solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 through 11.3.6.*

11.2.3 Add 2 mL (1+1) HNO_3 and 1.0 mL of (1+1) HCl to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note). The beaker should be covered with an elevated watch glass or other

necessary steps should be taken to prevent sample contamination from the fume hood environment.

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

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. <u>DO NOT BOIL</u>. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge).

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

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

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

11.3 Solid sample preparation–Total recoverable analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion to a tared weighing dish. For samples with <35% estimated moisture, a 20 g portion is sufficient. For samples with estimated moisture >35%, a larger aliquot 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 mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.

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

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

NOTE: *For proper heating, adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C). Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.*

11.3.4 Heat the sample and gently reflux for 30 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 (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 the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration). The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

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

11.4 Sludge sample preparation–Total recoverable analytes.

NOTE: *It may be possible to use the solids digestion (Section 11.3) for sludge samples, depending on the composition of the sludge sample and the analyte(s) of interest. Under this performance-based method, it is admissible to change the digestion technique as long as all quality control and assurance tests meet the criteria published in Tables 4 and 5. This method has been validated using the sludge sample digestion in Section 11.4 of this method, and it works for all the analytes listed in Section 1.1.*

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

11.4.1.1 Mix the sample thoroughly and transfer a portion to a tared weighing dish. For samples with <35% estimated moisture a 20 g portion is sufficient. For samples with estimated 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 mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.

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

11.4.1.3 Add 10 mL of (1+1) HNO_3 to the beaker and cover the lip of 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, place on a hot plate, and reflux for 30 minutes. Repeat this last step once. Remove the beaker from the hot plate and allow the sample to cool. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. Place the beaker on a hot plate and heat the sample until a gentle effervescence is observed. Once the reaction has subsided, additional 1 mL aliquots of the 30% H_2O_2 should be added until no effervescence is observed, but to no more than a total of 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 volume 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 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 large amounts 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. Then remove the watch glass and reduce the sample volume to 3 mL, again adjusting upwards if necessary.

11.4.2.3   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.

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

11.5   Sample analysis.

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

11.5.2 Configure the instrument system.

11.5.2.1   Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100 - 1200 watts forward power, 15 - 16 mm viewing height, 15 - 19 L/min. argon coolant flow, 0.6 - 1 L/min. argon aerosol flow, 1 - 1.8 mL/min. sample pumping rate with a one minute preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors (Reference 17).

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

11.5.2.3   Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000 µg/mL solution of yttrium (Section 7.10.32), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 - 20 mm above the top of the work coil (Reference 18). Record the nebulizer gas flow rate or pressure setting for future reference.

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

11.5.2.5 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 11.5.2.3 and 11.5.2.4, and aspirate the plasma solution (Section 7.16), containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 - 18 mm above the top of the work coil. This region of the plasma is commonly referred to as the analytical zone (Reference 19). Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

11.5.2.6 The instrument operating condition finally selected as optimum should provide the lowest reliable method detection limits.

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

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

"hard" (Pb 220.353 nm) and "soft" (Cu 324.754) lines is illustrated in Figure 1.

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

11.5.4 Prior to and during the analysis of samples, the laboratory must comply with the required QA/QC procedures (Section 9). QA/QC data must be generated using the same instrument operating conditions (Section 11.5) and calibration routine (Section 10) in effect for sample analysis. The data must be documented and kept on file so that they are available for review by the data user.

11.5.5 A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.12.1) for a minimum of 60 seconds (Section 4.4) between all standard or sample solutions, OPRs, MS, MSD, and check solutions.

11.5.6 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and analyzed again.

11.5.7 Also, for the inter-element spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended. If another approved method is unavailable, the sample may be diluted with acidified reagent water and reanalyzed.

11.5.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5.4 and 11.6 are recommended.

11.5.9 Report data as directed in Section 12.0.

11.6 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates

for enhancement or depression of an analyte signal by a matrix (Reference 21). It will not correct for additive interferences such as contamination, inter-element interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated with Equation 8.

Equation 8

$$C_S = \frac{S_2 * V_1 * C}{(S_1 - S_2) * V_2}$$

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 (L) used for MSA*

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

12.0 Data Analysis and Calculations

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

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

12.3 For total recoverable aqueous analytes (Section 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce

the 50 mL final solution, and report data as instructed in Section 12.4. If an aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration.

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

12.5 For total recoverable analytes in solid and sludge samples (Sections 11.3 and 11.4), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using Equation 9.

Equation 9

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

where:

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

Do not report analyte data below the solids MDL.

12.6 To report percent solids or mg/kg of solid and sludge samples, use the procedure in Appendix A.

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

13.0 **Method Performance**

13.1 MDLs and MLs will be determined in a validation study. Preliminary MDL values are given in Table 4. The ML for each analyte can be calculated by multiplying

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the MDL by 3.18 and rounding to the number nearest ($2, 5,$ or 10×10^n) where n is a positive or negative integer.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation (e.g., Section 7.10). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

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

15.0 Waste Management

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

16.0 References

1.   U.S. Environmental Protection Agency. Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes-Method 200.7, Dec. 1982. EPA-600/4-79-020, revised March 1983.

2.   U.S. Environmental Protection Agency. Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010, SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition, 1986.

3.   U.S. Environmental Protection Agency. Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, revision 3.3, EPA 600 4-91/010 June 1991.

4.   U.S. Environmental Protection Agency. Inductively Coupled Plasma-Atomic Emission Spectrometry Method for the Analysis of Waters and Solids, EMMC, July 1992.

5.   Fassel, V.A. et al. Simultaneous Determination of Wear Metals in Lubricating Oils by Inductively-Coupled Plasma Atomic Emission Spectrometry. Anal. Chem. 48:516-519, 1976.

6.   Merryfield, R.N. and R.C. Loyd. Simultaneous Determination of Metals in Oil by Inductively Coupled Plasma Emission Spectrometry. Anal. Chem. 51:1965-1968, 1979.

7.   Winge, R.K. et al. Inductively Coupled Plasma-Atomic Emission Spectroscopy: An Atlas of Spectral Information, Physical Science Data 20. Elsevier Science Publishing, New York, New York, 1985.

8.   Boumans, P.W.J.M. Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry, 2nd edition. Pergamon Press, Oxford, United Kingdom, 1984.

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

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

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

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

13. Rohrbough, W.G. et al. Reagent Chemicals, American Chemical Society Specifications, 7th edition. American Chemical Society, Washington, D.C., 1986.

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

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

16.   Maxfield, R. and B. Mindak. EPA Method Study 27, Method 200.7 Trace Metals by ICP, Nov. 1983. Available from National Technical Information Service (NTIS) as PB 85-248-656.

17.   Botto, R.I., Quality Assurance in Operating a Multielement ICP Emission Spectrometer. Spectrochim. Acta, 39B(1):95-113, 1984.

18.   Wallace, G.F., Some Factors Affecting the Performance of an ICP Sample Introduction System. Atomic Spectroscopy, Vol. 4, p. 188-192, 1983.

19.   Koirtyohann, S.R. et al. Nomenclature System for the Low-Power Argon Inductively Coupled Plasma, Anal. Chem. 52:1965, 1980.

20.   Deming, S.N. and S.L. Morgan. Experimental Design for Quality and Productivity in Research, Development, and Manufacturing, Part III, pp 119-123. Short course publication by Statistical Designs, 9941 Rowlett, Suite 6, Houston, TX 77075, 1989.

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

22.   Jones, C.L. et al. An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050. EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, Nevada, 1987.

23.   Martin, T.D., E.R. Martin and S.E. Long. Method 200.2: Sample Preparation Procedure for Spectrochemical Analyses of Total Recoverable Elements, EMSL ORD, USEPA, 1989.

24.   *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*; U.S. Environmental Protection Agency. EMSL-Cincinnati, OH, March 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

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

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

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

[b]These estimated 3-sigma instrumental detection limits are provided only as a guide to instrumental limits (Reference 16). The method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits for solids can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

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

[d]Calculated from 2-sigma data (Reference 5).

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

TABLE 2: ON-LINE METHOD INTER-ELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant[a]
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

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

TABLE 3: MIXED STANDARD SOLUTIONS

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

TABLE 4: TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)[a]

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

[a] Table will be changed after interlaboratory validation of Method 200.7.

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

[c] Estimated, calculated from aqueous MDL determinations.

[d] Boron not reported because of glassware contamination. Silica not determined in solid samples.

[e] Elevated value due to fume-hood contamination.

TABLE 5: PERFORMANCE CRITERIA FOR METHOD 200.7 (TO BE DETERMINED DURING INTERLABORATORY VALIDATION)
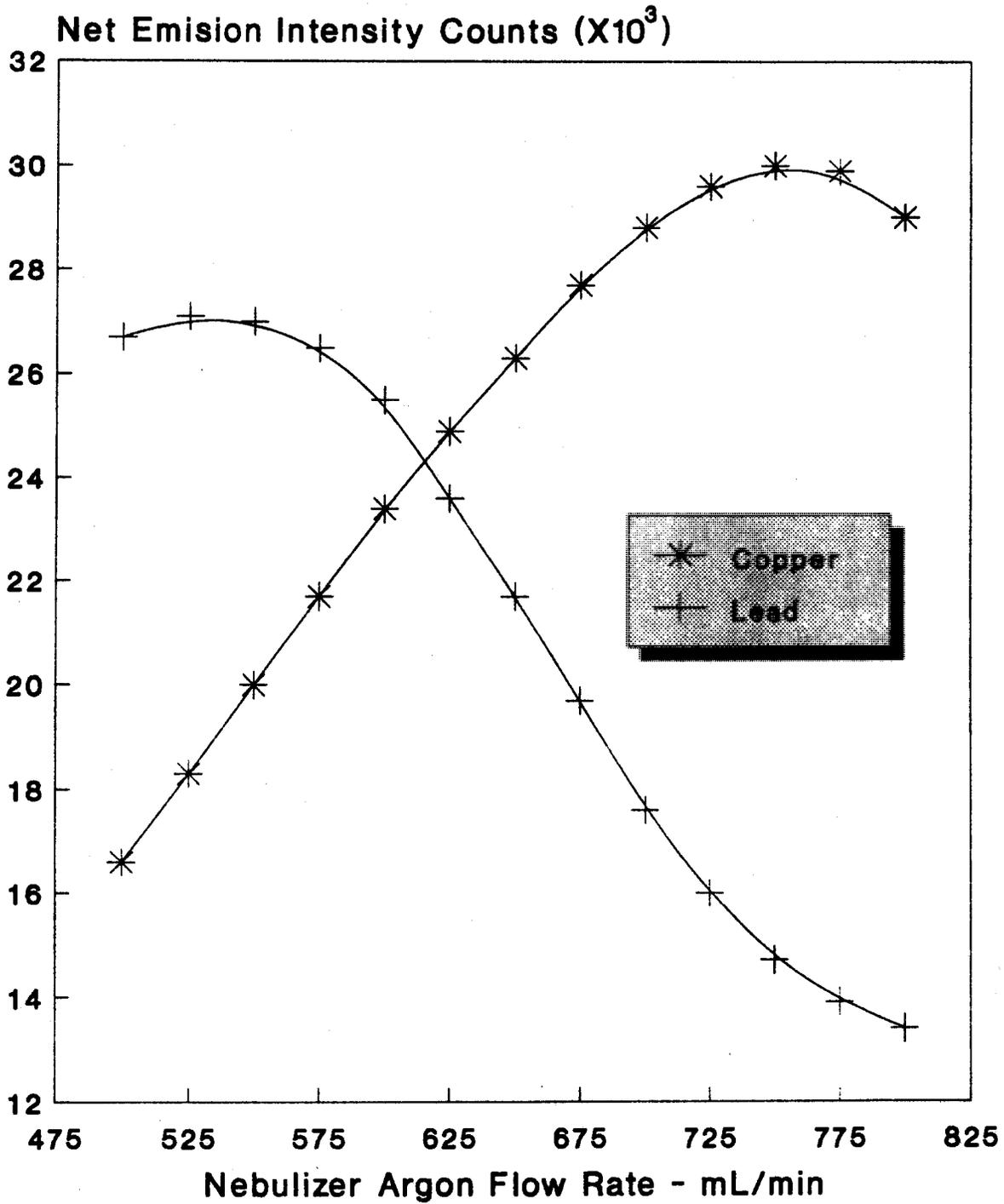
Pb-Cu ICP-AES EMISSION PROFILE

Figure 1

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 200.7.

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 200.7.

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 200.7 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 200.7.

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

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

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 200.7.

15.0 Waste Management

15.1 Waste management details are given in Section 15 of Method 200.7.

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.