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Method 1639: Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption

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Disclaimer

This method has been reviewed and approved for publication by 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.

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Introduction

This analytical method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge about the physical fate (e.g., concentration and dispersal) of pollutants, and their effects on ecological and human health, and biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within their boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and those required to support technology-based permits. Therefore, EPA developed new sampling and analysis methods to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, on which the new sampling and analysis methods are based. Method 1639 was specifically developed to provide reliable measurements of six of these metals at EPA WQC levels using stabilized temperature graphite furnace atomic absorption techniques.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This analytical method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

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Note: This method is intended to be performance based, and the laboratory is permitted to omit any step or modify any procedure provided that *all* performance requirements set forth in this method are met. The laboratory is *not* allowed to omit any quality control analyses. The terms "must," "may," and "should" are included throughout this method and are intended to illustrate the importance of the procedures in producing verifiable data at water quality criteria levels. The term "must" is used to indicate that researchers in trace metals analysis have found certain procedures essential in successfully analyzing samples and avoiding contamination; however, these procedures can be modified or omitted if the laboratory can demonstrate that data quality is not affected.

Method 1639

Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption

1.0 Scope and Application

1.1 This method provides procedures to determine dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using stabilized temperature graphite furnace atomic absorption (GFAA). It may also be used to determine total recoverable element concentrations in these waters. This method was developed by integrating the analytical procedures contained in EPA Method 200.9 with the stringent quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels. This method contains QC procedures that will ensure that contamination will be detected when blanks accompanying samples are analyzed. This method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (the "Sampling Method"). The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process.

1.2 This method is applicable to the following analytes:

Analyte	***Symbol***	***Chemical Abstract Services Registry Number (CASRN)***
Antimony	(Sb)	7440-36-0
Cadmium	(Cd)	7440-43-9
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Trivalent Chromium	(Cr^{3+})	16065-83-1
Zinc	(Zn)	7440-66-6

Table 1 lists the EPA WQC levels, the Method Detection Limit (MDL) for each metal, and the Minimum Level (ML) set for each metal in this method. Instrument operating conditions for the applicable elements are listed in Table 3. They are intended as a guide and are typical of a system optimized for the element employing commercial instrumentation. However, actual linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.3 This method is not intended to determine metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range.

1.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination. These suggestions are given in Section 4.0, "Contamination and Interferences," and are based on findings of researchers performing trace metals analyses (References 1–8). Additional suggestions for improving existing facilities can be found in EPA's *Guidance for Establishing Trace Metals Clean Rooms in Existing Facilities*, which is available from the National Center for Environmental Publications and Information (NCEPI) at the address listed in the introduction to this document.

1.5 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this method, however, because they lack an exact definition. However, the information provided in this method is consistent with and is copied from summary guidance on clean and ultraclean techniques (Reference 9).

1.6 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 10).

1.7 This method is "performance based"; i.e., an alternate procedure or technique may be used, as long as the performance requirements in the method are met. Section 9.1.2 gives details of the tests and documentation required to support equivalent performance.

1.8 For dissolved metal determinations, samples must be filtered through a 0.45-µm capsule filter at the field site. The filtering procedures are described in the Sampling Method. Except for trivalent chromium, the filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in the Sampling Method; procedures for laboratory preservation are provided in this method. To determine trivalent chromium, a field preparation step, which is described in the Sampling Method, is used to isolate the trivalent chromium.

1.9 To determine total recoverable analytes in ambient water samples, a digestion/extraction is required before analysis when the elements are not in solution (e.g., aqueous samples that may contain particulate and suspended solids).

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

1.11 This method should be used by analysts experienced in the use of graphite furnace atomic absorption spectroscopy, the interpretation of spectral and matrix interferences, and procedures for their correction, and only by personnel thoroughly trained in handling and analyzing samples to determine metals at EPA WQC levels. A minimum of six months' experience with commercial instrumentation is recommended.

1.12 This method is accompanied by a data verification and validation guidance document titled *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitoring*. Data users should state the data quality objectives (DQOs) required for a project before using this method.

2.0 Summary of Method

2.1 An aliquot of a well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, mixed, and centrifuged or allowed to settle overnight prior to analysis. To determine dissolved analytes in a filtered aqueous sample aliquot, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analytes listed in this method are determined by stabilized temperature platform graphite furnace atomic absorption (STPGFAA). In STPGFAA, the sample and the matrix modifier are first pipeted onto the platform or a device that provides delayed atomization. The furnace chamber is then purged with a continuous flow of a premixed gas (95% argon/5% hydrogen) and the sample is dried at a relatively low temperature (about 120°C) to avoid spattering. Once dried, the sample is pretreated in a char or ashing step, which is designed to minimize the interference effects caused by the concomitant sample matrix. After the char step, the furnace is allowed to cool before atomization. The atomization cycle is characterized by rapid heating of the furnace to a temperature in which the metal (analyte) is atomized from the pyrolytic graphite surface into a stopped gas flow atmosphere of argon containing 5% hydrogen. (Only selenium is determined in an atmosphere of high-purity argon.) The resulting atomic cloud absorbs the element-specific atomic emission produced by a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL). Following analysis, the furnace is subjected to a cleanout period of high temperature and continuous argon flow. Because the resulting absorbance usually has a nonspecific component associated with the actual analyte absorbance, an instrumental background correction device is required to subtract from the total signal the component that is nonspecific to the analyte. In the absence of interferences, the background corrected absorbance is directly related to the concentration of the analyte. Interferences relating to STPGFAA (Section 4.0) must be recognized and corrected. Suppressions or enhancements of instrument response caused by the sample matrix must be corrected by the method of standard addition (Section 12.5).

3.0 Definitions

3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

3.2 Other definitions of terms are given in the glossary (Section 18) at the end of this method.

4.0 Contamination and Interferences

4.1 Preventing contamination of ambient water samples during the sampling and analytical process constitutes one of the greatest difficulties encountered with trace metals determinations. Over the last two decades, marine chemists have recognized that much of the historical data regarding the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. More recently, historical trace metals data collected from freshwater rivers and streams have been shown to be similarly biased because of contamination during sampling and analysis (Reference 15). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 Samples may become contaminated by numerous routes. Potential sources of trace metals contamination during sampling include metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.3 Contamination Control

4.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain metals.

4.3.1.1 The integrity of the results cannot be compromised by contamination of samples. Requirements and suggestions for control of sample contamination are given in this method and in the Sampling Method.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. Requirements and suggestions for protecting the laboratory are given in this method.

4.3.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this method and in the Sampling Method.

4.3.2 Avoid contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known or thought to be free from contamination. Two of the most important factors in avoiding or reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Therefore it is imperative that the procedures described in this method be carried out by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class 100 clean room (Section 6.1.1). If a clean room is not available, all sample preparation must be performed in a class 100 clean bench or a nonmetal glove box fed by particle-free air or nitrogen. Digestions must be performed in a nonmetal fume hood, ideally situated in the clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions must only be opened or exposed in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

4.3.5 Clean work surfaces—Before processing a given batch of samples, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.3.6 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.9.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.3.7 Use metal-free Apparatus—All Apparatus used for metals determinations at ambient WQC levels must be nonmetallic and/or free of material that may contain metals.

4.3.7.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials resulting either in contamination or low-biased results (Reference 3). All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures described in Section 11 and must be known to be clean and metal free before proceeding.

4.3.7.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample itself, *unless* these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 12).

4.3.7.3 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to injection into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected.

4.3.7.4 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.3.8 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.3.8.1 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. To reduce carryover, the sample introduction system may be rinsed between samples with dilute acid and reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a laboratory blank to check for carryover. For samples containing high levels of metals, it may be necessary to acid clean or replace the connecting tubing or inlet system to ensure that contamination will not affect subsequent measurements. Samples known or suspected to contain the lowest concentration of metals should be analyzed first followed by samples containing higher levels. For instruments containing autosamplers, the laboratory should keep track of which station is used for a given sample. When an unusually high concentration of a metal is detected in a sample, the station used for that sample should be cleaned more thoroughly to prevent contamination of subsequent samples, and the results for subsequent samples should be checked for evidence of the metal(s) that occurred in high concentration.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of inorganic substances are processed and analyzed. As stated in Section 1.0, this method is not intended for these samples, and samples containing high concentrations should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.

4.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the

bag and then subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in collecting, processing, and analyzing ambient water samples be cleaned as specified in Section 11.

4.3.8.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, samples should be processed and analyzed as far as possible from sources of airborne contamination.

4.4 Interferences—Several interference sources may cause inaccuracies in determining trace elements by GFAA. These interferences can be classified into three major subdivisions, namely spectral, matrix, and memory.

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

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

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

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

4.4.2.1 Matrix interferences can be chemical or physical. In this method the use of a delayed atomization device that provides stabilized temperatures is required. These devices provide an environment that is more conducive to the formation of free analyte atoms and thereby minimize this type of interference. This type of interference can be detected by analyzing the sample plus a sample aliquot fortified with a known concentration of the analyte. If the determined concentration of the analyte addition is outside a designated range, a possible matrix effect should be suspected (Section 9.3).

4.4.2.2 The use of nitric acid is preferred for GFAA analyses to minimize vapor state anionic chemical interferences; however, in this method hydrochloric acid is required to maintain stability in solutions containing antimony. When hydrochloric acid is used, the chloride ion vapor state interferences must be reduced using an appropriate matrix modifier. In this method a combination modifier of palladium, magnesium nitrate, and a hydrogen (5%)/argon (95%) gas mixture is used for this purpose. The effects and benefits of using this modifier are discussed in detail in Reference 13 (Section 17.0). Listed in Section 4.4.3 are some typical observed effects.

4.4.3 Specific element interferences

Antimony: Antimony suffers from an interference produced by K_2SO_4 (Reference 14). In the absence of hydrogen in the char cycle (1300°C), K_2SO_4 produces a relatively high (1.2 abs) background absorbance, which can produce a false signal, even with Zeeman background correction. However, this background level can be dramatically reduced (0.1 abs) by the use of a hydrogen/argon gas mixture in the char step. This reduction in background is strongly influenced by the temperature of the char step. Because the actual furnace temperature may vary from instrument to instrument, it should be determined on an individual basis.

Cadmium: The HCl present from the digestion procedure can influence the sensitivity for Cd. The use of 20 µL of a 1% HCl solution with Pd as a modifier results in a 80% loss in sensitivity relative to the analyte in a 1% HNO_3 solution. The use of $Pd/Mg/H_2$ as a matrix modifier reduces this suppression to less than 10% (Reference 13).

Selenium: Iron has been shown to suppress Se response with continuum background correction (Reference 14). In addition, the use of hydrogen as a purge gas during the dry and char steps can cause a suppression in Se response if not purged from the furnace before atomization.

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

5.0 Safety

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable.

5.1.1 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 15–18). A reference file of material safety data sheets should also be available to all personnel involved in the chemical analysis. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and make the results available to the analyst. The references and bibliography at the end of Reference 18 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.1.2 Concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. These reagents should be used in a fume hood whenever possible. If eyes or skin are touched, they must be flushed with a large volume of water. Protective clothing should always be worn along with safety glasses or a shield for eye protection, and proper mixing of these reagents must be observed.

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

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

5.4 The graphite tube during atomization emits intense UV radiation. Suitable precautions should be taken to protect personnel from such a hazard.

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

6.0 Apparatus, Equipment, and Supplies

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

6.1 Facility

6.1.1 Clean room—Class 100, 200-ft^2 minimum, with down-flow, positive-pressure ventilation, air-lock entrances, and pass-through doors

6.1.1.1 Construction materials—Nonmetallic, preferably plastic sheeting attached without metal fasteners. If painted, paints that do not contain the metal(s) of interest must be used.

6.1.1.2 Adhesive mats, for use at entry points to control dust and dirt from shoes

6.1.2 Fume hoods, nonmetallic, two minimum, with one installed internal to the clean room

6.1.3 Clean benches, class 100, one installed in the clean room; the other adjacent to the analytical instrument(s) for preparation of samples and standards

6.2 Graphite furnace atomic absorbance spectrophotometer

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

6.2.2 Single-element HDLs or single-element EDLs along with the associated power supplies

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

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

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

6.3 Analytical balance, with capability to measure to 0.1 mg, to weigh solids and to prepare standards

6.4 A temperature-adjustable hot plate capable of maintaining a temperature of 95°C

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

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

6.7 Alkaline detergent—Liquinox®, Alconox®, or equivalent

6.8 pH meter or pH paper

6.9 Labware—To determine trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust and other contaminants. A clean laboratory work area should be designated for trace element sample handling. Sample containers can introduce positive and negative errors in determining trace elements by contributing contaminants through surface desorption or leaching, and depleting element concentrations through adsorption processes. All labware must be metal free. Suitable construction materials are fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, and polypropylene. Fluoropolymer should be used when samples are to be analyzed for mercury. All labware should be cleaned according to the procedure in Section 11.4. Gloves, plastic wrap, storage bags, and filters may all be used new without additional cleaning unless results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an alternate supplier must be obtained or the materials must be cleaned.

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

6.9.1 Volumetric flasks, graduated cylinders, funnels and centrifuge tubes

6.9.2 Assorted calibrated pipets

6.9.3 PTFE (or other suitable material) beakers, 250 mL with PTFE covers

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

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

6.9.6 Tongs—For removal of Apparatus from acid baths. Coated metal tongs may not be used.

6.9.7 Gloves—Clean, nontalc polyethylene, latex, or vinyl; various lengths. Heavy gloves should be worn when working in acid baths as baths will contain hot, strong acids.

6.9.8 Buckets or basins—5–50 L capacity, for acid soaking of the Apparatus

6.9.9 Nonmetallic brushes for scrubbing Apparatus

6.9.10 Storage bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes) for storage of Apparatus

6.9.11 Plastic wrap—Clean, colorless polyethylene to store Apparatus

6.10 Sampling Equipment—The sampling team may contract with the laboratory or a cleaning facility that is responsible for cleaning, storing, and shipping all sampling devices, sample bottles, filtration equipment, and all other Apparatus used to collect ambient water samples. Before shipping the equipment to the field site, the laboratory or facility must generate an

acceptable equipment blank (Section 9.5.3) to demonstrate that the sampling equipment is free from contamination.

6.10.1 Sampling devices—Before ambient water samples are collected, consideration should be given to the type of sample to be collected and the devices to be used (grab, surface, or subsurface samplers). The laboratory or cleaning facility must clean all devices used for sample collection. Various types of samplers are described in the Sampling Method. Cleaned sampling devices should be stored in polyethylene bags or wrap.

6.10.2 Sample bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL with lids. Cleaned sample bottles should be filled with 0.1% HCl (v/v) until use.

NOTE: *If mercury is a target analyte, fluoropolymer or glass bottles must be used.*

6.10.3 Filtration apparatus

6.10.3.1 Filters, Gelman Supor 0.45-µm, 15-mm diameter filter capsules (Gelman 12175), or equivalent

6.10.3.2 Peristaltic pump—115-V a.c., 12-V d.c., internal battery, variable speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent).

6.10.3.3 Tubing for use with peristaltic pump—Styrene/ethylene/butylene/silicone (SEBS) resin, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06464-18, or approximately 1/4-in i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent). Tubing is cleaned by soaking in 5–10% HCl solution for 8–24 h, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

7.0 Reagents and Standards

Reagents may contain elemental impurities that might affect analytical data. Only high-purity reagents should be used. If the purity of a reagent is in question, it should be analyzed 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 subboiling distillation are acceptable.

7.1 Reagents for cleaning Apparatus, sample bottle storage, and sample preservation and preparation

7.1.1 Nitric acid, concentrated (sp gr 1.41), Seastar or equivalent

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

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

7.1.4 Nitric acid (1+9)—Add 100 mL concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.

7.1.5 Hydrochloric acid, concentrated (sp gr 1.19)

7.1.6 Hydrochloric acid (1+1)—Add 500 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid (1+4)—Add 200 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.8 Hydrochloric acid (HCl): 1N trace metal grade

7.1.9 Hydrochloric acid (HCl): 10% wt, trace metal grade

7.1.10 Hydrochloric acid (HCl): 1% wt, trace metal grade

7.1.11 Hydrochloric acid (HCl): 0.5% (v/v), trace metal grade

7.1.12 Hydrochloric acid (HCl): 0.1% (v/v) ultrapure grade

7.1.13 Tartaric acid (CASRN 87-69-4)

7.2 Reagent water—Reagent water is demonstrably free of the metal(s) of interest and potentially interfering substances at the MDL for that metal listed in Table 1. It is prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other technique that removes the metal(s) and potential interferent(s).

7.3 Matrix modifier—Dissolve 300 mg palladium (Pd) powder in concentrated HNO_3 (1 mL of HNO_3, adding 0.1 mL of concentrated HCl, if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in reagent water. Pour the two solutions together and dilute to 100 mL with reagent water.

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

7.4 Standard stock solutions—Stock standards may be purchased or prepared from ultra high-purity grade chemicals (99.99% to 99.999% pure). All compounds must be dried for 1 h at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards can not be verified.

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

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

From pure element,

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

From pure compound,

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

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

7.4.1 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.

7.4.2 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.

7.4.3 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.

7.4.4 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.

7.4.5 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.

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

7.5 Preparation of calibration standards—Fresh calibration standards should be prepared every 2 weeks, or as needed. Dilute each of the stock standard solutions to levels appropriate to the operating range of the instrument using the appropriate acid diluent (see note). Calibration standards should be prepared at a minimum of three concentrations, one of which must be at the ML (Table 1), and another of which must be near the upper end of the linear dynamic range. Calibration standards should be initially verified using a quality control sample (Section 7.7).

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

7.6 Blanks—The laboratory should prepare the following types of blanks. A calibration blank is used to establish the analytical calibration curve; the laboratory (method) blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background; and the rinse blank is used to flush the instrument autosampler uptake system. All diluent acids should be made from concentrated acids (Section 7.1) and reagent water (Section 7.2). In addition to these blanks, the laboratory may be required to analyze field blanks (Section 9.5.2) and equipment blanks (Section 9.5.3).

7.6.1 Calibration blank—The calibration blank consists of the appropriate acid diluent (Section 7.5 note) (HCl/HNO_3) in reagent water. The calibration blank should be stored in a FEP bottle.

7.6.2 Laboratory blank—The laboratory blank must contain all the reagents in the same volumes as used in processing the samples. The laboratory blank must be carried through the same entire preparation scheme as the samples including digestion, when applicable (Section 9.5.1).

7.6.3 The rinse blank is prepared as needed by adding 1.0 mL of concentrated HNO_3 and 1.0 mL of concentrated HCl to 1 L of reagent water.

7.7 Quality control sample (QCS)—The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards (Section 7.5 note). The concentration of the analytes in the QCS solution should be such that the resulting solution will provide an absorbance reading of approximately 0.1. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.8 Ongoing precision and recovery (OPR) sample—The OPR should be prepared in the same acid mixture as the calibration standards (Section 7.5 note) by combining method analytes at

appropriate concentrations. The OPR must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable (Section 9.6).

8.0 Sample Collection, Filtration, Preservation, and Storage

8.1 Before an aqueous sample is collected, 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 before aliquoting for processing or direct analysis to ensure the sample has been properly preserved. If properly acid-preserved, the sample can be held up to 6 months before analysis.

8.2 Sample collection—Samples are collected as described in the Sampling Method.

8.3 Sample filtration—For dissolved metals, samples and field blanks are filtered through a 0.45-µm capsule filter at the field site. Filtering procedures are described in the Sampling Method. For the determination of total recoverable elements, samples are *not* filtered but should be preserved according to the procedures in Section 8.4.

8.4 Sample preservation—Preservation of samples and field blanks for both dissolved and total recoverable elements may be performed in the field at time of collection or in the laboratory. However, to avoid the hazards of strong acids in the field and transport restrictions, to minimize the potential for sample contamination, and to expedite field operations, the sampling team may prefer to ship the samples to the laboratory within 2 weeks of collection. Samples and field blanks should be preserved at the laboratory immediately upon receipt. For all metals, preservation involves the addition of 10% HNO_3 (Section 7.1.3) to bring the sample to pH < 2. For samples received at neutral pH, approximately 5 mL of 10% HNO_3 per liter will be required.

8.4.1 Wearing clean gloves, remove the cap from the sample bottle, add the volume of reagent grade acid that will bring the pH to < 2, and recap the bottle immediately. If the bottle is full, withdraw the necessary volume using a clean pipet and then add the acid. Record the volume withdrawn and the amount of acid used.

NOTE: *Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood (Section 5.2).*

8.4.2 Store the preserved sample for a minimum of 48 h at 0–4°C to allow the acid to completely dissolve the metal(s) adsorbed on the container walls. The sample should then verified to be pH < 2 just before 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 h until verified to be pH < 2 (Section 8.1).

8.4.3 With each sample set, preserve a method blank and an OPR sample in the same way as the sample(s).

8.4.4 Store sample bottles in polyethylene bags at 0–4°C until analysis.

8.5 Samples collected to determine trivalent chromium

8.5.1 Samples to determine trivalent chromium are prepared at the field site by isolating the trivalent chromium using a iron hydroxide coprecipitation technique. These procedures are described in the Sampling Method.

8.5.2 The sampling team is also responsible for the preparation of laboratory blanks, OPRs, and MS/MSD samples for trivalent chromium as described in the Sampling Method.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 19). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared with established performance criteria to determine that results of the analysis meet the performance characteristics of the method.

9.1.1 The analyst will demonstrate 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, concentration, and cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as substituting a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in the method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in the method for the analytes of interest.

9.1.2.1 Each time a modification is made to the method, the analyst is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, 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 calibration will be affected by the change, the analyst must recalibrate the instrument according to Section 10.

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

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

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

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

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

(a) Calibration
(b) Calibration verification
(c) Initial precision and recovery (Section 9.2)
(d) Analysis of blanks
(e) Accuracy assessment

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

(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 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 (auto sampler, flow injection system, etc.)
(m) Operating conditions (background corrections, temperature program, flow rates, etc.)
(n) Detector (type, operating conditions, etc.)
(o) Mass spectra, printer tapes, and other recordings of raw data
(p) 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. The required types, procedures, and criteria for analysis of blanks are described in Section 9.5.

9.1.4 The laboratory will spike at least 10% of the samples with the metal(s) of interest to monitor method performance. This test is described in Section 9.3 of this method. 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 for spikes 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 will, on an ongoing basis, demonstrate through calibration verification and through analysis of the ongoing precision and recovery aliquot that the analytical system is in control. These procedures are described in Sections 10.7 and 9.6 of this method.

9.1.6 The laboratory shall maintain records to define the quality of data that are generated. Development of accuracy statements is described in Section 9.3.4.

9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect the trace metals of interest, the analyst shall determine the MDL for each analyte accoding to the procedure in 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Table 1, or one-third the regulatory compliance limit, whichever is greater. MDLs should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that they be redetermined.

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

9.2.2.1 Analysis of four aliquots of reagent water spiked with the metal(s) of interest at two to three times the ML (Table 1), according to the procedures in Section 12. All digestion, extraction, and concentration steps, and the containers, labware, and reagents that will be used with samples, must be used in this test.

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

9.2.2.3 For each metal, comparison of s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X for all metal(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that metal. The problem must be corrected and the test repreated (Section 9.2.2.1).

9.2.3 Linear dynamic range (LDR)—The upper limit of the LDR must be established for the wavelength used for each analyte by determining the signal responses from a minimum of six different concentration standards across the range, two of which are close to the upper limit of the LDR. Determined LDRs must be documented and kept on file. The linear calibration range that may be used for the analysis of samples should be judged

by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from the four lower standards. The LDRs should be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions dictates that they be redetermined.

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

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

9.2.4 Quality control sample (QCS)—When beginning the use of this method, on a quarterly basis or as required to meet data quality needs, the calibration standards and acceptable instrument performance must be verified with the preparation and analyses of a QCS (Section 7.7). To verify the calibration standards, the determined mean concentration from three analyses of the QCS must be within ± 10% of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the calibration standards and/or acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored, or at least one MS sample analysis and one MSD sample analysis must be performed for each sample batch (samples collected from the same site at the same time, to a maximum of 10 samples), whichever is more frequent. Blanks (e.g., field blanks) may not be used for MS/MSD analysis.

9.3.1 Determine the concentration of the MS and MSD as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of a specific metal in the sample is being checked against a regulatory concentration limit, the spike must be at that limit or at one to five times the background concentration, whichever is greater.

9.3.1.2 If the concentration is not being checked against a regulatory limit, the concentration must be at one to five times the background concentration or at one to five times the ML in Table 1, whichever is greater.

9.3.2 Assess spike recovery

9.3.2.1 Determine the background concentration (B) of each metal by analyzing one sample aliquot according to the procedure in Section 12.

9.3.2.2 If necessary, prepare a QC check sample concentrate that will produce the appropriate level (Section 9.3.1) in the sample when the concentrate is added.

9.3.2.3 Spike a second sample aliquot with the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each metal.

9.3.2.4 Calculate each percent recovery (P) as 100(A - B)/T, where T is the known true value of the spike.

9.3.3 Compare the percent recovery (P) for each metal with the corresponding QC acceptance criteria found in Table 2. If any individual P falls outside the designated range for recovery, that metal has failed the acceptance criteria.

9.3.3.1 For a metal that has failed the acceptance criteria, analyze the ongoing precision and recovery standard (Section 9.6). If the OPR is within its respective limit for the metal(s) that failed (Table 2), the analytical system is in control and the problem is attributable to the sample matrix.

9.3.3.2 For samples that exhibit matrix problems, further isolate the metal(s) from the sample matrix using dilution, chelation, extraction, concentration, hydride generation, or other means and repeat the accuracy test (Section 9.3.2).

9.3.3.3 If the recovery for the metal remains outside the acceptance criteria, the analytical result for that metal in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

9.3.4 Assess recovery for samples and maintain records.

9.3.4.1 After the analysis of five samples of a given matrix type (river water, lake water, etc.) for which the metal(s) pass the tests in Section 9.3.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (SR) for the metal(s). Express the accuracy assessment as a percent recovery interval from R - 2SR to R + 2SR for each matrix. For example, if R = 90% and SR = 10% for five analyses of river water, the accuracy interval is expressed as 70–110%.

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

9.4 Precision of MS and MSD

9.4.1 Calculate the relative percent difference (RPD) between the MS and MSD according to the equation below using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 100\frac{(|D1-D2|)}{(D1+D2)/2}$$

Where:
D1 = concentration of the analyte in the MS sample
D2 = concentration of the analyte in the MSD sample

9.4.2 The relative percent difference between the MS and the MSD must be less than 20 percent. If this criterion is not met, the analytical system is judged to be out of control. Correct the problem and reanalyze all samples in the sample batch associated with the MS/MSD that failed the RPD test.

9.5 Blanks—Blanks are analyzed to demonstrate freedom from contamination.

9.5.1 Laboratory (method) blank

9.5.1.1 Prepare a method blank with each sample batch (samples of the same matrix started through the sample preparation process (Section 12) on the same 12-hour shift, to a maximum of 10 samples). To demonstrate freedom from contamination, analyze the blank immediately after analysis of the OPR (Section 9.6).

9.5.1.2 If the metal of interest or any potentially interfering substance is found in the blank at a concentration equal to or greater than the MDL (Table 1), sample analysis must be halted, the source of the contamination determined, the samples and a new method blank prepared, and the sample batch and fresh method blank reanalyzed.

9.5.1.3 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.

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

9.5.2 Field blank

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

9.5.2.2 If the metal of interest or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater,

then results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.5.2.3 Alternatively, if a sufficient number 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.

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

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

9.5.3.1 Bottle blanks—After undergoing appropriate cleaning procedures (Section 11.4), 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 h. 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 recleaned.

9.5.3.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

9.5.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.2) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method). 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.

9.5.3.2.2 The sampler check blank must be analyzed using the procedures given in this method. If any metal of interest or any potentially interfering substance is detected in the blank,

the source of contamination/ interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

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

9.6 Ongoing precision and recovery

9.6.1 Prepare an ongoing precision and recovery sample (laboratory fortified method blank) identical to the initial precision and recovery aliquots (Section 9.2) with each sample batch (samples of the same matrix started through the sample preparation process (Section 12) on the same 12-hour shift, to a maximum of 10 samples) by spiking an aliquot of reagent water with the metal(s) of interest.

9.6.2 Analyze the OPR sample before analyzing the method blank and samples from the same batch.

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

9.6.4 For each metal, compare the concentration with the limits for ongoing recovery in Table 2. If all metals meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual recovery falls outside of the range given, the analytical processes are not being performed properly for that metal. Correct the problem, prepare the sample batch again, and repeat the ongoing precision and recovery test (Section 9.6).

9.6.5 Add results that pass the specifications in Section 9.6.4 to initial and previous ongoing data for each metal in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each metal in each matrix type by calculating 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 = 95% and SR = 5%, the accuracy is 85–105%.

9.7 The specifications contained in this method can be met if the instrument used is calibrated properly and then maintained in a calibrated state. A given instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of metals by this method.

9.8 Depending on specific program requirements, the laboratory may be required to analyze field duplicates collected to determine the precision of the sampling technique. The RPD between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate it to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

10.0 Calibration and Standardization

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

10.2 Before using this method, optimize the instrument operating conditions. The analyst should follow the instructions provided by the manufacturer while using the conditions listed in Table 3 as a guide. Of particular importance is the determination of the charring temperature limit for each analyte. This limit is the furnace temperature setting where a loss in analyte will occur before atomization. This limit should be determined by conducting char temperature profiles for each analyte and when necessary, in the matrix of question. The charring temperature selected should minimize background absorbance while providing some furnace temperature variation without loss of analyte. For routine analytical operation the charring temperature is usually set at least 100°C below this limit. The optimum conditions selected should provide the lowest reliable MDLs and be similar to those listed in Table 3. Once the optimum operating conditions are determined, they should be recorded and available for daily reference.

10.3 Before an initial calibration, determine the linear dynamic range of the analyte (Section 9.2.3) using the optimized instrument operating conditions (Section 10.2). For all determinations, allow an instrument and hollow cathode lamp warm-up period of not less than 15 minutes. If an EDL is to be used, allow 30 minutes for warm-up.

10.4 Before daily calibrating the instrument, inspect the graphite furnace, the sample uptake system, and the autosampler injector for any change in the system that would affect instrument performance. Clean the system and replace the graphite tube and/or platform when needed or daily.

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

10.6 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Section 7.6.1) and calibration standards (Section 7.5) prepared at three or more concentrations, one of which must be at the ML (Table 1), and another that must be near the upper end of the linear dynamic range.

10.6.1 Calculate the response factor (RF) for each metal in each CAL solution using the following equation and the height or area produced by the metal.

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

Where:

R_x = *height or area of the signal for the metal*
C_x = *concentration of compound injected* (µg/L)

10.6.2 For each metal, calculate the mean RF (M), the standard deviation (SD) of the RF, and the relative standard deviation (RSD) of the mean, where RSD = 100 x SD/M.

10.6.3 Linearity–If the RSD of the mean RF for any metal is less than 25% over the calibration range, an averaged RF may be used for that analyte. Otherwise, a calibration curve for that metal must be used over the calibration range.

10.7. Calibration verification—Immediately following calibration, perform an initial calibration verification. Adjustment of the instrument is performed until verification criteria are met. Only after these criteria are met may blanks and samples be analyzed.

10.7.1 Analyze the midpoint calibration standard (Section 10.6).

10.7.2 Compute the percent recovery of each metal using the average RF or the calibration curve obtained in the initial calibration.

10.7.3 For each metal, compare the recovery with the corresponding limit for calibration verification in Table 2. If all metals meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue using the response from the initial calibration. If any individual value falls outside the range given, system performance is unacceptable for that compound. Locate and correct the problem and/or prepare a new calibration check standard and repeat the test (Sections 10.7.1–10.7.3), or recalibrate the system according to Section 10.6.

10.7.4 Verify calibration following every 10 samples by analyzing the midpoint calibration standard. If the recovery does not meet the acceptance criteria specified in Table 2, analysis must be halted, the problem corrected, and the instrument recalibrated. All samples after the last acceptable calibration verification must be reanalyzed.

10.8 Analyze a calibration blank following every calibration verification to demonstrate that there is no carryover of the analytes of interest and that the analytical system is free from contamination. If the concentration of an analyte in the blank result exceeds the MDL, correct the problem, verify the calibration (Section 10.7), and repeat the analysis of the calibration blank.

11.0 Procedures for Cleaning the Apparatus

11.1 All sampling equipment, sample containers, and labware should be cleaned in a designated cleaning area that has been demonstrated to be free of trace element contaminants. Such areas may include class 100 clean rooms as described by Moody (Reference 20), labware cleaning areas as described by Patterson and Settle (Reference 6), or clean benches.

11.2 Materials, such as gloves (Section 6.9.7), storage bags (Section 6.9.10), and plastic wrap (Section 6.9.11) may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an alternate supplier must be obtained or the materials must be cleaned.

11.3 Cleaning procedures—Proper cleaning of the Apparatus is extremely important, because the Apparatus may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the container surface.

NOTE: *If laboratory, field, and equipment blanks (Section 9.5) from Apparatus cleaned with fewer cleaning steps than those detailed below show no levels of analytes above the MDL, than those cleaning steps that do not eliminate these artifacts may be omitted provided all performance criteria outlined in Section 9 are met.*

11.3.1 Bottles, labware, and sampling equipment

11.3.1.1 Fill a clean basin (Section 6.9.8) with a sufficient quantity of a 0.5% solution of liquid detergent (Section 6.7), and completely immerse each piece of ware. Allow to soak in the detergent for at least 30 minutes.

11.3.1.2 Using a pair of clean gloves (Section 6.9.7) and clean nonmetallic brushes (Section 6.9.9), thoroughly scrub down all materials with the detergent.

11.3.1.3 Place the scrubbed materials in a clean basin. Change gloves.

11.3.1.4 Thoroughly rinse the inside and outside of each piece with reagent water until there is no sign of detergent residue (e.g., until all soap bubbles disappear).

11.3.1.5 Change gloves, immerse the rinsed equipment in a hot (50–60°C) bath of concentrated reagent grade HNO_3 (Section 7.1.1) and allow to soak for at least 2 h.

11.3.1.6 After soaking, use clean gloves and tongs to remove the Apparatus and thoroughly rinse with distilled, deionized water (Section 7.2).

11.3.1.7 Change gloves and immerse the Apparatus in a hot (50–60°C) bath of 1N trace metal grade HCl (Section 7.1.8), and allow to soak for at least 48 h.

11.3.1.8 Thoroughly rinse all equipment and bottles with reagent water. Proceed to Section 11.3.2 for labware and sampling equipment. Proceed to Section 11.3.3 for sample bottles.

11.3.2 Labware and sampling equipment

11.3.2.1 After cleaning, air-dry in a class 100 clean air bench.

11.3.2.2 After drying, wrap each piece of ware/equipment in two layers of polyethylene film.

11.3.3 Fluoropolymer sample bottles—These bottles should be used if mercury is a target analyte.

11.3.3.1 After cleaning, fill sample bottles with 0.1% (v/v) ultrapure HCl (Section 7.1.11) and cap tightly. It may be necessary to use a strap wrench to ensure a tight seal.

11.3.3.2 After capping, double-bag each bottle in polyethylene zip-type bags. Store at room temperature until sample collection.

11.3.4 Bottles, labware, and sampling equipment (polyethylene or material other than fluoropolymer)

11.3.4.1 Apply the steps outlined above in Section 11.3.1.1–11.3.1.8 to all bottles, labware, and sampling equipment. Proceed to Section 11.3.4.2 for bottles or Section 11.3.4.3 for labware and sampling equipment.

11.3.4.2 After cleaning, fill each bottle with 0.1% (v/v) ultrapure HCl (Section 7.1.12). Double-bag each bottle in a polyethylene bag to prevent contamination of the surfaces with dust and dirt. Store at room temperature until sample collection.

11.3.4.3 After rinsing labware and sampling equipment, air-dry in a class 100 clean air bench. After drying, wrap each piece of ware/equipment in two layers of polyethylene film.

NOTE: *Polyethylene bottles cannot be used to collect samples that will be analyzed for mercury at trace (e.g., 0.012 µg/L) levels because of the potential of vapors diffusing through the polyethylene.*

11.3.4.4 Polyethylene bags—If polyethylene bags need to be cleaned, clean according to the following procedure:

11.3.4.4.1 Partially fill with cold, (1+1) HNO_3 (Section 7.1.2) and rinse with distilled deionized water (Section 7.2).

11.3.4.4.2 Dry by hanging upside down from a plastic line with a plastic clip.

11.3.5 Silicone tubing, fluoropolymer tubing, and other sampling apparatus—Clean any silicone, fluoropolymer, or other tubing used to collect samples by rinsing with 10% HCl (Section 7.1.9) and flushing with water from the site before sample collection.

11.3.6 Extension pole—Submerging the 2-m polyethylene extension pole (used in with the optional grab sampling device) in acid solutions as described above is impractical because of its length. If such an extension pole is used, a nonmetallic brush (Section 6.9.9) should be used to scrub the pole with reagent water and the pole wiped down with acids as described in Section 11.3.4 above. After cleaning, the pole should be wrapped in polyethylene film.

11.4 Storage—Store each piece or assembly of the Apparatus in a clean, single polyethylene zip-type bag. If shipment is required, place the bagged apparatus in a second polyethylene zip-type bag.

11.5 All cleaning solutions and acid baths should be periodically monitored for accumulation of metals that could lead to contamination. When levels of metals in the solutions become too high, the solutions and baths should be changed and the old solutions neutralized and discarded in compliance with state and federal regulations.

12.0 Procedures for Sample Preparation and Analysis

12.1 Aqueous sample preparation—dissolved analytes (except trivalent chromium)

12.1.1 To determine dissolved analytes in ground and surface waters, pipet an aliquot (≥ 20 mL) of the filtered, acid-preserved sample into a clean 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20-mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

12.2 Aqueous sample preparation—total recoverable analytes (except trivalent chromium)

NOTE: *To preclude contamination during sample digestion, it may be necessary to perform the open-beaker, total-recoverable digestion procedure described in Sections 12.2.1–12.2.6 in a fume hood that is located in a clean room. An alternate digestion procedure is provided in Section 12.2.7; however, this procedure has not undergone interlaboratory testing.*

12.2.1 To determine total recoverable analytes in ambient water samples, transfer a 100-mL (± 1 mL) aliquot from a well-mixed, acid-preserved sample to a 250-mL Griffin beaker (Section 6.9.3). If appropriate, a smaller sample volume may be used.

12.2.2 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker and place the beaker on the hot plate for digestion. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but not higher than 85°C. (See the following note.) Cover the beaker or take other necessary steps to prevent sample contamination from the fume hood environment.

NOTE: *For proper heating, adjust the temperature control of the hot plate so that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature of approximately but not higher than 85°C. (Once the beaker is covered with a watch glass, the temperature of the water will rise to approximately 95°C.)*

12.2.3 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. Do not boil. This step takes about 2 h for a 100-mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

12.2.4 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.)

12.2.5 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-mL volumetric flask or 50-mL class A stoppered graduated cylinder, make to volume with reagent water, stopper, and mix.

12.2.6 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If, after centrifuging or standing overnight, the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered to remove the solids before 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.

12.2.7 Alternate total recoverable digestion procedure

12.2.7.1 Open the preserved sample under clean conditions. Add ultrapure nitric and hydrochloric acid at the rate of 10 mL/L and 5 mL/L, respectively. Remove the cap from the original container only long enough to add each aliquot of acid. The sample container should not be filled to the lip by the addition of the acids. However, only minimal headspace is needed to avoid leakage during heating.

12.2.7.2 Tightly recap the container and shake thoroughly. Place the container in an oven preheated to 85°C. The container should be placed on an insulating piece of material such as wood rather than directly on the typical metal grating. After the samples have reached 85°C, heat for two hours. (Total time will be 2.5–3 h depending on the sample size).

Temperature can be monitored using an identical sample container with distilled water and a thermocouple to standardize heating time.

12.2.7.3 Allow the sample to cool. The sample is now ready for analysis. Remove aliquots for analysis under clean conditions.

12.3 Sample preparation for trivalent chromium

12.3.1 When the samples are received at the laboratory, shake the vial until the precipitate on the filter dissolves.

12.3.2 After the precipitate dissolves, add 4 mL of reagent water.

12.3.3 Samples are now ready for analysis according to Section 12.4.

12.4 Sample Analysis

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

12.4.2 Use an autosampler to introduce all solutions into the graphite furnace. Once the standard, sample or QC solution plus the matrix modifier is injected, the furnace controller completes furnace cycles and cleanout period as programmed. Analyte signals must be integrated and collected as peak area measurements. Background absorbances, background corrected analyte signals, and determined analyte concentrations on all solutions must be able to be displayed on a CRT for immediate review by the analyst and be available as hard copy for documentation to be kept on file. Flush the autosampler solution uptake system with the rinse blank (Section 7.6.3) between each solution injected.

12.4.3 Analyze samples in the same operational manner used in the calibration routine.

12.4.4 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9 and 10.

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

12.4.6 Determined sample analyte concentrations that are 90% or more of the upper limit of calibration must either be diluted with acidified reagent water and reanalyzed with concern for memory effects (Section 4.4.4), or determined by another approved test procedure.

12.4.7 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the MSA described in Section 12.5 is recommended.

12.4.8 Report data as directed in Section 13.

12.5 Standard Additions—If the MSA is required, the following procedure is recommended:

12.5.1 The MSA (Reference 21) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference, which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows: Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration C_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

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

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

1. The response vs amount must be linear.

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

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

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

13.0 Data Analysis and Calculations

13.1 Sample data should be reported in units of µg/L (parts-per-billion; ppb). Report results at or above the ML for metals found in samples and determined in standards. Report all results for metals found in blanks, regardless of level.

13.2 Compute the concentration of each analyte in the sample using the averaged RF determined from the calibration data (Section 10.6) according to the following equation:

$$C_x\ (\mu g/L) = \frac{R_x}{RF}$$

where the terms are defined in Section 10.6.1.

13.3 For total recoverable aqueous analytes (Sections 12.2.1–12.2.6), multiply solution analyte concentrations by the dilution factor 0.5, when 100-mL aliquot is used to produce the 50-mL final solution. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding the upper limit of the calibration curve. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

13.4 For data values less than the ML, two significant figures should be used for reporting element concentrations. For data values greater than or equal to the ML, three significant figures should be used.

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

14.0 Method Performance

14.1 The MDLs listed in Table 1 and the quality control acceptance criteria listed in Table 2 were validated in three laboratories (Reference 22) for all dissolved analytes except trivalent chromium.

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that place pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, EPA recommends recycling as the next best option. The acids used in this method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.2 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 NW, Washington DC 20036, 202/872–4477.

16.0 Waste Management

16.1 EPA 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 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 Section 15.2.

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18.0 Glossary

Many of the terms and definitions listed below are used in the EPA 1600-series methods, but terms have been cross-referenced to terms commonly used in other methods where possible.

18.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

18.2 **Analyte**—A metal tested for by the methods referenced in this method. The analytes are listed in Table 1.

18.3 **Apparatus**—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.

18.4 **Calibration Blank**—A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument (Section 7.6.1).

18.5 **Calibration Standard (CAL)**—A solution prepared from a dilute mixed standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

18.6 **Dissolved Analyte**—The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter assembly before sample acidification (Section 8.3).

18.7 **Equipment Blank**—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before shipment to the field site. An acceptable equipment blank must be achieved before the sampling devices and apparatus are used for sample collection. In addition, equipment blanks should be run on random, representative sets of gloves, storage bags, and plastic wrap for each lot to determine if these materials are free from contamination before use.

18.8 **Field Blank**—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, storage, preservation, and all analytical procedures, which may include filtration. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

18.9 **Field Duplicates (FD1 and FD2)**—Two separate samples collected in separate sample bottles at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

18.10 **Initial Precision and Recovery (IPR)**—Four aliquots of the OPR standard analyzed to establish the ability to generate acceptable precision and accuracy. IPRs are performed before the first time a method is used and any time the method or instrumentation is modified.

18.11 **Instrument Detection Limit (IDL)**—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the selected analytical wavelength.

18.12 **Laboratory Blank**—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if method analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. (Sections 7.6.2 and 9.5.1).

18.13 **Laboratory Control Sample (LCS)**—See Ongoing Precision and Recovery (OPR) Standard.

18.14 **Laboratory Duplicates (LD1 and LD2)**—Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

18.15 **Laboratory Fortified Blank (LFB)**—See Ongoing Precision and Recovery (OPR) Standard.

18.16 **Laboratory Fortified Sample Matrix (LFM)**—See Matrix Spike and Matrix Spike Duplicate.

18.17 **Laboratory Reagent Blank (LRB)**—See Laboratory Blank.

18.18 **Linear Dynamic Range (LDR)**—The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

18.19 **Matrix Modifier**—A substance added to the graphite furnace along with the sample to minimize the interference effects by selective volatilization of either analyte or matrix components.

18.20 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an 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. Their purpose is to quantify the bias and precision caused by the sample matrix. 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 9.3).

18.21 **May**—This action, activity, or procedural step is optional.

18.22 **May Not**—This action, activity, or procedural step is prohibited.

18.23 **Method Blank**—See Laboratory Blank.

18.24 **Method Detection Limit (MDL)**—The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Section 9.2.1 and Table 1).

18.25 **Minimum Level (ML)**—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 9).

18.26 **Must**—This action, activity, or procedural step is required.

18.27 **Ongoing Precision and Recovery (OPR) Standard**—A laboratory blank spiked with known quantities of the method analytes. The OPR is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and to ensure that the results produced by the laboratory remain within the method-specified limits for precision and accuracy.

18.28 **Preparation Blank**—See Laboratory Blank.

18.29 **Primary Dilution Standard**—A solution containing the analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

18.30 **Quality Control Sample (QCS)**—A sample containing all or a subset of the method analytes at known concentrations. The QCS is obtained from a source outside of the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared outside of the normal preparation process.

18.31 **Reagent Water**—Water demonstrated to be free from the method analytes and potentially interfering substances at the MDL for that metal in the method.

18.32 **Should**—This action, activity, or procedural step is suggested but not required.

18.33 **Standard Addition**—The addition of a known amount of analyte to the sample 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.

18.34 **Stock Standard Solution**—A solution containing one or more method analytes that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

18.35 **Total Recoverable Analyte**—The concentration of analyte determined by analysis of the solution extract of an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Section 12.2).

Table 1
List of Analytes Amenable to Analysis Using Method 1639: Lowest Water Quality Criterion for Each Metal Species, Method Detection Limits, and Minimum Levels

Metal	Lowest EPA Water Quality Criterion (µg/L)[1]	Method Detection Limit (MDL) and Minimum Level (ML); µg/L	
		MDL[2]	ML[3]
Antimony	14	1.9	5
Cadmium	0.37	0.023	0.05
Chromium (III)	57	0.1	0.2
Nickel	8.2	0.65	2
Selenium	5	0.83	2
Zinc	32	0.14	0.5

Notes:

1. Lowest of the freshwater, marine, or human health WQC at 40 *CFR* Part 131 (57 *FR* 60848 for human health criteria and 60 *FR* 22228 for aquatic criteria). Hardness-dependent freshwater aquatic life criteria also calculated to reflect a hardness of 25 mg/L $CaCO_3$, and all aquatic life criteria, except chronic criteria for Se, have been adjusted to reflect dissolved levels in accordance with the equations provided in 60 *FR* 22228. Hardness dependent dissolved criteria conversion factors for Cd were also calculated at a hardness of 25 mg/L per 60 *FR* 22228.

2. Method Detection Limit (MDL) as determined by 40 *CFR* Part 136, Appendix B.

3. Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc. in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

Table 2

Quality Control Acceptance Criteria for Performance Tests[1]

Method	Metal	Initial Precision and Recovery (Section 9.2) s	Initial Precision and Recovery (Section 9.2) X	Calibration Verification (Section 10.7)	Ongoing Precision and Recovery (Section 9.6)	Spike Recovery (Section 9.3)
200.9	Antimony	60	24–144	54–114	18–150	18–150
	Cadmium	11	67–142	86–123	64–145	64–145
	Chromium	26	76–129	89–116	74–131	74–131
	Nickel	36	69–141	87–123	65–145	65–145
	Selenium	31	60–128	77–111	56–131	56–131
	Zinc	19	67–142	86–123	67–142	67–142

1. All specifications expressed as percent.

TABLE 3

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

Element	Wavelength	Slit	Temperature °C[4]	
			Char	Atom
Sb[6]	217.6	0.7	1100	2000
Cd	228.8	0.7	800	1600
Cr	357.9	0.7	1650	2600[5]
Ni	232.0	0.2	1400	2500
Se[6]	196.0	2.0	1000	2000

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

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

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

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

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

6 An electrodeless discharge lamp was used for this element.