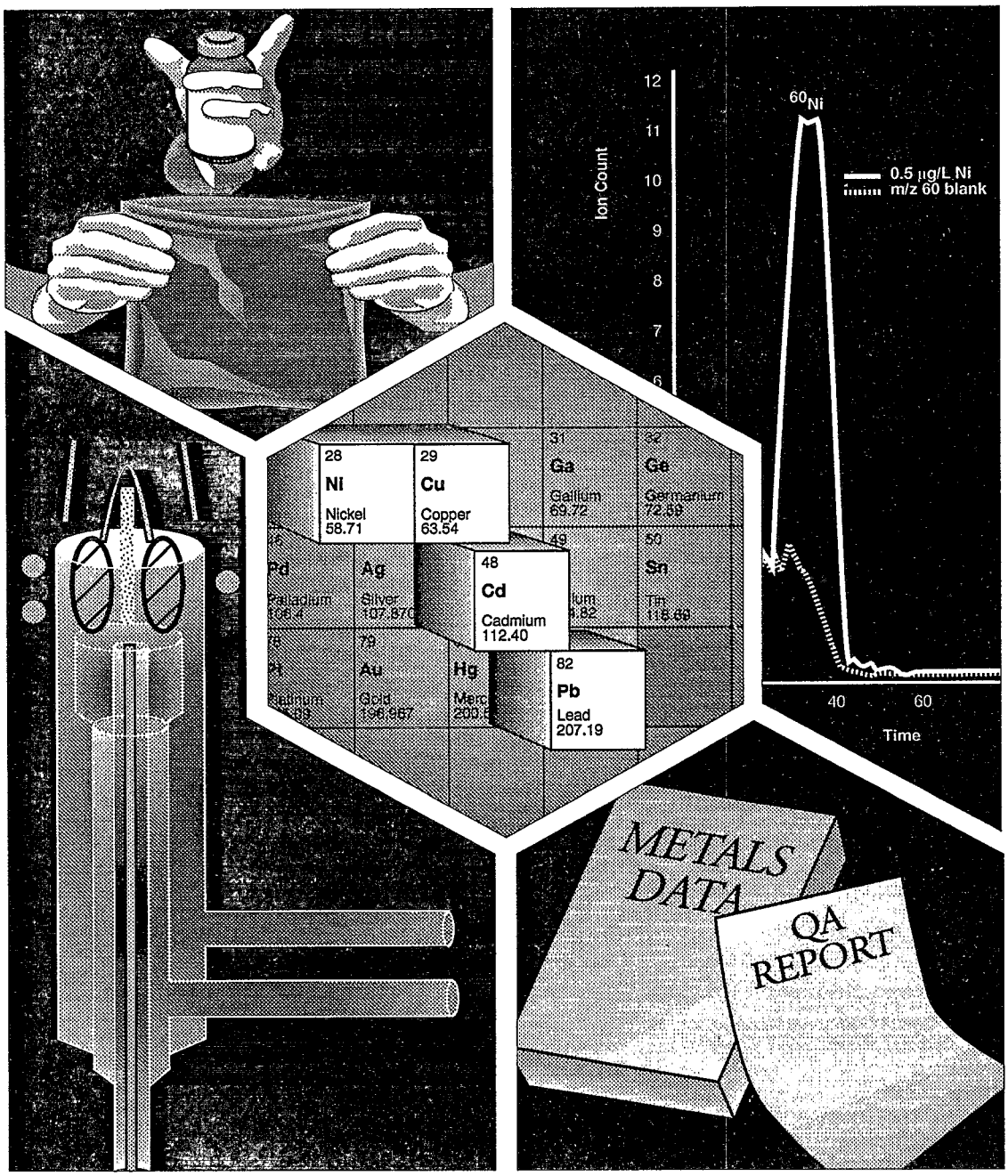
United States
Environmental Protection
Agency

Office of Water
(4303)

EPA 821-R-95-033
April 1995

EPA

Method 1640: Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry



Printed on Recycled Paper

EPA

Method 1640: Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry

Printed on Recycled Paper

Acknowledgments

Method 1640 was prepared under the direction of William A. Telliard of the U.S. Environmental Protection Agency's (EPA's) Office of Water (OW), Engineering and Analysis Division (EAD). The method was prepared under EPA Contract 68-C3-0337 by the DynCorp Environmental Programs Division with assistance from Interface, Inc.

The following researchers contributed to the philosophy behind this method. Their contribution is gratefully acknowledged:

Shier Berman, National Research Council, Ottawa, Ontario, Canada
Nicholas Bloom, Frontier Geosciences Inc, Seattle, Washington
Paul Boothe and Gary Steinmetz, Texas A&M University, College Station, Texas
Eric Crecelius, Battelle Marine Sciences Laboratory, Sequim, Washington
Russell Flegal, University of California/Santa Cruz, California
Gary Gill, Texas A&M University at Galveston, Texas
Carlton Hunt and Dion Lewis, Battelle Ocean Sciences, Duxbury, Massachusetts
Carl Watras, Wisconsin Department of Natural Resources, Boulder Junction, Wisconsin
Herb Windom and Ralph Smith, Skidaway Institute of Oceanography, Savannah, Georgia

In addition, the following personnel at the EPA Office of Research and Development's Environmental Monitoring Systems Laboratory in Cincinnati, Ohio, are gratefully acknowledged for the development of the analytical procedures described in this method:

J.T. Creed
T.D. Martin
S.E. Long (DynCorp, formerly Technology Applications, Inc.)

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.

Questions concerning this method or its application should be addressed to:

W.A. Telliard
USEPA Office of Water
Analytical Methods Staff
Mail Code 4303
401 M Street, SW
Washington, DC 20460
Phone: 202/260–7120
Fax: 202/260–7185

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 concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on 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 its 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 that can be achieved using existing EPA methods and 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). This rule includes water quality criteria for 13 metals, and it is these criteria on which the new sampling and analysis methods are based. Method 1640 was specifically developed to provide reliable measurements of four of these metals at EPA WQC levels using on-line chelation preconcentration and inductively coupled plasma-mass spectrometry 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.

Requests for additional copies should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489–8190

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 show that data quality is not affected.

Method 1640

Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry

1.0 Scope and Application

1.1 This method is for the determination of dissolved elements in ambient waters at EPA water quality criteria (WQC) levels using on-line chelation preconcentration and inductively coupled plasma-mass spectrometry (ICP-MS). It may also be used for determination of total recoverable element concentrations in these waters. This method was developed by integrating the analytical procedures contained in EPA Method 200.10 with the 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 assure 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 elements:

Analyte	***Symbol***	***Chemical Abstract Services Registry Number (CASRN)***
Cadmium	(Cd)	7440-43-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Nickel	(Ni)	7440-02-0

Table 1 lists the EPA WQC levels, the method detection limit (MDL) for each metal, and the minimum level (ML) for each metal in this method. Linear working ranges will be dependent on the instrumentation and selected operating conditions but should be essentially independent of the matrix because elimination of the matrix is a feature of the method.

1.3 This method is not intended for determination of 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 and are based on findings of researchers performing trace metals analyses (References 1–8). Additional suggestions for improvement of existing facilities may 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 because they lack an exact definition. However, the information provided in this method is consistent with the 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 and document equivalent performance.

1.8 For dissolved metal determinations, samples must be filtered through a 0.45-μm capsule filter at the field site. The Sampling Method describes the filtering procedures. 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; provides procedures for laboratory preservation are provided in this method.

1.9 Acid solubilization is required before the determination of total recoverable elements to aid breakdown of complexes or colloids that might influence trace element recoveries.

1.10 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), including the interpretation of spectral and matrix interferences and procedures for their correction; and should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of metals at EPA WQC levels. A minimum of six months' experience with commercial instrumentation is recommended.

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

2.0 Summary of Method

2.1 This method is used to preconcentrate trace elements using an iminodiacetate functionalized chelating resin (References 11–12). Following acid solubilization, the sample is buffered prior to the chelating column using an on-line system. Group I and II metals, as well as most

anions, are selectively separated from the analytes by elution with ammonium acetate at pH 5.5. The analytes are subsequently eluted into a simplified matrix consisting of dilute nitric acid and are determined by ICP-MS using a directly coupled on-line configuration.

2.2 The determinative step in this method is ICP-MS (Reference 13-15). Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge (m/z) ratio by a mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height at m/z 300. An electron multiplier or Faraday detector detects ions transmitted through the mass analyzer, and a data handling system processes the resulting current. Interferences relating to the technique (Section 4) must be recognized and corrected. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrumental drift must be corrected for by the use of internal standardization.

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 ambient water samples from becoming contaminated during the sampling and analytical process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on 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 16). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 There are numerous routes by which samples may become contaminated. 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 produced cannot be compromised by contamination of samples. Requirements and suggestions for control of sample contamination are given in this method and 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 Although 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 the Sampling Method.

4.3.2 Avoiding 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 to be free from contamination. Two of the most important factors in avoiding/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 should be performed in a class 100 clean bench or a nonmetal glove box fed by particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally, in the clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only 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 a given batch of samples is processed, 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 6.10.7) 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 determination of metals at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

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 should not contact the sample or be used to hold liquids that contact the sample, *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 17).

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 application to 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 the collection, processing, and analysis of 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, sample processing and analysis should occur as far as possible from sources of airborne contamination.

4.4 Interferences—Interference sources that may cause inaccuracies in the determination of trace elements by ICP-MS are given below and must be recognized and corrected for. Internal standards should be used to correct for instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix.

4.4.1 Isobaric elemental interferences—Are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal m/z and that cannot be resolved by the mass spectrometer. All elements determined by this method have, at a

minimum, one isotope free of isobaric elemental interferences. If an alternative isotope that has a higher natural abundance is selected to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the contribution the isotope of interest based on the relative abundance of the alternate isotope and isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the relative abundance used in the equation for data calculations. Relative abundances should be established before any corrections are applied.

4.4.2 Abundance sensitivity—Is a property defining the degree to which the wings of a mass peak contribute to adjacent m/z's. Ion energy and quadruple operating pressure affect the abundance sensitivity. Wing overlap interferences may result when a small m/z peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.4.3 Isobaric polyatomic ion interferences—Are caused by ions consisting of more than one atom which have the same nominal m/z as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Such interferences must be recognized, and when they cannot be avoided by selecting alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence because the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.4.4 Physical interferences—Are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Internal standardization may be effectively used to compensate for many physical interference effects (Reference 18). Internal standards ideally should have similar analytical behavior to the elements being determined.

4.4.5 Memory interferences—Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur depends on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.6.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated before it is analyzed. This estimation may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated

intervals. The length of time required to reduce analyte signals below the ML should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if the memory effect was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period.

4.4.6 A principal advantage of this method is the selective elimination of species giving rise to polyatomic spectral interferences on certain transition metals (e.g., removal of the chloride interference on vanadium). As most of the sample matrix is removed, matrix-induced physical interferences are also substantially reduced.

4.4.7 Low recoveries may be encountered in the preconcentration cycle if the trace elements are complexed by competing chelators in the sample or are present as colloidal material. Acid solubilization pretreatment is used to improve analyte recovery and to minimize adsorption, hydrolysis, and precipitation effects.

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 for the safe handling of the chemicals specified in this method (References 19–22). A reference file of material safety data sheets (MSDSs) 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 that the results of this monitoring be made available to the analyst. The references and bibliography at the end of Reference 22 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. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear protective clothing and safety glasses or a shield for eye protection, and observe proper mixing when working with these reagents.

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

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

5.4 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

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 should 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 Preconcentration system—System containing no metal parts in the analyte flow path, configured as shown in Figure 1.

NOTE: *An alternate preconcentration system to the one described below may be used provided that all performance criteria listed in this method can be met. If low recoveries are encountered in the preconcentration cycle for a particular analyte, it may be necessary to use an alternate preconcentration system.*

6.2.1 Column—Macroporous iminodiacetate chelating resin (Dionex Metpac CC-1 or equivalent).

6.2.2 Sample loop—10-mL loop constructed from narrow-bore, high-pressure inert tubing, Tefzel ETFE (ethylene tetra-fluoroethylene) or equivalent.

6.2.3 Eluent pumping system (P1)—Programmable-flow, high-pressure pumping system, capable of delivering either one of two eluents at a pressure up to 2000 psi and a flow rate of 1–5 mL/min.

6.2.4 Auxiliary pumps

6.2.4.1 On-line buffer pump (P2)—Piston pump (Dionex QIC pump or equivalent) for delivering 2M ammonium acetate buffer solution.

6.2.4.2 Carrier pump (P3)—Peristaltic pump (Gilson Minipuls or equivalent) for delivering 1% nitric acid carrier solution.

6.2.4.3 Sample pump (P4)—Peristaltic pump for loading sample loop.

6.2.5 Control valves—Inert, double-stack, pneumatically operated four-way slider valves with connectors.

6.2.6 Argon gas supply regulated at 80–100 psi

6.2.7 Solution reservoirs—Inert containers, e.g., high density polyethylene (HDPE), for holding eluent and carrier reagents.

6.2.8 Tubing—High pressure, narrow bore, inert tubing (e.g., Tefzel ETFE or equivalent) for interconnection of pumps and valve assemblies and a minimum length for connection of the preconcentration system to the ICP-MS instrument.

6.3 Inductively coupled plasma mass spectrometer

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

6.3.2 Radio-frequency generator compliant with FCC regulations.

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

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

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

6.3.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted before analysis.

6.4 Analytical balance—with capability to measure to 0.1 mg, for use in weighing solids and for preparing standards.

6.5 Temperature-adjustable hot plate—capable of maintaining a temperature of 95°C.

6.6 Centrifuge with guard bowl, electric timer, and brake (optional)

6.7 Drying oven—gravity convection, with thermostatic control capable of maintaining 105°C (± 5°C).

6.8 Alkaline detergent—Liquinox®, Alconox®, or equivalent.

6.9 pH meter or pH paper

6.10 Labware—For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area should be designated for handling trace element samples. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All 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.*

6.10.1 Volumetric flasks, graduated cylinders, funnels, and centrifuge tubes

6.10.2 Assorted calibrated pipets

6.10.3 Beakers—fluoropolymer (or other suitable material), 250-mL with fluoropolymer covers.

6.10.4 Storage bottles—Narrow-mouth, fluoropolymer with fluoropolymer screw closure, 125- to 250-mL capacities.

6.10.5 Wash bottle—One-piece stem fluoropolymer, with screw closure, 125-mL capacity.

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

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

6.10.8 Buckets or basins—5- to 50-L capacity, for acid soaking of the Apparatus.

6.10.9 Brushes—Nonmetallic, for scrubbing Apparatus.

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

6.10.11 Plastic wrap—Clean, colorless polyethylene for storage of Apparatus.

6.11 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 for the collection of ambient water samples. Before the equipment is shipped to the field site, the laboratory or facility must generate an acceptable equipment blank (Section 9.6.3) to demonstrate that the sampling equipment is free from contamination.

6.11.1 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.

6.11.2 Sample bottles—Fluoropolymer, 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.*

6.11.3 Filtration Apparatus

6.11.3.1 Filter—Gelman Supor 0.45-µm, 15-mm diameter capsule filter (Gelman 12175, or equivalent).

6.11.3.2 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).

6.11.3.3 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 the integrity of analytical data. Because of the high sensitivity of ICP-MS, high-purity reagents should be used. Each reagent lot should be tested for the metals of interest by diluting and analyzing an aliquot from the lot using the techniques and instrumentation to be used for analysis of samples. The lot will be acceptable if the concentration of the metal of interest is below the MDL listed in this method. All acids used for this method must be ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation.

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

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

7.1.4 Nitric acid 1.25M—Dilute 79 mL (112 g) concentrated nitric acid to 1000 mL with reagent water.

7.1.5 Nitric acid 1%—Dilute 10 mL concentrated nitric acid to 1000 mL with reagent water.

7.1.6 Hydrochloric acid—concentrated (sp gr 1.19).

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

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

7.1.9 Hydrochloric acid (HCl)—1N trace metal grade

7.1.10 Hydrochloric acid (HCl)—10% wt, trace metal grade

7.1.11 Hydrochloric acid (HCl)—1% wt, trace metal grade

7.1.12 Hydrochloric acid (HCl)—0.5% (v/v), trace metal grade

7.1.13 Hydrochloric acid (HCl)—0.1% (v/v) ultrapure grade

7.1.14 Acetic acid, glacial (sp gr 1.05)

7.1.15 Ammonium hydroxide (20%)

7.1.16 Ammonium acetate buffer 1M, pH 5.5—Add 58 mL (60.5 g) of glacial acetic acid to 600 mL of reagent water. Add 65 mL (60 g) of 20% ammonium hydroxide and mix. Check the pH of the resulting solution by withdrawing a small aliquot and testing with a calibrated pH meter, adjusting the solution to pH 5.5 (± 0.1) with small volumes of acetic acid or ammonium hydroxide as necessary. Cool and dilute to 1 L with reagent water.

7.1.17 Ammonium acetate buffer 2M, pH 5.5—Prepare as for Section 7.1.16 using 116 mL. (121 g) glacial acetic acid and 130 mL (120 g) 20% ammonium hydroxide, diluted to 1000 mL with reagent water.

NOTE: *The ammonium acetate buffer solutions may be further purified by passing them through the chelating column at a flow rate of 5.0 mL/min. With reference to Figure 1, pump the buffer solution through the column using pump P1, with valves A and B off and valve C on. Collect the purified solution in a container at the waste outlet. Then elute the collected contaminants from the column using 1.25M nitric acid for 5 min at a flow rate of 4.0 mL/min.*

7.1.18 Oxalic acid dihydrate (CASRN 6153-56-6), 0.2M—Dissolve 25.2 g reagent grade $C_2H_2O_4.2H_2O$ in 250 mL reagent water and dilute to 1000 mL with reagent water.

CAUTION: *Oxalic acid is toxic; handle with care.*

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

7.3 Standard stock solutions—May be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99–99.999% pure). All salts should be dried for 1 h at 105°C, unless otherwise specified.

CAUTION: *Many metal salts are extremely toxic if inhaled or swallowed. (Wash hands thoroughly after handling.) Stock solutions should be stored in plastic bottles.*

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

NOTE: *Some metals, particularly those that form surface oxides, require cleaning before they are weighed. This may be achieved by pickling the surface of the metal in acid. An amount over the desired weight should be pickled repeatedly, rinsed with water, dried, and weighed until the desired weight is achieved.*

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

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

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

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

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

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

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

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

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

7.4 Multielement stock standard solution—When multielement stock standards are prepared, care must be taken that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities that might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-cleaned, new FEP or HDPE bottles for storage and monitored periodically for stability. A multielement stock standard solution containing cadmium, copper, lead, and nickel (1 mL = 10 µg) may be prepared by diluting 1 mL of each single element stock in the list to 100 mL with reagent water containing 1% (v/v) nitric acid.

7.4.1 Preparation of calibration standards—Fresh multielement calibration standards should be prepared every 2 weeks or as needed. Dilute the stock multielement standard solution to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. Calibration standards should be prepared at a minimum of three 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. If the direct addition procedure is being used (Method A, Section 10.3), add internal standards

(Section 7.5) to the calibration standards and store in fluoropolymer bottles. Calibration standards should be verified initially using a quality control sample (Section 7.8).

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

NOTE: *Bismuth should not be used as an internal standard using the direct addition method (Method A, Section 10.3) because it is not efficiently concentrated on the iminodiacetate column.*

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 between samples in order to reduce memory interferences. In addition to these blanks, the laboratory may be required to analyze field blanks (Section 9.6.2) and equipment blanks (Section 9.6.3).

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

7.6.2 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 9.6.1). If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to the solution after preparation is complete.

7.6.3 Rinse blank—Consists of 1% (v/v) nitric acid in reagent water.

7.7 Tuning solution—This solution is used for instrument tuning and mass calibration before analysis (Section 10.2). The solution is prepared by mixing nickel, yttrium, indium, terbium, and lead stock solutions (Section 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 µg/L of each element. Internal standards are not added to this solution. (Depending on the sensitivity of the instrument, this solution may need to be diluted 10-fold.)

7.8 Quality control sample (QCS)—The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS, dilute an appropriate aliquot of analytes to a concentration $\leq$ 100 µg/L in 1% (v/v) nitric acid. Because of lower sensitivity, selenium may be diluted to a concentration of $<$ 500 µg/L. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards after dilution, mix, and store in a FEP bottle. The QCS should be analyzed as needed to meet data quality needs and a fresh solution should be prepared quarterly or more frequently as needed.

7.9 Ongoing precision and recovery (OPR) Sample—To an aliquot of reagent water, add aliquots of the multielement stock standard (Section 7.4) to prepare the OPR. The OPR must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable (Section 9.7). If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to this solution after preparation has been completed.

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 they are aliquotted 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 when the samples are collected 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 when they are received. 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, approx 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 precleaned 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, the sample should be acidified in a fume hood. See 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 pH should be verified as <2 immediately before an aliquot is withdrawn 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. See Section 8.1.

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

8.4.4 Sample bottles should be stored in polyethylene bags at 0–4°C until analysis.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 23). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine that results of the analysis meet the performance characteristics of the method.

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

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, preconcentration, cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in 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 the method is modified, the analyst is required to repeat the procedure in Section 9.2. If the the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDL (40 *CFR* Part 136, Appendix B) is lower than the MDL for that analyte in this method, or one-third the regulatory compliance level, whichever is higher. If the change will affect calibration, 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 to this method, including:

(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:

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

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. Section 9.6 describes the required types, procedures, and criteria for analysis of blanks.

9.1.4 The laboratory shall spike at least 10% of the samples with the metal(s) of interest to monitor method performance. Section 9.3 describes this test. 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 shall, 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 10.5 and 9.7 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 according to the procedure in 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Table 1, 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 shall perform the following operations.

9.2.2.1 Analyze four aliquots of reagent water spiked with the metal(s) of interest at 2–3 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, compute the average percent recovery (X) for the metal(s) in each aliquot and the standard deviation of the recovery (s) for each metal.

9.2.2.3 For each metal, compare s and X with the corresponding limits for 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. Correct the problem and repeat the test (Section 9.2.2.1).

9.2.3 Linear calibration ranges—Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The analyst should judge the linear calibration range that may be used for the analysis of samples from the resulting data. The upper limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper limit must be diluted and reanalyzed. The upper limits should be verified whenever, in the judgement of the

analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.4 Quality control sample (QCS)—When beginning the use of this method, quarterly or as required to meet data quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.8). To verify the calibration standards the determined mean concentration from 3 analyses of the QCS must be within ± 10% of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the calibration standards, acceptable instrument performance, or both 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 The concentration of the MS and MSD is determined 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 1–5 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 1–5 times the background concentration or at 1–5 times the ML in Table 1, whichever is greater.

9.3.2 Assessing 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 9.7). 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 can be attributed 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 Recovery for samples should be assessed and records maintained.

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 five to ten new measurements).

9.4 Precision of matrix spike and duplicate

9.4.1 Calculate the relative percent difference (RPD) between the MS and MSD per 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 matrix spike and the matrix spike duplicate must be less than 20%. If this criterion is not met, the analytical system is be judged to be out of control. In this case, correct the problem and reanalyze all samples in the sample batch associated with the MS/MSD that failed the RPD test.

9.5 Internal standards responses—The analyst is expected to monitor the responses from the internal standards throughout the sample batch being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards, or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60–125% of the original response in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of 2, add the internal standards, and reanalyze. If, after flushing, the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

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

9.6.1 Laboratory (method) blank

9.6.1.1 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). Analyze the blank immediately after the OPR is analyzed (Section 9.7) to demonstrate freedom from contamination.

9.6.1.2 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.

9.6.1.3 Alternatively, if a sufficient number of blanks (3 minimum) are analyzed to characterize the nature of a blank, the average concentration plus two standard deviations must be less than the regulatory compliance level.

9.6.1.4 If the result for a single blank remains above the 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.

9.6.2 Field blank

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

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

9.6.2.3 Alternatively, if a sufficient number of field blanks (3 minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

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

9.6.3 Equipment Blanks—Before any sampling equipment is used at a given site, 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.

9.6.3.1 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.

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

9.6.3.2.1 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.

9.6.3.2.2 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 or 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.

9.6.3.2.3 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.

9.7 Ongoing precision and recovery

9.7.1 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.

9.7.2 Analyze the OPR sample before the method blank and samples from the same batch are analyzed.

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

9.7.4 For each metal, compare the concentration to 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, reprepare the sample batch, and repeat the ongoing precision and recovery test (Section 9.7).

9.7.5 Add results that pass the specifications in Section 9.7.4 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%.

9.8 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.

9.9 Depending on specific program requirements, the laboratory may be required to analyze field duplicates collected to determine the precision of the sampling technique. The relative percent

difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate this 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 Operating conditions—Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. The analyst is responsible for verifying that the instrument configuration and operating conditions satisfy the quality control requirements in this method. Table 5 lists instrument operating conditions that may be used as a guide for analysts in determining instrument configuration and operating conditions.

10.2 Precalibration routine—The following precalibration routine should be completed before calibrating the instrument until it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.

10.2.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 min for the instrument to warm up. During this period, conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by nickel isotopes 60, 61, 62. Resolution at high mass is indicated by lead isotopes 206, 207, 208. For good performance, adjust the spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.2.2 Instrument stability must be demonstrated by running the tuning solution (Section 7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 10%.

10.3 Internal standardization—Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, a minimum of three internal standards must be used. Internal standards must be present in all samples, standards, and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank, or sample solution (Method A), or alternatively by mixing with the solution before nebulization using a second channel of the peristaltic pump and a mixing coil (Method B). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Internal standards should be added to blanks, samples, and standards in a like way so that dilution effects resulting from the addition may be disregarded.

NOTE: *Bismuth should not be used as an internal standard using the direct addition method (Method A, Section 10.3) because it is not efficiently concentrated on the iminodiacetate column.*

10.4 Calibration—Before initial calibration, set up proper instrument software routines for quantitative analysis and connect the ICP-MS instrument to the preconcentration apparatus.

The instrument must be calibrated at a minimum of three points for each analyte to be determined.

10.4.1 Inject the calibration blank (Section 7.6.1) and calibration standards A and B (Section 7.4.1) 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. The calibration solutions should be processed through the preconcentration system using the procedures described in Section 12. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

10.4.2 Compute the response factor at each concentration, as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:
C_s = *concentration of the analyte in the standard or blank solution*
C_{is} = *concentration of the internal standard in the solution*
A_s = *height or area of the response at the m/z for the analyte*
A_{is} = *height or area of the m/z for the internal standard*

10.4.3 Using the individual response factors at each concentration, compute the mean RF for each analyte.

10.4.4 Linearity—If the RF over the calibration range is constant (< 20% RSD), the RF can be assumed to be invariant and the mean RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

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

10.5.1 Analyze the mid-point calibration standard (Section 10.4).

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

10.5.3 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. In this event, locate and correct the problem and/or prepare a new calibration check standard and repeat the test (Sections 10.5.1–10.5.3), or recalibrate the system according to Section 10.4.

10.5.4 Calibration must be verified following every ten samples by analyzing the mid-point 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.

10.6 A calibration blank must be analyzed 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 10.5), 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 24), labware cleaning areas as described by Patterson and Settle (Reference 6), or clean benches.

11.2 Materials, such as gloves (Section 6.10.7), storage bags (Section 6.10.10), and plastic wrap (Section 6.10.11), 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 9.6) from the Apparatus cleaned with fewer cleaning steps than those detailed below show no levels of analytes above the MDL, those cleaning steps that do not eliminate these artifacts may be omitted if all performance criteria outlined in Section 9 are met.*

11.3.1 Bottles, labware, and sampling equipment

11.3.1.1 Fill a precleaned basin (Section 6.10.8) with a sufficient quantity of a 0.5% solution of liquid detergent (Section 6.8), and completely immerse each piece of ware. Allow to soak in the detergent for at least 30 min.

11.3.1.2 Using a pair of clean gloves (Section 6.10.7) and clean nonmetallic brushes (Section 6.10.9), thoroughly scrub down all materials with the detergent.

11.3.1.3 Place the scrubbed materials in a precleaned 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 7.1.9), and allow to soak for at least 48 h.

11.3.1.8 Thoroughly rinse all equipment and bottles with reagent water. Proceed with Section 11.3.2 for labware and sampling equipment. Proceed with 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 or 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 7.1.13) and cap tightly. It may be necessary to use a strap wrench to assure 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 in Sections 11.3.1.1–11.3.1.8 to all bottles, labware, and sampling equipment. Proceed with 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 7.1.13). 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 or 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 for vapors tp diffuse 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 7.1.10) and flushing with water from the site before sample collection.

11.3.6 Extension pole—Because of its length, it is impractical to submerse the 2-m polyethylene extension pole (used in with the optional grab sampling device) in acid solutions as described above. If such an extension pole is used, a nonmetallic brush (Section 6.10.9) should be used to scrub the pole with reagent water and the pole wiped down with acids described in Section 11.3.4. 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

12.1.1 For determination of 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). Add the internal standards, 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

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 For the determination of 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 6.10.3). If appropriate, a smaller sample volume may be used.

12.2.2 Add 2 mL (1+1) nitric 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 no higher than 85°C. (See the following note.) The beaker should be covered or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

NOTE: *For proper heating, adjust the temperature control of the hot plate 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 approximately but no higher than 85°C. (Once the beaker is covered with a watch glass, the temperature of the water will rise to approximately 95°C.)*

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 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 min. (Slight boiling may occur, but vigorous boiling must be avoided.)

12.2.5 Allow the beaker to cool. Quantitatively transfer the sample solution to a 100-mL volumetric flask, 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 acid at the rate of 10 mL/L. Remove the cap from the original container only long enough to add the aliquot of acid. The sample container should not be filled to the lip by the addition of the acid. 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 2 h. (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. Add the internal standards and mix. The sample is now ready for analysis. Remove aliquots for analysis under clean conditions.

12.3 Before first use, the preconcentration system should be thoroughly cleaned and decontaminated using 0.2M oxalic acid.

12.3.1 Place approximately 500 mL 0.2M oxalic acid in all the eluent/solution containers and fill the sample loop with 0.2M oxalic acid using the sample pump (P4) at a flow rate of 3–5 mL/min. With the preconcentration system disconnected from the ICP-MS instrument, use the pump program sequence listed in Table 3, to flush the complete system with oxalic acid. Repeat the flush sequence three times.

12.3.2 Repeat the sequence described in Section 12.3.1 using 1.25M nitric acid and again using reagent water in place of the 0.2M oxalic acid.

12.3.3 Rinse the containers thoroughly with reagent water, fill them with their designated reagents (see Figure 1), and run through the sequence in Table 3 once to prime the pump and all eluent lines with the correct reagents.

12.4 Sample Analysis

12.4.1 Initiate ICP-MS instrument operating configuration. Tune the instrument for the analytes of interest (Section 10).

12.4.2 Establish instrument software run procedures for quantitative analysis. Because the analytes are eluted from the preconcentration column in a transient manner, it is recommended that the instrument software be configured in a rapid scan/peak hopping mode. The instrument is now ready to be calibrated.

12.4.3 Reconnect the preconcentration system to the ICP-MS instrument. With valves A and B in the off position and valve C in the on position, load the sample through the sample loop to waste using pump P4 for 4 min at 4 mL/min. Switch on the carrier

pump (P3) and pump 1% nitric acid to the nebulizer of the ICP-MS instrument at a flow rate of 0.8–1.0 mL/min.

12.4.4 Switch on the buffer pump (P2), and pump 2M ammonium acetate at a flow rate of 1.0 mL/min.

12.4.5 Preconcentration of the sample may be achieved by running through an eluent pump program (P1) sequence similar to that illustrated in Table 3. The exact timing of this sequence should be modified according to the internal volume of the connecting tubing and the specific hardware configuration used.

12.4.5.1 Inject sample—With valves A, B and C on, load sample from the loop onto the column using 1M ammonium acetate for 4.5 min at 4.0 mL/min. The analytes are retained on the column, while most of the matrix is passed through to waste.

12.4.5.2 Elute analytes—Turn off valves A and B and begin eluting the analytes by pumping 1.25M nitric acid through the column at 4.0 mL/min, then turn off valve C and pump the eluted analytes into the ICP-MS instrument at 1.0 mL/min. Initiate ICP-MS software data acquisition and integrate the eluted analyte profiles.

12.4.5.3 Column Reconditioning—Turn on valve C to direct column effluent to waste, and pump 1.25M nitric acid, 1M ammonium acetate, 1.25M nitric acid and 1M ammonium acetate alternately through the column at 4.0 mL/min. During this process, the next sample can be loaded into the sample loop using the sample pump (P4).

12.4.6 Repeat the sequence described in Section 12.4.5 for each sample to be analyzed. At the end of the analytical run, leave the column filled with 1M ammonium acetate buffer until it is next used.

12.4.7 Samples having concentrations higher than the established linear dynamic range should be diluted into range with 1% HNO_3 (v/v) and reanalyzed.

13.0 Data Analysis and Calculations

13.1 Elemental equations recommended for sample data calculations are listed in Table 4. 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 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.

13.3 Compute the concentration of each analyte in the sample using the response factor determined from calibration data (Section 10.4) and the following equation:

$$C_s\ (mg/L) = \frac{A_s \times C_{is}}{A_{is} \times RF}$$

Where the terms are as defined in Section 10.4.2.

13.4 Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, because the chloride ion is a common constituent of environmental samples.

13.5 If an element has more than one monitored m/z, examination of the concentration calculated for each m/z, or the relative abundances, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary m/z's in the evaluation of the element concentration. In some cases, the secondary m/z may be less sensitive or more prone to interferences than the primary recommended m/z; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary m/z.

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

13.7 Do not perform blank subtraction on the sample results. Report results for samples and accompanying blanks.

14.0 Method Performance

14.1 The method detection limits (MDLs) listed in Table 1 and the quality control acceptance criteria listed in Table 2 were validated in two laboratories (Reference 25) for dissolved analytes.

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. Many opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option. 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 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in the Section 15.2.

17.0 References

1 Adeloju, S.B.; Bond, A.M. "Influence of Laboratory Environment on the Precision and Accuracy of Trace Element Analysis," *Anal. Chem.* **1985**, *57*, 1728.

2 Berman, S.S.; Yeats, P.A. "Sampling of Seawater for Trace Metals," *CRC Reviews in Analytical Chemistry* **1985**, *16*, 1.

3 Bloom, N.S. "Ultra-Clean Sampling, Storage, and Analytical Strategies for the Accurate Determination of Trace Metals in Natural Waters"; Presented at the 16th Annual EPA Conference on the Analysis of Pollutants in the Environment, Norfolk, VA, May 5, 1993.

4 Bruland, K.W. "Trace Elements in Seawater," *Chemical Oceanography* **1983**, *8*, 157.

5 Nriagu, J.O.; Larson, G.; Wong, H.K.T.; Azcue, J.M. "A Protocol for Minimizing Contamination in the Analysis of Trace Metals in Great Lakes Waters," *J. Great Lakes Research* **1993**, *19*, 175.

6 Patterson, C.C.; Settle, D.M. "Accuracy in Trace Analysis"; In *National Bureau of Standards Special Publication 422*; LaFleur, P.D., Ed., U.S. Government Printing Office, Washington, DC, 1976.

7 Fitzgerald, W.F.; Watras, C.J. *Science of the Total Environment* **1989**, *87/88*, 223.

8 Gill, G.A.; Fitzgerald, W.F. *Deep Sea Res.* **1985**, *32*, 287.

9 Prothro, Martha G., "Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria," EPA Memorandum to Regional Water Management and Environmental Services Division Directors, Oct. 1, 1993.

10 "Format for Method Documentation", Distributed by the EPA Environmental Monitoring Management Council, Washington, DC, Nov. 18, 1993.

11 Siraraks, A.; Kingston, H.M.; Riviello, J.M. *Anal Chem.* **1990**, *62*, 1185.

12 Heithmar, E.M., Hinners, T.A.; Rowan, J.T.; Riviello, J.M. *Anal Chem.* **1990**, *62*, 857.

13 Gray, A.L.; Date, A.R. *Analyst*, **1983**, *108*, 1033.

14 Houk, R.S. et al. *Anal Chem.* **1980**, *52*, 2283.

15 Houk, R.S. *Anal. Chem.* **1986**, *58*, 97A.

16 Windom, H.L; Byrd, J.T.; Smith, R.G., Jr.; Huan, F. "Inadequacy of NASQAN Data for Assessing Metal Trends in the Nation's Rivers," *Environ. Sci. Technol.* **1991**, *25*, 1137.

17 Zief, M.; Mitchell, J.W. "Contamination Control in Trace Metals Analysis"; In *Chemical Analysis* **1976,** Vol. 47, Chapter 6.

18 Thompson, J.J.; Houk, R.S. *Appl. Spec.* **1987**, *41*, 801.

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

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

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

22 "Proposed OSHA Safety and Health Standards, Laboratories, Occupational Safety and Health Administration," *Fed. Regist.*, July 24, 1986.

23 *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*; U.S. Environmental Protection Agency. EMSL-Cincinnati, OH, March 1979; EPA-600/4-79-019.

24 Moody, J.R. "NBS Clean Laboratories for Trace Element Analysis," *Anal. Chem.* **1982**, *54*, 1358A.

25 "Results of the Validation Study for Determination of Trace Metals at EPA Water Quality Criteria Levels," April 1995. Available from the Sample Control Center (operated by DynCorp), 300 N. Lee Street, Alexandria, VA 22314, 703/519–1140.

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 prior to 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 they are shipped 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 they are used.

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 ten replicate measurements of the calibration blank signal at the selected analytical mass(es).

18.12 **Internal Standard**—Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Sections 7.5 and 9.5).

18.13 **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 9.6.1).

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

18.15 **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.

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

18.17 **Laboratory Fortified Sample Matrix (LFM)**—See Matrix Spike (MS) and Matrix Spike Duplicate (MSD).

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

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

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 **m/z**—mass-to-charge ratio

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

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

18.24 **Method Blank**—See Laboratory Blank.

18.25 **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).

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

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

18.28 **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 assure that the results produced by the laboratory remain within the method-specified limits for precision and accuracy (Sections 7.9 and 9.7).

18.29 **Preparation Blank**—See Laboratory Blank.

18.30 **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.

18.31 **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 external to 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 external to the normal preparation process.

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

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

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).

18.36 **Tuning Solution**—A solution used to determine acceptable instrument performance before calibration and sample analyses (Section 7.7).

Table 1

List of Analytes Amenable to Analysis Using Method 1640: Lowest Water Quality Criterion for Each Metal Species, Method Detection Limits, Minimum Levels, and Recommended Analytical Masses

Metal	Lowest Ambient Water Quality Criterion (µg/L)[1]	Method Detection Limit (MDL) and Minimum Level (ML); µg/L		Recommended Analytical m/z
		MDL[2]	ML[3]	
Cadmium	0.32	0.0024	0.01	111
Copper	2.5	0.024	0.1	63
Lead	0.14	0.0081	0.02	206, 207, 208
Nickel	7.1	0.029	0.1	60

1. Lowest of the freshwater, marine, and human health WQC promulgated by EPA for 14 states at 40 *CFR* Part 131 (57 *FR* 60848), with hardness-dependent freshwater aquatic life criteria adjusted in accordance with 57 *FR* 60848 to reflect the worst case hardness of 25 mg/L $CaCO_3$ and all aquatic life criteria adjusted in accordance with the Oct. 1, 1993 Office of Water guidance to reflect dissolved metals criteria.

2. Method Detection Limit 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, 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 IN EPA METHOD 1640[1]

Metal	Initial Precision and Recovery (Section 9.2)		Calibration Verification (Section 10.5)	Ongoing Precision and Recovery (Section 9.7)	Spike Recovery (Section 9.3)
	s	X			
Cadmium	23	75–121	86–110	73–123	73–123
Copper	43	67–154	77–119	63–159	63–159
Lead	44	56–144	78–122	52–144	52–144
Nickel	27	74–128	87–115	71–130	71–130

1. **All specifications expressed as percent.**

TABLE 3: ELUENT PUMP PROGRAMMING SEQUENCE FOR PRECONCENTRATION OF TRACE ELEMENTS

Time (min)	Flow (mL/min)	Eluent	Valve A,B	Valve C
0.0	4.0	1M ammonium acetate	ON	ON
4.5	4.0	1.25M HNO_3	ON	ON
5.1	1.0	1.25M HNO_3	OFF	ON
5.5	1.0	1.25M HNO_3	OFF	OFF
7.5	4.0	1.25M HNO_3	OFF	ON
8.0	4.0	1M ammonium acetate	OFF	ON
10.0	4.0	1.25M HNO_3	OFF	ON
11.0	4.0	1M ammonium acetate	OFF	ON
12.5	0.0		OFF	ON

TABLE 4: RECOMMENDED ANALYTICAL ISOTOPES AND ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Isotope	Elemental Equation	Note
Cd	106,108,<u>111</u>,114	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(1)
Cu	<u>63</u>,65	$(1.000)(^{63}C)$	
Pb	<u>206,207,208</u>	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(2)
Ni	60	$(1.000)(^{60}C)$	

C—counts at specified m/Z.
(1)—correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
(2)—allowance for variability of lead isotopes.

NOTE: As a minimum, all isotopes listed should be monitored. Isotopes recommended for analytical determination are underlined.

TABLE 5: RECOMMENDED INSTRUMENTAL OPERATING CONDITIONS

Chromatography	
Instrument	Dionex chelation system
Preconcentration column	Dionex MetPac CC-1
ICP-MS Instrument Conditions	
Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Internal standards	Sc, Y, In, Tb
Data Acquisition	
Detector mode	Pulse counting
Mass range	45–240 amu
Dwell time	160 µs
Number of MCA channels	2048
Number of scan sweeps	250

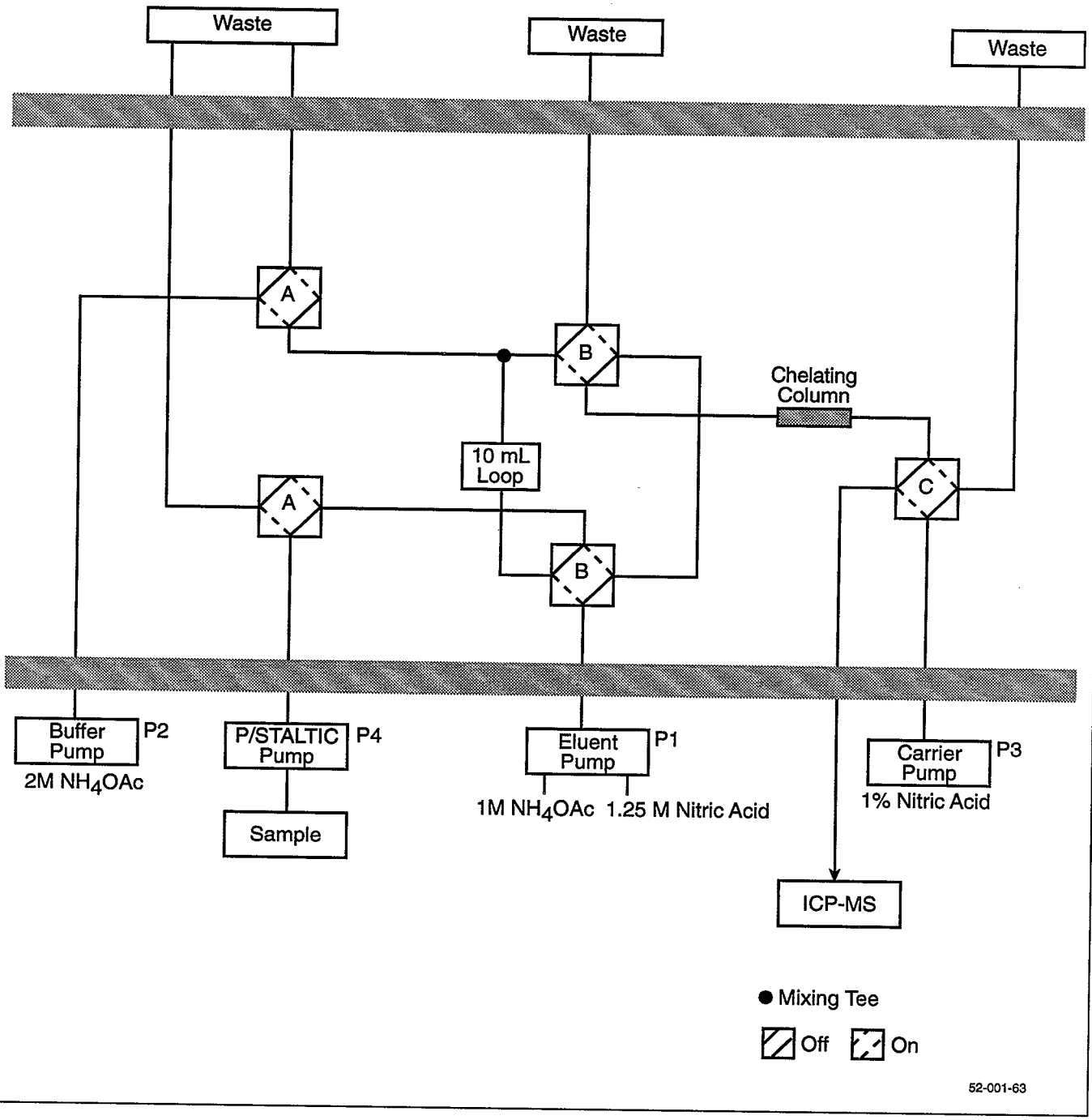



Figure 1. Configuration of Preconcentration System