

**METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY
NATIONAL WATER QUALITY LABORATORY—
DETERMINATION OF METALS IN WATER BY
INDUCTIVELY COUPLED PLASMA—MASS SPECTROMETRY**

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U.S. GEOLOGICAL SURVEY

Open-File Report 92-634



Denver, Colorado
1993

U.S. DEPARTMENT OF THE INTERIOR

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND ADDITIONAL ABBREVIATIONS

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
liter per minute (L/min)	0.265	gallon per minute
micrometer (µm)	3.3×10^{-6}	feet
milliliter (mL)	2.64×10^{-4}	gallon
milliliter per minute (mL/min)	3.38×10^{-2}	ounce per minute

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 9/5(^{\circ}\text{C}) + 32.$$

Abbreviated water-quality units used in this report:

mg/L	milligram per liter
µg/L	microgram per liter
µS/cm	microsiemens per centimeter at 25 degrees Celsius

Other abbreviations used in this report:

amu	atomic mass unit
ASTM	American Society for Testing and Materials
GFAAS	graphite furnace atomic absorption spectrometry
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma - atomic emission spectrometry
ICP-MS	inductively coupled plasma - mass spectrometry
kW	kilowatt
lb/in ²	pound per square inch
MHz	megahertz
MPV	most probable value
MPVSDV	most probable value standard deviation
m/z	mass-to-charge ratio
SDV	standard deviation
USEPA	U.S. Environmental Protection Agency

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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By LYNDA M. FAIRES

ABSTRACT

A method for the determination of dissolved concentration of 15 selected metals in water samples by inductively coupled plasma - mass spectrometry is described. Analysis requires only a few milliliters of sample solution and a few minutes of instrument time. Samples are filtered and acidified at time of collection. Specific conductance of samples is limited to less than 2,500 microsiemens per centimeter at 25 degrees Celsius or equivalent after dilution. The method reporting limits for routine analysis are 1 microgram per liter. Average short-term precision is 1.7 percent relative standard deviation for metal concentrations ranging from 25 to 50 micrograms per liter. The method may be used either as an alternative or as a supplement to existing methods for trace metal analysis in water samples.

INTRODUCTION

Dissolved concentrations of metals in water samples are commonly determined by either graphite furnace atomic absorption spectrometry (GFAAS) (Van Loon, 1985) or inductively coupled plasma - atomic emission spectrometry (ICP-AES) (Montaser and Golightly, 1987; Boumans, 1987; Thompson and Walsh, 1983). GFAAS is used to detect many metals at the microgram-per-liter or submicrogram-per-liter level, but the technique is slow, requiring a separate analysis for each element being determined. ICP-AES is a rapid multielement technique, but its detection limits are higher than GFAAS, sometimes by an order of magnitude or more. A new instrumental technique, inductively coupled plasma - mass spectrometry (ICP-MS) (Montaser and Golightly, 1987; Date and Gray, 1989), combines the low detection limits of GFAAS with the multielement speed of analysis of ICP-AES. ICP-MS is ideally suited to the determination of trace metals in water samples with low total-dissolved-solids content. Instrument detection limits are submicrogram per liter for most metals; method reporting limits

for routine analysis are set at 1 µg/L to ensure a high level of confidence in results from this method and to minimize problems with field or laboratory contamination at the submicrogram-per-liter level.

The ICP-MS technique was co-developed in laboratories in the United Kingdom and the United States in the late 1970s, and the first commercial instrument was available in 1983. Scientists soon began to publish a range of applications (Date and Gray, 1989), such as the certification of standard reference materials and the analysis of geologic and hydrologic samples. At present (1992) there are multiple manufacturers of the instrumentation and several hundred instruments being operated worldwide. The technology is accepted as a rugged and reliable tool for routine analysis and is operational in many government, academic, and commercial analytical laboratories. The U.S. Environmental Protection Agency (USEPA) is in the process of approving two independently developed methods for the analysis of water samples by ICP-MS: USEPA 6020 (Laing and others, 1992) and USEPA 200.8 (Long and Martin, 1992, p. 95-137). The American Society for Testing and Materials (ASTM) also is in the process of approving a standardized ICP-MS method for the analysis of water samples (Edward Zayhowski, U.S. Geological Survey, oral commun., 1992).

This report describes a method for determining dissolved concentrations in the range from 1.0 to 1,000 µg/L for 15 metals in filtered, acidified water samples with a specific conductance less than 2,500 µS/cm. This method is similar to both USEPA 200.8 (Long and Martin, 1992, p. 95-137) and the proposed ASTM method. The method can be used either as an alternative or as a supplement to existing methods at the U.S. Geological Survey's National Water Quality Laboratory (Fishman and Friedman, 1989):

- I-1472-87 (metals, atomic emission spectrometric, ICP),
- I-2138-87 (cadmium, atomic absorption spectrometric, graphite furnace),
- I-2243-87 (cobalt, atomic absorption spectrometric, graphite furnace),
- I-2274-87 (copper, atomic absorption spectrometric, graphite furnace),
- I-2403-87 (lead, atomic absorption spectrometric, graphite furnace),
- I-2503-87 (nickel, atomic absorption spectrometric, graphite furnace),
- I-2724-87 (silver, atomic absorption spectrometric, graphite furnace),
- I-1055-85 (antimony, atomic absorption spectrometric, hydride).

The ICP-MS method was implemented at the National Water Quality Laboratory in October 1992.

This report provides a detailed description of the method, including sampling and preservation, analysis, quality control, calculation, and reporting of results. Precision and accuracy data based on the analysis of standard reference materials, calculated instrument and method detection limits, method reporting limits, and comparison data based on the analysis of unspiked and spiked surface-water and ground-water samples by both ICP-

AES and ICP-MS are presented for 15 metals. The data in this report apply only to dissolved concentrations of 15 selected metals in filtered, acidified water samples. Subsequent reports may provide supporting data for the analysis of digested whole-water samples, digested tissue samples, or the determination of additional metals by the same analytical protocol.

ANALYTICAL METHOD

Parameters and Codes: Metals, dissolved, I-2477-92

[Lab, laboratory; WATSTORE, Water Data Storage and Retrieval System;
CAS, Chemical Abstract Services]

Parameter	Lab code	WATSTORE code	Method code	CAS registry number
Aluminum ($\mu\text{g/L}$ as Al)	1784	01106	G	7429-90-5
Antimony ($\mu\text{g/L}$ as Sb)	1785	01095	G	7440-36-0
Barium ($\mu\text{g/L}$ as Ba)	1786	01005	G	7440-39-3
Beryllium ($\mu\text{g/L}$ as Be)	1787	01010	G	7440-41-7
Cadmium ($\mu\text{g/L}$ as Cd)	1788	01025	G	7440-43-9
Chromium ($\mu\text{g/L}$ as Cr)	1789	01030	G	7440-47-3
Cobalt ($\mu\text{g/L}$ as Co)	1890	01035	G	7440-48-4
Copper ($\mu\text{g/L}$ as Cu)	1791	01040	G	7440-50-8
Lead ($\mu\text{g/L}$ as Pb)	1792	01049	G	7439-92-1
Manganese ($\mu\text{g/L}$ as Mn)	1793	01056	G	7439-96-5
Molybdenum ($\mu\text{g/L}$ as Mo)	1794	01060	G	7439-98-7
Nickel ($\mu\text{g/L}$ as Ni)	1795	01065	G	7440-02-0
Silver ($\mu\text{g/L}$ as Ag)	1796	01075	G	7440-22-4
Uranium ($\mu\text{g/L}$ as U)	1797	22703	G	7440-61-1
Zinc ($\mu\text{g/L}$ as Zn)	1798	01090	G	7440-66-6

1. Scope and application

This method is suitable for the single-element or multielement determination of dissolved concentrations of 15 selected trace metals (see table 1) in water. The method is applicable to surface-water, ground-water, drinking-water, and precipitation samples that have a measured specific conductance of less than 2,500 $\mu\text{S/cm}$ at 25°C. The method is applicable to metals in the concentration range from 1.0 to 1,000 $\mu\text{g/L}$. The use of new or upgraded instrumentation with an "extended dynamic range" option can extend the upper concentration limit to 200 mg/L. Also samples with a specific conductance greater than the specified limit may be analyzed after appropriate dilution to conform to the specified limit; however, method reporting limits for the original sample will be increased according to the dilution factor.

Table 1.--Metals, masses, detection and reporting limits

[amu, atomic mass unit; IDL, instrument detection limit;
MDL, method detection limit; MRL, method reporting limit]

Metal	Recommended masses (amu)	Limits measured in micrograms per liter		
		IDL	MDL	MRL
Ag silver	107, 109	0.03	0.07	1
Al aluminum	27	.12	1.18	1
Ba barium	137, 138	.10	.12	1
Be beryllium	9	.13	.07	1
Cd cadmium	111, 114	.17	.16	1
Co cobalt	59	.03	.07	1
Cr chromium	52	.11	.16	1
Cu copper	63, 65	.09	.10	1
Mn manganese	55	.06	.18	1
Mo molybdenum	95, 98	.06	.22	1
Ni nickel	60	.15	.19	1
Pb lead	206, 207, 208	.05	.18	1
Sb antimony	121, 123	.02	.26	1
U uranium	238	.01	.16	1
Zn zinc	64, 66	.12	.22	1

2. Summary of method

2.1 A generalized block diagram of an ICP-MS instrument is shown in figure 1.

2.2 Sample solution is pumped by a peristaltic pump into a pneumatic nebulizer (NEB in fig. 1) which generates a liquid aerosol. This aerosol is transported by argon gas flow into a water-cooled spray chamber where the large droplets are removed by gravity and condensation. The small droplets are further swept into a radiofrequency inductively coupled plasma (ICP) where evaporation, molecular dissociation, atomization, and ionization occur. The ions are physically extracted from the center of the plasma by a differentially pumped vacuum system, through a water-cooled sampler cone (SM in fig. 1) and skimmer cone (SK in fig. 1) assembly, which is in physical contact with the horizontally mounted ICP.

2.3 The extracted ions are focused by an electrostatic ion lens (IL in fig. 1) assembly and accelerated into a unit-resolution quadrupole mass spectrometer (QUAD in fig. 1). For a given combination of radiofrequency and direct current voltages applied to the quadrupoles, only ions of a specific

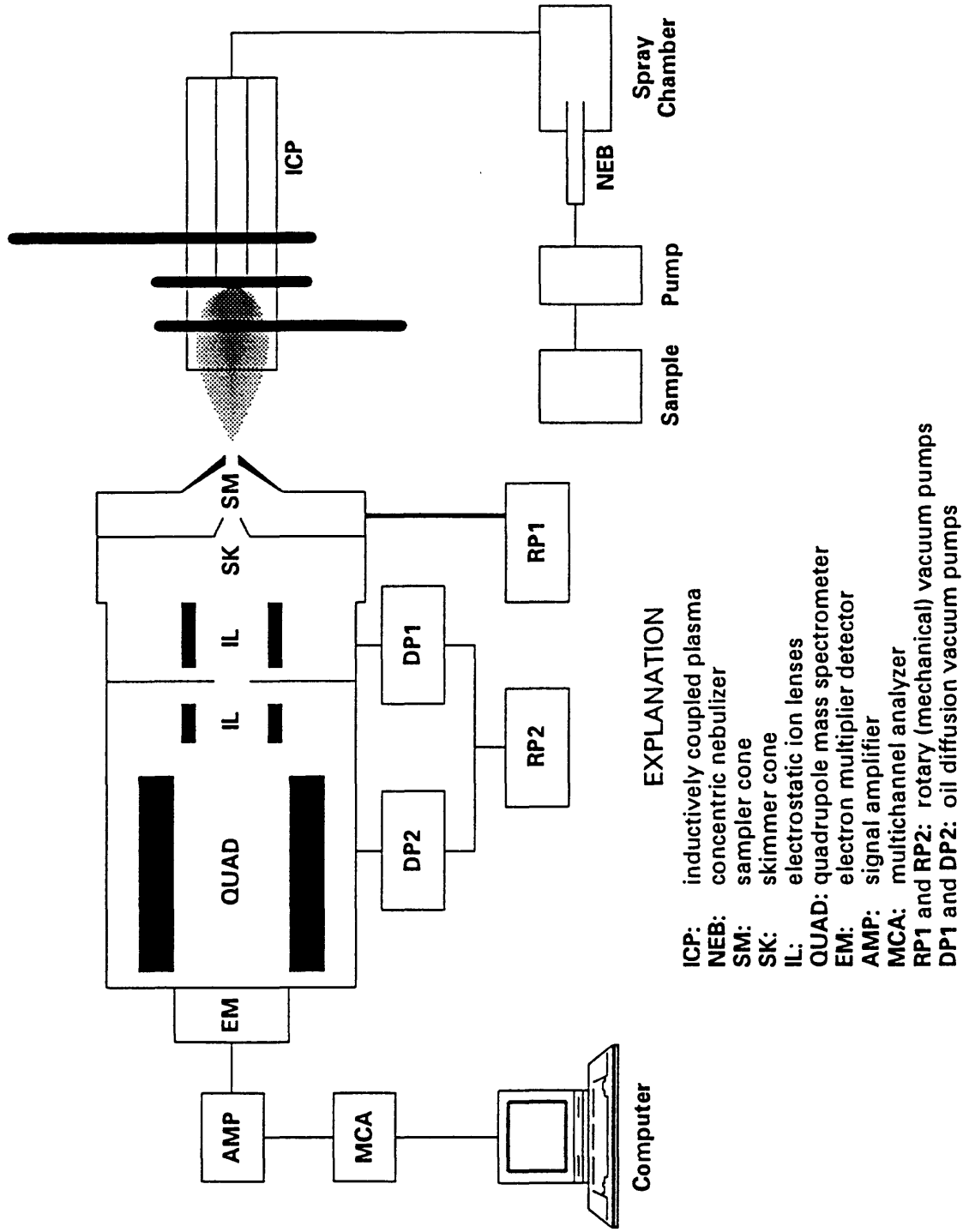


Figure 1.--Block diagram of inductively coupled plasma - mass spectrometer.

mass-to-charge ratio (m/z) pass through the quadrupoles and reach the detector. Rapidly scanning the voltages on the quadrupoles has the effect of rapidly scanning the mass spectrum at the detector. Selected mass values, where high ion signals are expected, can be pre-programmed to be skipped in the mass scan to avoid overload damage to the detector. The mass spectrometer alternatively can be operated in a peak-jumping mode, which rapidly changes the applied voltages to effectively jump to pre-selected masses instead of operating in the continuous mass-scanning mode already described. Mass-scanning is suggested in this method because the recorded spectrum can be recalled and qualitatively examined for the presence or absence of any analytes or potential interferences.

2.4 The ion signal is detected by a continuous dynode electron multiplier (EM in fig. 1) of the channeltron type. The physical impact of an ion on the detector surface produces a pulse of electrons. The resulting signal is processed in a digital, pulse-counting mode. New or upgraded instrumentation with an "extended dynamic range" option allows operation of the detector in an analog mode for high analyte concentrations. In either case, the ion signal is electronically amplified, and the resulting data are processed by a multichannel analyzer (MCA in fig. 1), or alternative data system, and computer.

2.5 Quantitative analysis is calibrated by generating a calibration curve using a calibration blank and multielement standard solutions of known concentrations. Internal standard spikes are added to all blanks, calibration standards, samples, and quality-control samples to correct for instrumental drift and suppression or enhancement of analyte signals because of matrix effects.

2.6 An "analysis procedure" is defined as a set of computer files, manual and automated operations, and calculations relating to a corresponding set of analytical solutions consisting of a calibration blank, calibration standards, samples, and quality-control samples.

3. Interferences

3.1 Several types of physical, chemical, or spectral interferences are recognized and documented for ICP-MS techniques (Date and Gray, 1989).

3.2 Isobaric elemental interferences are spectral overlaps caused when two or more isotopes of different elements form ions which have the same nominal mass-to-charge ratio. The analytes in this method all have at least one isotope that can be used for quantitative analysis which is free of potential isobaric elemental interference.

3.3 Isobaric polyatomic interferences are spectral overlaps caused when polyatomic ions formed by combinations of plasma gas, atmospheric gases, sample solvent, sample acid, or sample matrix constituents have the same nominal mass-to-charge ratio as the analyte isotope ion. These potential interferences have been systematically documented and tabulated (Tan and Horlick, 1986).

3.3.1 In the development of this method, isobaric spectral interferences occurred for copper in some samples containing sodium and for zinc in some samples containing sulfate. Copper analysis can be interfered by the formation of NaAr^+ at m/z 63, and zinc analysis can be interfered by the formation of SO_2^+ at m/z 64. These interferences were observed to be erratic and unpredictable with the parameters and instrumentation used in the development of this method, requiring the precautions described in Section 3.3.2.

3.3.2 In order to recognize isobaric spectral interferences, independently monitor two isotopes of each analyte, whenever possible, during quantitative analysis. If the calculated analytical results for each isotope of a given analyte agree within the acceptable method precision limits, then spectral interferences are not indicated. However, if the calculated analytical results for each isotope of a given analyte differ beyond the acceptable method precision limits, then spectral interferences are indicated for that analyte. In this case, the results for that analyte are not reported, and it needs to be reanalyzed or determined by an alternative approved method.

3.4 Physical interferences are associated with the physical processes of sample transport to the plasma, evaporation, dissociation, and ionization in the plasma, extraction of the ions from the plasma, and transmission of the ions through the mass spectrometer. Physical interferences cause the instrument response to be different, either suppressed or enhanced, for samples than for standard solutions, causing erroneous analytical results. High levels of dissolved salts can particularly cause physical interferences by affecting the sample transport or clogging the small orifice to the mass spectrometer.

3.4.1 In order to minimize physical interferences, the specific conductance of samples is limited to 2,500 $\mu\text{S}/\text{cm}$ or equivalent dilution prior to analysis. The use of internal standards compensates for minor physical interferences and also provides a means of detecting major physical interferences. The integrated counts (or calculated concentrations) for each sample replicate need to be printed and monitored during the analysis procedure. Changes in the integrated counts for the internal standards in excess of ± 30 percent (or changes in the calculated concentrations in excess

of acceptable method precision) alert the operator to the likely occurrence of physical interferences. Suspect samples need to be diluted and reanalyzed or analyzed by an alternative approved method.

3.5 Memory interferences result when constituents of a prior sample contribute to the measured signal of the current sample. These interferences are caused by sample deposition and subsequent release from the sample tubing, nebulizer, spray chamber, plasma torch, or sampler or skimmer cones.

3.5.1 Memory interferences are minimized by limiting the specific conductance of individual samples and by sufficient flushing of the system between samples with rinse blank. Memory interferences are suspected if the sequential replicate integrated counts (or calculated concentrations) for a given isotope in a sample decrease consecutively while the other isotopes for the sample vary only within acceptable method precision limits. In that case the concentration of that analyte in the previous sample needs to be checked to determine if it was high. If so, the system needs to be thoroughly flushed and the affected sample reanalyzed.

4. Instrumentation and equipment

The instrumentation and equipment needed for this method are listed as follows. Specific brands and models used during the development of this method along with typical operating parameters, where applicable, used to obtain the data in this report, are listed in table 2. Equivalent instrumentation and equipment, demonstrating equivalent or superior performance, may be substituted.

4.1 *Inductively coupled plasma-mass spectrometry system.*

4.1.1 Capable of scanning the mass range from 1 to 280 amu.

4.1.2 Minimum resolution capability of 1 amu peak width at 5 percent of maximum peak height.

4.1.3 Capable of skipping preselected amu values during scan or with "extended dynamic range" option.

4.1.4 Digital pulse-counting detection system or "extended dynamic range" option.

4.1.5 Radio-frequency generator--27.1 or 40 MHz, minimum power 1.5 kW.

4.1.6 Mass flow controller on nebulizer gas supply.

Table 2.--*Typical instrument operating parameters*

Parameter	Unit, value, or instrument manufacturer
Inductively coupled plasma - mass spectrometer	Fisons/VG Instruments, UK, model PlasmaQuad PQ-1
Radiofrequency generator	Henry, 1.25 kilowatts
Inductively coupled plasma torch	Fassel type, quartz
Inductively coupled plasma spray chamber	Scott type, water cooled at 5°C by Neslab RBC-3
Inductively coupled plasma nebulizer	Meinhard type, concentric
Coolant flow rate	13 liters per minute argon
Auxiliary flow rate	0.6 liter per minute argon
Nebulizer flow rate	0.7 liter per minute argon
Solution uptake rate	0.7 milliliter per minute
Peristaltic pump	Ismatec
Vacuum water chiller temperature	15°C
Detector mode	Channeltron type, pulse-counting
Replicate integrations	3
Mass range	5-240 atomic mass units
Multichannel analyzer	2,048 channels
Dwell time	320 microseconds
Scans per integration	100
Time per integration	1 minute
Sample uptake time	2 minutes
Rinse time	1 minute
Data acquisition time	3 minutes
Total sample cycle time	6 minutes
Data processing system	Compaq Deskpro 386/20
Printer	Epson FX-86e

4.1.7 ICP glassware--Nebulizer, water-cooled spray chamber, quartz plasma torch.

4.2 *Instrument control and data processing system.*

4.2.1 Capable of acquiring and storing data during analytical procedure, performing calculations, storing, displaying, and printing acquired spectra, printing real-time integrations of sample counts or real-time calculated concentrations, and printing calculated results.

4.2.2 Data transfer system for archiving data.

4.2.3 On-line printer.

4.3 *Peristaltic pump*: Capable of pumping aqueous solutions at adjustable rates ranging from 0.2 to 2.0 mL/min; minimum of four channels.

4.4 *Argon gas regulator*: Capable of delivery of high-purity (99.99 percent) grade argon at variable rates from 0 to 25 L/min with constant back pressure of 80 lb/in².

4.5 *Autosampler*: Capable of holding 10-mL sample tubes, with continuously flushing sample probe rinse.

4.6 *Labware*: For trace metal analysis, particular attention is necessary to avoid contamination or loss of analytes, both in the field and in the laboratory. Sample bottles, sample tubes, pipette tips, volumetric ware, and storage ware need to be Teflon, polytetrafluoroethylene, fluorinated ethylene propylene, high density polyethylene, or similar materials. These items need to be acid-cleaned using ASTM Type I water and ultrapure grade nitric acid prior to use.

4.7 *Operating parameters*: Refer to the manufacturers' operating manuals for installation, performance testing, tuning procedures, optimization, and routine maintenance of all instrumentation and equipment used by this method; operating parameters will be specific to a given model and make of instrumentation. The parameters found to be optimum for the equipment used in the development of this method are listed in table 2.

5. Materials, reagents, and standards

5.1 For trace metal analysis, high-purity or ultrapure-grade reagents need to be used. All acids for sample preservation or solution preparation need to be ultrapure grade; nitric acid (HNO₃) is the acid of choice, whenever possible, to minimize isobaric polyatomic spectral interferences and to matrix-match standards and samples.

5.2 *Argon gas supply* (99.99-percent purity).

5.3 *Water*, ASTM Type I reagent water (American Society for Testing and Materials, 1992) or equivalent deionized water.

5.4 *Nitric acid* (HNO₃), concentrated, specific gravity 1.41.

5.5 *Nitric acid, 2 percent (volume/volume)*: Dilute 20 mL of concentrated nitric acid to 1,000 mL with ASTM Type I reagent water. Use for rinse blank and calibration blank.

5.6 *Calibration standard and internal standard Stock I solutions*: Commercially prepared and certified single-element or multielement Stock I solutions may be used, or they may be prepared from high-purity chemicals and metals according to approved U.S. Geological Survey methods (Fishman and Friedman, 1989) such as those listed in table 3, approved USEPA methods (Long and Martin, 1992), or approved ASTM methods (American Society for Testing and Materials, 1992). A convenient concentration for Stock I solutions is 1,000 mg/L in 5-percent (volume/volume) nitric acid. These Stock I solutions are stable at room temperature for extended periods (up to 1 year). Stock I solutions need to be analyzed for possible contamination prior to further use.

NOTE: Chemicals combined in any multielement solutions must be chemically compatible and stable.

5.7 *Calibration standard and internal standard Stock II solutions*: Commercially prepared and certified single-element or multielement Stock II solutions may be used, or they may be prepared by dilution from Stock I solutions. A convenient concentration for Stock II solutions is 10 mg/L in 5-percent (volume/volume) nitric acid. Stock II solutions are stable at room temperature for extended periods (up to 1 year).

5.7.1 *Calibration standards*: Single-element or multielement calibration standards of the desired concentrations need to be prepared fresh at the start of each analytical procedure by diluting Stock II solutions to the appropriate concentrations using 2-percent (volume/volume) nitric acid. Single-point calibration can be used, but multipoint calibration is suggested, with concentrations of the standards distributed over the anticipated range of analyte concentrations.

5.7.2 *Internal standards*: Internal standards are added in equal concentrations to all blanks, standards, and samples in an analysis procedure. This may be done by manually spiking each solution with an aliquot of the internal standard Stock II solution or by using a second channel of the peristaltic pump for continuous on-line addition. A convenient resultant concentration for the internal standard spike in the sample solution is 100 µg/L of each internal standard used. Indium may be used as a single internal standard, but the use of three or more internal standards, distributed across the mass range, is suggested. Commonly used internal standards include scandium, yttrium, indium, terbium, and bismuth. Any element may be used as an internal standard if it is similar in mass and chemical behavior to the analyte element and if it is not already present in the sample.

5.8 *Tuning solution*: A multielement solution, distributed across the mass range, in 2-percent (volume/volume) nitric acid is used for daily instrument tuning, mass calibration, resolution, and sensitivity checks. Commonly used elements are beryllium, magnesium, cobalt, indium, and lead. A convenient concentration of the tuning solution is 100 µg/L of each element. Prepare this solution by dilution from Stock I or Stock II solutions. Tuning solution is stable at room temperature for extended periods (up to 1 year).

6. Sample collection and preparation

Filter surface- or ground-water samples collected for the determination of dissolved concentrations of metals through a 0.45-µm filter and acidify to pH less than 2.0 with ultrapure-grade nitric acid as soon after collection as possible. Samples are then stable for moderate periods (up to 6 months) without refrigeration, although extreme temperatures need to be avoided. To avoid contamination, collect and store samples in previously acid-rinsed Teflon, polytetrafluoroethylene, fluorinated ethylene propylene, high density polyethylene, or similar containers, following appropriate field protocols for clean sampling at the microgram-per-liter level.

7. Instrument performance

7.1 *Analytical productivity*: According to the typical operating parameters used in the development of this method (table 2), each sample requires 6 minutes for a complete sample analysis cycle (uptake, three replicate integrations, rinse). A typical analysis procedure of 38 solutions could include 1 blank, 3 calibration standards, 4 quality-control samples, and 30 samples. This setup would require a total analysis time of 3 hours, 48 minutes. On the basis of an 8-hour working day for the analyst, approximately 50 to 60 samples per day can be analyzed using the typical parameters listed in table 2. Productivity can be increased by (a) reducing the scanning time for each integration, (b) reducing the number of replicate integrations for each sample, or (c) increasing the number of samples within each analysis procedure (each calibration). Some loss of accuracy and precision, compared to the data presented in this report, will result from such changes in the operating parameters.

7.2 *Instrument performance evaluation*: Evaluate and optimize instrument performance each day for sensitivity, resolution, and mass calibration using the tuning solution (Section 5.8). Instructions for instrument performance evaluation are given in Procedure (Section 8.2). After tuning, instrument sensitivity needs to be at least 100,000 counts/sec for 100 µg/L solution of indium; instrument resolution needs to be at least 0.75 amu at 5-percent peak height; and mass calibration needs to be within 0.1 amu to proceed with analysis. If the software allows, determine the instrument stability during the course of an analysis procedure by monitoring the integration counts of the internal standards, which need to remain within ±30 percent of their starting values to proceed with analysis.

Table 3.--*Preparation of Stock I solutions*

[°C, degree Celsius; mg/L, milligram per liter; g, gram; mL, milliliter;
ASTM, American Society for Testing and Materials]

Obtain ultrahigh-purity grade chemicals or metals from reputable commercial sources. Dry all salts for 1 hour at 105°C and cool in a desiccator, unless otherwise specified. All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1992). Prepare Stock I solutions with concentrations of 1,000 mg/L from the following directions.

Aluminum: Dissolve 1.000 g aluminum metal in 100 mL concentrated HCl and 20 mL concentrated HNO₃. Heat to increase rate of dissolution. Continue heating until volume is reduced to 40 mL. Cool and add 40 mL water. Heat until volume is reduced to 20 mL. Cool and dilute to 1,000 mL with water.

Antimony: Dissolve 1.000 g antimony powder in 20 mL (1+1) nitric acid and 5 mL concentrated HCl. Heat to increase rate of dissolution. Cool, add 200 mL water and 1.5 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 1,000 mL with water.

Barium: Dissolve 1.512 g BaCl₂, dried at 180°C for 1 hour, in a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, slowly add 100 mL concentrated HNO₃ with stirring. After the BaCl₂ has dissolved, dilute to 1,000 mL with water.

Beryllium: Wash 1.000 g beryllium flakes into a 1,000-mL volumetric flask with a minimum amount of water. Use a well-ventilated hood. Heat to increase rate of dissolution. Add 90 mL concentrated HNO₃ and 10 mL HCl. Cool and dilute to 1,000 mL with water.

Cadmium: Wash 1.000 g cadmium spatters into a 1,000-mL volumetric flask with a minimum amount of water. Add 50 mL concentrated HCl and stir. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

Chromium: Wash 1.000 g chromium metal into a 1,000-mL volumetric flask with a minimum amount of water. Add 50 mL concentrated HCl and stir. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

Cobalt: Wash 1.000 g cobalt powder into a 1,000-mL volumetric flask with a minimum amount of water. Add 100 mL concentrated HNO₃. Place in an ultrasonic bath to increase rate of dissolution. Dilute to 1,000 mL with water.

Table 3.--Preparation of Stock I solutions--Continued

Copper: Wash 1.000 g copper powder into a 1,000-mL volumetric flask with a minimum amount of water. Slowly add 100 mL concentrated HNO₃ with stirring. If necessary, heat to increase rate of dissolution. Dilute to 1,000 mL with water.

Lead: Wash 1.000 g lead powder into a 1,000-mL volumetric flask with a minimum amount of water. Place flask in an ultrasonic bath in a well-ventilated hood and add 15 mL concentrated HCl. Periodically add 1-mL increments of concentrated HNO₃ for a total volume of 85 mL. Dilute to 1,000 mL with water.

Manganese: Wash 1.000 g manganese flakes into a 1,000-mL volumetric flask with a minimum amount of water. In a well-ventilated hood, slowly add 100 mL concentrated HNO₃. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

Molybdenum: Wash 1.000 g molybdenum powder into a 1,000-mL volumetric flask with a minimum amount of water. In a well-ventilated hood, while stirring, slowly add 10 mL concentrated HNO₃. After fumes dissipate, add an additional 90 mL of concentrated HNO₃ and 20 mL water. Heat to increase rate of dissolution. If solution turns cloudy and a precipitate appears, increase heat and stir for an additional 15 to 30 minutes. Cool and dilute to 1,000 mL with water.

Nickel: Wash 1.000 g nickel powder into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, while stirring, slowly add 100 mL concentrated HNO₃. Heat and stir for 30 minutes or until dissolution is complete. Cool and dilute to 1,000 mL with water.

Silver: Wash 1.000 g silver powder into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, while stirring, slowly add 100 mL concentrated HNO₃. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water. Store in an opaque bottle.

Uranium: Dissolve 2.110 g UO₂(NO₃)₂•6H₂O (do not dry) in 200 mL water and dilute to 1,000 mL with water.

Zinc: Wash 1.000 g zinc powder into a 1,000-mL volumetric flask containing 200 mL water. While stirring, slowly add 100 mL concentrated HNO₃. Dilute to 1,000 mL with water.

8. Procedure

8.1 Begin operating the instrument and data system. Allow at least 30 minutes for instrument warm-up and stabilization prior to starting analysis.

8.2 Check the instrument performance to meet the specifications in Section 7.2. Using the tuning solution, tune the ion lenses for maximum sensitivity of the indium 115 peak. Obtain a survey scan of the tuning solution and check the resolution and mass calibration at low-, middle-, and high-mass values; adjust if necessary.

8.3 Set up the appropriate software routines to perform the analysis procedure.

8.4 Prepare blanks, standards, and samples for analysis by pipetting aliquots into tubes for the autosampler rack. If the internal standard is added manually by spiking, then the sample aliquots need to be pipetted to an exact volume. A convenient volume for analysis is 10 mL, but smaller volumes can be analyzed by the use of appropriate tubes and racks. Internal standards are added, either manually or on-line, in equal concentration to all blanks, standards, and samples; the exact concentration need not be known as long as it is consistent in all solutions within a given analysis procedure.

8.5 Calibrate for the analysis procedure by using a calibration blank and one or more single-element or multielement standard solutions at one or more concentration levels for each metal. The first sample in the analytical procedure needs to be a quality-control sample to verify the calibration.

8.6 Analyze the samples. Allow sufficient uptake time for each sample prior to data acquisition for sample transport and signal stabilization. Obtain replicate integrations for each sample. Allow sufficient time to flush the system with rinse blank between samples.

8.7 Verify the on-going operation of the analytical system by inserting quality-control samples after the calibration standards, after every 10 samples or fewer, and at the end of the analysis procedure. The measured concentrations for the quality-control samples need to be within acceptable limits of the expected concentrations to verify the analysis of each subset of samples between two quality-control samples. Reanalyze samples not bracketed by acceptable quality-control samples.

8.8 Print the integrated counts (or calculated concentrations) for each sample replicate during the course of the analysis procedure. The analyst needs to review these values for any abnormalities that indicate interferences (see Sections 3.3.2, 3.4.1, 3.5.1).

9. Calculations

9.1 Obtain replicate integrations for each blank, standard, and sample.

9.2 Specify standards and sample to be blank-subtracted in the setup of the analytical procedure.

9.3 Request full statistics so that results are calculated independently for each isotope specified in the analysis procedure.

9.4 Calibration and calculations are performed by the instrument data system. Integrated counts for analyte isotopes are compared to the appropriate internal standards during the calculation of the results.

9.5 If dilutions were made, apply the appropriate multiplication factors to the sample results and to the method reporting limits for that sample.

9.6 Review the results to determine if the independently calculated values for two isotopes of the same analyte in the same sample are within the acceptable method precision. If so, then report the abundance-weighted average of the two isotope results. If not, the result is not acceptable, and the sample will need to be reanalyzed or analyzed by an alternative approved method for that metal.

10. Reporting of results

Report dissolved concentrations of metals as follows: less than 10 µg/L, two significant figures; 10 to 100 µg/L, three significant figures; 100 to 1,000 µg/L, four significant figures. Report results less than 1.0 µg/L as "less than method reporting limit."

DISCUSSION OF RESULTS

11. Detection limits and reporting limits

11.1 Instrument detection limits are listed in table 4. These values were obtained by analyzing seven aliquots of calibration blank solution (2-percent ultrapure HNO₃ in ASTM Type I water) consecutively in a single analysis procedure, following the procedure described in Section 8. The results were not blank-subtracted, in order to have nonzero numbers for the calculations. The standard deviation of each metal for the seven replicate analyses was multiplied by the appropriate t-value for 99-percent confidence level to obtain the corresponding instrument detection limit. The average instrument detection limit for the 15 analytes was 0.08 µg/L.

11.2 Method detection limits are listed in table 5. These values were obtained by analyzing seven aliquots of a laboratory-prepared multielement solution with concentrations of the metals near the expected detection limit

Table 4.--*Instrument detection limits*

[meas. conc., measured concentration; IDL, instrument detection limit.
All measurements in micrograms per liter]

Metal	Average meas. conc.	Standard deviation	IDL
Ag	0.03	0.01	0.03
Al	.58	.04	.12
Ba	.07	.03	.10
Be	.22	.04	.13
Cd	.14	.06	.17
Co	.07	.01	.03
Cr	1.49	.03	.11
Cu	.20	.03	.09
Mn	.23	.02	.06
Mo	.08	.02	.06
Ni	.62	.05	.15
Pb	.09	.02	.05
Sb	.05	.01	.02
U	.01	.00	.01
Zn	.39	.04	.12

Samples were not blank-subtracted.

Number of replicates = 7.

Degrees of freedom = 6.

t-value (99-percent confidence) = 3.143.

Average IDL = 0.08 µg/L.

of the method. The seven aliquots were analyzed consecutively in a single analysis procedure, following the procedure described in Section 8. The results were blank-subtracted. The standard deviation of each analyte for the seven replicate analyses was multiplied by the appropriate t-value for 99-percent confidence level to obtain the corresponding method detection limit. The average method detection limit for the 15 analytes was 0.22 µg/L.

11.3 Method reporting limits for routine analysis following the procedure described in Section 8 are suggested to be 1 µg/L for each metal. This method reporting limit is approximately five times greater than the average determined method detection limit. The purpose of using method reporting limits rather than method detection limits is to minimize the problems associated with field and laboratory contamination at the submicrogram-per-liter level and to ensure a high degree of confidence in

Table 5.--*Method detection limits*

[meas. conc., measured concentration; MDL, method detection limit.
All measurements in micrograms per liter]

Metal	Nominal concentration	Average meas. conc.	Standard deviation	MDL
Ag	2	2.06	0.02	0.07
Al	2	2.21	.38	1.18
Ba	2	2.10	.04	.12
Be	1	.91	.02	.07
Cd	1	1.00	.05	.16
Co	1	.96	.02	.07
Cr	2	1.87	.05	.16
Cu	1	.94	.03	.10
Mn	1	.93	.06	.18
Mo	1	1.05	.07	.22
Ni	1	.91	.06	.19
Pb	1	.97	.06	.18
Sb	1	1.01	.08	.26
U	1	1.10	.05	.16
Zn	2	1.91	.07	.22

Number of replicates = 7.

Degrees of freedom = 6.

t-value (99-percent confidence) = 3.143.

Average MDL = 0.22 µg/L.

analytical results from the routine mode of operation. Reporting limits less than the suggested 1 µg/L method reporting limit could be used in the case of custom analyses where particular care is taken in both the field and laboratory work associated with the samples and the analyses.

12. Accuracy and precision

12.1 The accuracy of the method was verified by the analyses of standard reference water samples with certified or most probable values for the dissolved concentrations of the constituent analytes. The results for U.S. Geological Survey standard reference water sample T-101 (trace constituents) are shown in table 6, and the results for National Institute of Standards and Technology SRM 1643b (trace elements in water) are listed in table 7.

Table 6.--Analyses of U.S. Geological Survey
standard reference water sample T-101

[MPV, most probable value; MPVSDV, most probable value standard deviation; meas. conc., measured concentration; SDV, measured standard deviation; NC, not certified. All measurements in micrograms per liter]

Metal	MPV	MPVSDV	Average meas. conc.	SDV
Ag	4.94	1.11	4.89	0.23
Al	87.65	13.62	81.46	8.51
Ba	65.00	15.93	60.38	3.44
Be	14.45	2.24	14.56	1.04
Cd	9.93	1.49	9.42	.26
Co	11.94	3.50	9.55	.73
Cr	18.00	3.22	15.27	.34
Cu	49.96	6.62	48.45	4.69
Mn	50.41	4.09	50.02	1.32
Mo	49.50	3.29	48.82	3.16
Ni	31.81	5.78	31.60	2.32
Pb	17.90	6.08	18.58	.54
Sb	10.28	1.42	10.93	.52
U	NC	NC	13.57	.59
Zn	66.25	7.58	76.45	6.74

Twenty-one analyses over 9 days.

These results were obtained from multiple analyses over several days, following the procedure described in Section 8. Agreement was found between the most probable values and the average measured concentrations. In most cases, the average measured concentration was within two times the most probable standard deviation of the most probable value. Also in most cases, the measured standard deviation was less than, or similar to, the most probable standard deviation.

12.2 Short-term (single-operator, within-day) precision was determined by analyzing seven aliquots each of two laboratory-prepared multielement solutions consecutively in a single analysis procedure following the procedure described in Section 8. The results are listed in tables 8 and 9. Relative standard deviation at the 1- and 2- $\mu\text{g/L}$ concentration level ranged from 1 to 8 percent, with the exception of Al which was about 17 percent

Table 7.--Analyses of National Institute of Standards and Technology SRM 1643b

[MPV, most probable value; MPVSDV, most probable value standard deviation; meas. conc., measured concentration; SDV, measured standard deviation; NC, not certified; <MRL, less than method reporting limit. All measurements in micrograms per liter]

Metal	MPV	MPVSDV	Average meas. conc.	SDV
Ag	9.80	0.80	10.76	1.23
Al	NC	NC	3.04	2.11
Ba	44.00	2.00	41.03	2.80
Be	19.00	2.00	18.62	1.66
Cd	20.00	1.00	19.61	.53
Co	26.00	1.00	26.36	1.93
Cr	18.60	.40	16.74	.48
Cu	21.90	.40	21.26	2.27
Mn	28.00	2.00	28.97	1.28
Mo	85.00	3.00	95.98	7.90
Ni	49.00	3.00	47.89	4.11
Pb	23.70	.70	20.66	.89
Sb	NC	NC	<MRL	<MRL
U	NC	NC	<MRL	<MRL
Zn	66.00	2.00	68.89	5.36

Twenty-one analyses over 9 days.

(table 8). The average relative standard deviation at this concentration level for the 15 metals was 5.2 percent. Relative standard deviations at the 25- and 50- $\mu\text{g}/\text{L}$ concentration level ranged from 1 to 4 percent (table 9). The average relative standard deviation at this concentration level for the 15 metals was 1.7 percent. Short-term precision and accuracy results for U.S. Geological Survey standard reference water sample T-113 are given in table 10.

12.3 Long-term (single-operator, multiday) precision was determined by analyzing several aliquots of a laboratory-prepared multielement solution in several analysis procedures on multadays. The results are listed in table 11. The relative standard deviations at the 25- and 50- $\mu\text{g}/\text{L}$ concentration level ranged from 2 to 9 percent. The average relative standard deviation at this concentration level for the 15 metals was 4.6 percent. Long-term precision data also are listed in tables 6 and 7 for the analyses of standard reference water samples.

Table 8.--Short-term precision at 1- and 2-micrograms-per-liter concentration level

[meas. conc., measured concentration; µg/L, microgram per liter]

Metal	Nominal concentration (µg/L)	Average meas. conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
Ag	2	2.06	0.02	1.15
Al	2	2.21	.38	16.99
Ba	2	2.10	.04	1.78
Be	1	.91	.02	2.46
Cd	1	1.00	.05	5.06
Co	1	.96	.02	2.26
Cr	2	1.87	.05	2.78
Cu	1	.94	.03	3.47
Mn	1	.93	.06	6.30
Mo	1	1.05	.07	6.70
Ni	1	.91	.06	6.51
Pb	1	.97	.06	5.75
Sb	1	1.01	.08	8.12
U	1	1.10	.05	4.72
Zn	2	1.91	.07	3.70

Number of replicates = 7.

Average precision = 5.2 percent relative standard deviation.

13. Method comparison

A surface-water sample was collected from the South Platte River, near Henderson, Colorado. A ground-water sample was collected from a U.S. Geological Survey well in Jefferson County, Colorado. Each water sample was filtered and acidified at time of collection and subsequently split into four subsamples, which were analyzed by ICP-MS and ICP-AES to compare analytical performance of the two methods. One subsample was unspiked; one subsample was spiked at 20 µg/L for each metal; one subsample was spiked at 100 µg/L for each metal; and one subsample was spiked at 500 µg/L for each metal. Each subsample was analyzed in replicates of seven aliquots consecutively within an analysis procedure. Results for the surface-water study are presented in table 12, and results for the ground-water study are presented in table 13. U.S. Geological Survey standard reference water sample T-113 (trace constituents) was used in all the analyses as a quality-control sample. The results for both ICP-MS and ICP-AES analyses of T-113 are presented in table 14.

Table 9.--Short-term precision at 25- and 50-micrograms-per-liter concentration level

[meas. conc., measured concentration; $\mu\text{g/L}$, microgram per liter]

Metal	Nominal concentration ($\mu\text{g/L}$)	Average meas. conc. ($\mu\text{g/L}$)	Standard deviation ($\mu\text{g/L}$)	Relative standard deviation (percent)
Ag	50	50.76	0.48	0.94
Al	50	46.04	.83	1.79
Ba	50	49.40	.81	1.64
Be	25	23.65	.25	1.05
Cd	25	24.88	.42	1.69
Co	25	24.74	.31	1.26
Cr	50	47.75	.40	.84
Cu	25	23.78	.24	1.02
Mn	25	24.15	.15	.63
Mo	25	26.06	.81	3.11
Ni	25	23.96	.38	1.58
Pb	25	26.06	1.10	4.21
Sb	25	25.08	.41	1.63
U	25	28.32	.71	2.51
Zn	50	49.25	.64	1.30

Number of replicates = 7.

Average precision = 1.7 percent relative standard deviation.

Analyses of unspiked and spiked surface-water and ground-water samples and U.S. Geological Survey standard reference water sample T-113 by ICP-MS and ICP-AES were in agreement. The concentrations of several metals were less than the method reporting limit for ICP-AES in the unspiked samples, but all analytes were within the detection range of both techniques in the spiked samples.

Some disagreement in the results for Al by the two techniques was observed. On the basis of the measured recoveries in the spiked samples, the Al results by ICP-AES probably are more accurate than by ICP-MS. Al results by ICP-MS have a greater degree of uncertainty than the other metals included in the method, as indicated by the data in tables 5, 8, 11, and 12. During development of this method, it was observed that the quality of results for Al was variable. This problem might be instrument dependent rather than technique or method dependent. Also, it was observed that Al and Zn contamination at the 1- to 2- $\mu\text{g/L}$ level can occur easily and randomly

Table 10.-*Within-day analyses of U.S. Geological Survey standard reference water sample T-113*

[MPV, most probable value; MPVSDV, most probable value standard deviation; meas. conc., measured concentration; SDV, measured standard deviation; NR, not reported; NC, not certified; <MRL, less than method reporting limits. All measurements in micrograms per liter]

Metal	MPV	MPVSDV	Average meas. conc.	SDV
Ag	5.00	0.30	5.43	0.22
Al	317.00	8.00	331.00	6.56
Ba	70.00	2.00	73.07	2.16
Be	10.00	.90	10.99	.72
Cd	4.23	.18	4.40	.29
Co	10.20	.40	10.19	.27
Cr	2.50	.70	1.05	.25
Cu	47.00	1.00	NR	NR
Mn	65.00	1.00	63.06	1.08
Mo	34.00	2.00	37.00	1.37
Ni	2.10	.30	2.76	.37
Pb	1.30	1.30	.43	.08
Sb	18.90	1.60	20.40	.61
U	NC	NC	<MRL	<MRL
Zn	55.50	1.30	50.09	1.70

Eighteen analyses within-day.

in noncleanroom laboratory conditions. Quality-control sample results need to be carefully monitored during use of this method to ensure reliable results for all metals, especially Al.

Measured recoveries in the spiked samples were good for all metals except Ag, which was observed to be low by both techniques. This result is assumed to be due to the presence of chloride in the natural-water samples, causing the Ag to be lost from solution by precipitation. The recoveries by ICP-MS for Ag were lower than by ICP-AES probably because the samples were analyzed by ICP-MS later than by ICP-AES, and more Ag had been lost by precipitation during the interval. Unspiked natural-water samples are unlikely to contain Ag at concentrations greater than a few micrograms per liter, and loss by precipitation is not anticipated to be a problem.

Table 11.--Long-term precision at 25- and 50-micrograms-per-liter concentration level

[meas. conc., measured concentration; $\mu\text{g/L}$, microgram per liter]

Metal	Nominal concentration ($\mu\text{g/L}$)	Average meas. conc. ($\mu\text{g/L}$)	Standard deviation ($\mu\text{g/L}$)	Relative standard deviation (percent)
Ag	50	52.95	1.59	3.01
Al	50	51.85	2.55	4.92
Ba	50	49.53	2.03	4.09
Be	25	27.73	1.81	6.51
Cd	25	27.13	1.16	4.28
Co	25	24.91	.61	2.44
Cr	50	50.83	1.60	3.15
Cu	25	25.78	.76	2.94
Mn	25	25.53	.74	2.91
Mo	25	25.00	.96	3.85
Ni	25	25.76	.87	3.38
Pb	25	23.56	2.20	9.34
Sb	25	26.31	.87	3.31
U	25	23.34	2.19	9.40
Zn	50	54.94	3.05	5.56

Number of replicates = 7.

Average precision = 4.6 percent relative standard deviation.

CONCLUSIONS

From the data presented in this report, inductively coupled plasma - mass spectrometry is shown to be a useful and reliable analytical method for the determination of trace metals in water. This report presents a method for the routine analysis of 15 metals in natural-water samples with a specific conductance less than 2,500 $\mu\text{S/cm}$ or equivalent after dilution. Method reporting limits are set at 1 $\mu\text{g/L}$ to ensure reliability of analytical results and avoid problems of sample contamination at the submicrogram-per-liter level. Average short-term, single-operator, within-day precision is 5.2 percent at the 1- and 2- $\mu\text{g/L}$ concentration level and 1.7 percent at the 25- and 50- $\mu\text{g/L}$ concentration level. Average long-term, single-operator, multiday precision is 4.6 percent at the 25- and 50- $\mu\text{g/L}$ concentration level.

Table 12.--Analyses of surface-water samples

[ICP-AES, inductively coupled plasma - atomic emission spectrometry; ICP-MS, inductively coupled plasma - mass spectrometry; µg/L, microgram per liter; <MRL, less than method reporting limit; NA, not analyzed]

Metal	ICP-AES (µg/L)				ICP-MS (µg/L)			
	Unspiked	Low	Medium	High	Unspiked	Low	Medium	High
Average measured concentrations								
Ag	<MRL	17.7	85.0	421.9	<MRL	16.5	77.9	344.8
Al	21.9	41.2	118.6	524.2	7.1	22.1	124.1	495.7
Ba	40.4	60.2	136.4	530.4	43.0	63.3	147.0	565.0
Be	<MRL	20.3	99.8	507.3	<MRL	19.1	111.4	516.8
Cd	<MRL	20.6	95.8	491.9	<MRL	19.0	102.1	502.3
Co	<MRL	20.3	100.9	504.5	<MRL	19.3	109.7	429.6
Cr	<MRL	23.7	99.5	499.2	1.6	19.3	109.7	197.5
Cu	<MRL	23.3	102.9	498.4	3.5	20.5	105.6	460.6
Mn	290.5	315.0	389.8	770.7	298.0	312.7	442.6	786.1
Mo	27.1	47.4	120.5	528.7	24.3	44.4	136.9	572.3
Ni	<MRL	27.7	106.4	499.2	10.4	27.4	92.1	480.0
Pb	<MRL	20.0	104.1	497.6	<MRL	21.3	103.9	502.3
U	NA	NA	NA	NA	10.3	34.6	116.2	601.0
Zn	28.5	51.1	126.9	523.2	30.4	48.7	147.4	486.0
Standard deviations of average measured concentrations								
Ag	<MRL	0.3	1.1	3.5	<MRL	0.4	1.1	4.4
Al	1.8	2.5	3.1	6.7	.7	.8	2.1	5.2
Ba	.1	.1	.3	1.8	.4	1.0	1.8	4.4
Be	<MRL	.1	.3	2.1	<MRL	.3	2.5	5.3
Cd	<MRL	.4	1.0	2.8	<MRL	.5	.6	3.9
Co	<MRL	.5	.9	2.4	<MRL	.3	1.1	3.4
Cr	<MRL	.5	1.3	3.0	.1	.3	1.3	3.8
Cu	<MRL	.3	.3	2.2	.1	.6	1.4	6.2
Mn	.6	.5	2.2	4.3	3.3	4.5	5.4	6.6
Mo	2.2	1.6	1.6	2.2	.5	1.2	.7	5.6
Ni	5.5	1.7	1.4	3.3	.2	.8	1.1	4.4
Pb	<MRL	1.5	4.6	3.9	<MRL	.3	.6	5.1
U	NA	NA	NA	NA	.2	.7	2.7	5.5
Zn	1.1	1.4	1.3	5.4	.5	.5	2.3	6.5
Recovery of spike additions								
	ICP-AES (percent)			ICP-MS (percent)				
	Low	Medium	High	Low	Medium	High		
Ag	88.4	85.0	84.4	82.6	77.9	69.0		
Al	96.4	96.7	100.5	75.3	117.1	97.7		
Ba	99.0	95.9	98.0	101.4	104.0	104.4		
Be	101.2	99.7	101.4	95.6	111.4	103.4		
Cd	102.8	95.8	98.4	93.8	101.8	100.4		
Co	101.6	100.9	100.9	91.8	108.8	85.7		
Cr	114.8	98.8	99.7	88.8	108.1	99.2		
Cu	116.4	102.9	99.7	84.8	102.1	91.4		
Mn	122.6	99.3	96.0	73.9	144.6	97.6		
Mo	101.4	93.4	100.3	100.4	112.5	109.6		
Ni	121.2	103.0	99.2	84.8	81.7	93.9		
Pb	100.2	104.1	99.5	103.0	103.2	100.3		
U	NA	NA	NA	121.6	105.9	118.1		
Zn	113.1	98.4	98.9	91.4	117.0	91.1		

Table 13.--Analyses of ground-water samples

[ICP-AES, inductively coupled plasma - atomic emission spectrometry; ICP-MS, inductively coupled plasma - mass spectrometry; µg/L, microgram per liter; <MRL, less than method reporting limit; NA, not analyzed]

Metal	ICP-AES (µg/L)				ICP-MS (µg/L)			
	Unspiked	Low	Medium	High	Unspiked	Low	Medium	High
Average measured concentrations								
Ag	<MRL	18.1	66.5	219.7	<MRL	18.4	31.9	141.4
Al	2.7	19.6	95.5	492.6	<MRL	12.8	106.9	486.6
Ba	118.2	133.6	211.5	585.4	133.1	156.3	230.7	619.2
Be	<MRL	19.7	99.7	498.8	<MRL	20.7	114.5	520.0
Cd	<MRL	21.3	98.9	492.0	<MRL	20.1	100.6	495.4
Co	<MRL	20.1	99.0	491.4	<MRL	17.8	106.0	491.1
Cr	<MRL	22.2	100.4	491.3	<MRL	17.1	112.2	512.5
Cu	<MRL	18.1	96.6	477.4	1.3	19.6	100.3	458.1
Mn	263.8	279.9	345.2	737.2	218.0	225.4	407.5	785.5
Mo	<MRL	22.9	102.8	506.2	1.0	17.8	109.2	526.1
Ni	<MRL	19.8	99.6	484.6	12.1	32.7	109.5	481.9
Pb	<MRL	20.0	97.2	492.2	<MRL	19.0	103.1	510.8
U	NA	NA	NA	NA	<MRL	18.4	107.7	565.9
Zn	<MRL	23.6	97.3	494.4	4.2	24.3	112.7	493.4
Standard deviations of average measured concentrations								
Ag	<MRL	0.5	0.8	2.3	<MRL	0.2	3.2	12.8
Al	1.6	2.7	2.1	6.2	<MRL	.3	1.0	6.4
Ba	1.6	1.1	.5	3.4	2.8	1.3	2.6	4.9
Be	<MRL	.2	.5	4.8	<MRL	.3	1.1	11.8
Cd	<MRL	.8	2.0	8.8	<MRL	.3	1.2	3.8
Co	<MRL	.3	1.1	5.8	<MRL	.2	.9	2.3
Cr	<MRL	1.2	1.9	6.9	<MRL	.1	1.4	2.0
Cu	<MRL	.3	.6	2.4	.5	.3	1.6	4.7
Mn	12.7	7.0	4.4	9.7	5.4	5.7	6.1	5.4
Mo	<MRL	2.0	1.5	6.9	.1	.2	1.7	3.8
Ni	<MRL	1.1	2.7	7.8	2.5	1.2	1.7	2.6
Pb	<MRL	1.4	4.3	5.8	<MRL	.4	1.3	3.3
U	NA	NA	NA	NA	<MRL	.7	2.0	11.0
Zn	<MRL	1.9	2.5	9.5	.6	.8	2.9	7.0
Recovery of spike additions								
	ICP-AES (percent)			ICP-MS (percent)				
	Low	Medium	High	Low	Medium	High		
Ag	90.3	66.5	43.9	91.8	31.9	28.3		
Al	84.7	92.8	98.0	64.0	106.9	97.3		
Ba	77.0	93.3	93.4	116.0	97.6	97.2		
Be	98.3	99.7	99.8	103.4	114.5	104.0		
Cd	106.6	98.9	98.4	100.2	100.6	99.1		
Co	100.7	99.0	98.3	85.6	105.4	98.1		
Cr	110.8	100.4	98.3	80.7	111.2	102.3		
Cu	90.4	96.6	95.5	91.2	99.0	91.4		
Mn	80.5	81.4	94.7	37.0	189.4	113.5		
Mo	114.3	102.8	101.2	83.6	108.2	105.0		
Ni	98.9	99.6	96.9	102.8	97.4	94.0		
Pb	100.0	97.2	98.4	95.0	103.1	102.2		
U	NA	NA	NA	91.0	107.5	113.1		
Zn	117.8	97.3	98.7	100.7	108.5	97.8		

Table 14.--Analyses of U.S. Geological Survey
standard reference water sample T-113

[MPV, most probable value; ICP-AES, inductively coupled plasma - atomic emission spectrometry; ICP-MS, inductively coupled plasma - mass spectrometry; <MRL, less than method reporting limit; NC, not certified; NA, not analyzed.
All measurements in micrograms per liter]

Metal	MPV	Average measured concentration	
		ICP-AES	ICP-MS
Ag	5.0	5.9	5.1
Al	317.0	319.3	315.5
Ba	70.0	68.2	71.3
Be	10.0	10.5	11.5
Cd	4.2	4.4	4.5
Co	10.2	11.5	10.6
Cr	2.5	<MRL	1.6
Cu	47.0	46.4	46.4
Mn	65.0	65.0	63.0
Mo	34.0	36.4	35.0
Ni	2.1	<MRL	3.1
Pb	1.3	<MRL	<MRL
Sb	18.9	NA	19.6
U	NC	NA	<MRL
Zn	55.5	56.0	60.7

ICP-AES: 12 analyses on 4 days.

ICP-MS: 11 analyses on 4 days.

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