Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium Using Inductively Coupled Plasma–Mass Spectrometry

---

Open-File Report 99–093

U.S. Department of the Interior
U.S. Geological Survey

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium Using Inductively Coupled Plasma–Mass Spectrometry

By John R. Garbarino

U.S. Geological Survey
Open-File Report 99–093

Denver, Colorado
1999

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

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

For additional information write to:

U.S. Geological Survey
Chief, National Water Quality Laboratory
Box 25046, Mail Stop 407
Federal Center
Denver, CO 80225-0046

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Federal Center
Denver, CO 80225-0286

CONTENTS

FIGURES

FIGURES—Continued

TABLES

CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, OTHER ABBREVIATIONS, AND DEFINITIONS

Multiply	By	To obtain
gram (g)	3.53×10^{-2}	ounce
liter (L)	2.64×10^{-1}	gallon
microgram (µg)	3.53×10^{-8}	ounce
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon

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

$$°F = 9/5\ (°C) + 32.$$

Abbreviated water-quality units used in this report are as follows:

mg/L	milligram per liter
µg/L	microgram per liter
µS/cm	microsiemens per centimeter at 25°C

Other abbreviations also used in this report:

amu	atomic mass unit
ASTM	American Society for Testing and Materials
CC	catalyzed colorimetry
DCP–AES	direct current plasma–atomic emission spectrometry
F–AAS	flame–atomic absorption spectrophotometry
FEP	fluorinated ethylene propylene (Teflon)
GF–AAS	graphite furnace–atomic absorption spectrophotometry
HG–AAS	hydride generation–atomic absorption spectrophotometry
ICP–MS	inductively coupled plasma–mass spectrometry
ICP–AES	inductively coupled plasma–atomic emission spectrometry, also known as inductively coupled plasma–optical emission spectrometry (ICP–OES)
MDL(s)	method detection limit(s)
MRL(s)	minimum reporting level(s)
MPV(s)	most probable value(s)
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
SRWS(s)	U.S. Geological Survey Standard Reference Water Sample(s)
SOP	standard operating procedure
USGS	U.S. Geological Survey
>	greater than
<	less than
≤	less than or equal to
±	plus or minus

Definitions:

MDL	The method detection limit (MDL) is defined as the minimum concentration of an element that can be measured and reported with 99-percent confidence that the concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the element of interest (U.S. Environmental Protection Agency, 1997).
MPV	The most probable value (MPV) is equal to the median value for numerous interlaboratory analyses from multiple analytical methods.

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium Using Inductively Coupled Plasma–Mass Spectrometry

By John R. Garbarino

ABSTRACT

The inductively coupled plasma–mass spectrometric (ICP–MS) methods have been expanded to include the determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium in filtered, acidified natural water. Method detection limits for these elements are now 10 to 200 times lower than by former U.S. Geological Survey (USGS) methods, thus providing lower variability at ambient concentrations. The bias and variability of the method was determined by using results from spike recoveries, standard reference materials, and validation samples. Spike recoveries at 5 to 10 times the method detection limit and 75 micrograms per liter in reagent-water, surface-water, and ground-water matrices averaged 93 percent for seven replicates, although selected elemental recoveries in a ground-water matrix with an extremely high iron sulfate concentration were negatively biased by 30 percent. Results for standard reference materials were within 1 standard deviation of the most probable value. Statistical analysis of the results from about 60 filtered, acidified natural-water samples indicated that there was no significant difference between ICP–MS and former USGS official methods of analysis.

INTRODUCTION

The U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) offers several methods for the determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium in filtered, acidified water samples. Former USGS methods use single-element quantification, such as flame– (F–AAS), graphite furnace– (GF–AAS), and hydride generation–atomic absorption spectrophotometry (HG–AAS), direct current plasma–atomic emission spectrometry (DCP–AES), catalyzed colorimetry (CC), or the simultaneous multielement technique of inductively coupled plasma–atomic emission spectrometry (ICP–AES). This report provides data that validates the addition of the aforementioned elements to the existing inductively coupled plasma–mass spectrometric (ICP–MS) method.

Elements that are being added to the existing multielement ICP–MS method and their corresponding former USGS methods of analysis are listed in the following table: Dissolved arsenic, boron, lithium, strontium, thallium, and vanadium are validated for use in ICP–MS method I-2477-92 (see Faires, 1993; Garbarino and Taylor, 1994).

Element	CC	F–AAS	GF–AAS	HG–AAS	DCP–AES	ICP–AES
Arsenic			✓	✓		
Boron					✓	✓
Lithium		✓				✓
Selenium			✓	✓		
Strontium		✓				✓
Thallium			✓			
Vanadium	✓					✓

ICP–MS is compared to one former method from the list in the preceding table. In all comparisons, the most current (as of January 1998) former method is used. Dissolved arsenic and selenium ICP–MS results are compared to HG–AAS. The HG–AAS methods require that the sample be digested to oxidize organocompounds. The former HG–AAS method for dissolved arsenic is based on an online sulfuric acid/potassium persulfate digestion. The former HG–AAS method for dissolved selenium is based on an offline hydrochloric acid/potassium persulfate digestion. No such digestions are necessary to determine dissolved elements by the ICP–MS method because the high-temperature plasma dissociates organometallic species. The ICP–MS method for dissolved boron, lithium, strontium, and vanadium is compared to ICP–AES. The ICP–MS thallium method was compared to GF–AAS.

The objectives of this report are as follows:

- To determine whether ICP–MS results are biased with respect to former USGS methods of analysis for determination of the new elements in filtered natural water. Multiple strategies are used in the statistical analysis of the experimental data to provide a practical estimate of the expected accuracy.

- To compare the variability of the ICP–MS method to former USGS methods of analysis.

- To estimate potential effects of using results from the ICP–MS method on long-term water-quality studies.

The revised methods were developed by the USGS for use at the NWQL. These methods supplement other official USGS inorganic methods (Fishman, 1993; Fishman and Friedman, 1989). The new elements will be available in the ICP–MS schedules.

ANALYTICAL METHOD

1. Application

The determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium in filtered, acidified natural water has been added to the ICP–MS method (I-2477-92). Table 1 lists the new lab code, parameter code, method code, and reporting unit for every element. A report by Garbarino and Taylor (1994) describes the determination of these elements in filtered, acidified natural water; therefore, only supplementary information and validation data are provided here. Filtered, acidified natural water is processed as described in Horowitz and others (1994).

Table 1. Inorganic constituents and parameter codes

Metals, Dissolved, Method I-2477-92

Element	Lab code	Parameter and method codes
Arsenic, µg/L	2503	01000D
Boron, µg/L	2504	01020G
Lithium, µg/L	2505	01130C
Selenium, µg/L	2506	01145C
Strontium, µg/L	2507	01080I
Thallium, µg/L	2508	01057I
Vanadium, µg/L	2509	01085E

The short-term method detection limits (MDLs) and analytical concentration ranges are listed in table 2. Even though the upper calibration standard is listed as 200 µg/L or less, the elemental linear dynamic range is extended to at least 1 mg/L by calibrating both the pulse and analog measurement modes. Short-term MDLs were calculated by using the U.S. Environmental Protection Agency's (1997) definition and represent pooled averages on the basis of four MDLs determined on different days over several weeks. The MDLs have not been established for most former methods, therefore, minimum-reporting levels (MRLs) are listed that are probably within a factor of 5 of the MDL.

2. Summary of Method

The ICP–MS methods have been described previously in Faires (1993) and Garbarino and Taylor (1994). The following sections only provide additional information specific to the elements that are being added to the method.

3. Interferences

Several types of physical and spectral interference are recognized and documented for ICP–MS techniques (see Horlick and Shao, 1992; Garbarino and Taylor, 1994). Physical interferences are associated primarily with sample introduction and are minimized by using the internal standardization technique. Isotopes measured in this procedure have been selected specifically to minimize spectral interferences from isobaric, doubly charged, and molecular ions. Multiple isotopes can be measured for selected elements that have potential isobaric or molecular ion interference. The analyst must be aware of these interferences because they might be present with certain types of sample matrices.

3.1 *Physical interferences.* The use of the ratio of elemental ion intensity to the internal standard element ion intensity for calibration reduces the effects of sample transport, instrumental drift, and matrix-induced fluctuations in plasma characteristics. Accurate results depend on having a constant internal standard ion intensity throughout the analysis of all standards and samples. Stable internal standard ion intensity requires that any interference associated with the internal standard element can be corrected and that the internal standard element is not naturally present in the samples being analyzed. Groups of elements with similar response characteristics or mass-to-charge ratios are often referenced to an internal standard element with similar characteristics.

Three internal standard elements are routinely used to cover the mass range from 6 to 240—for example, $^{72}Ge^+$, $^{115}In^+$, and $^{209}Bi^+$ (Garbarino and Taylor, 1994). Alternative isotopes may be substituted after ensuring that there are no spectral interferences associated with the new selections.

Memory effects related to sample transport are negligible for most elements that are normally present in natural water. Carryover from samples that have arsenic,

Table 2. Former methods and ICP–MS method detection limits and calibration limits for new elements determined in filtered, acidified natural water

[All concentrations are in micrograms per liter; MRL, minimum reporting level; MDL, method detection limit; CC, catalyzed colorimetry; DCP–AES, direct current plasma–atomic emission spectrometry; F–AAS, flame–atomic absorption spectrophotometry; GF–AAS, stabilized temperature graphite furnace–atomic absorption spectrophotometry; HG–AAS, hydride generation–atomic absorption spectrophotometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry]

	Former methods			ICP–MS	
Element	**Technique**	**MRL**	**Upper concentration limit (without dilution)**	**Short-term MDL**	**Upper calibration standard[1]**
Arsenic	GF–AAS	0.9	50	0.07	200
	HG–AAS	1	20		
Boron	ICP–AES	16	10,000	[2] 0.5	100
Lithium	F–AAS	10	1,000	0.03	200
	ICP–AES	4	100,000		
Selenium	GF–AAS	1	50	0.1	200
	HG–AAS	1	20		
Strontium	F–AAS	10	5,000	0.008	200
	ICP–AES	1	10,000		
Thallium	GF–AAS	1	9	0.005	200
Vanadium	CC	1	40	0.08	200
	ICP–AES	10	10,000		

[1] Upper concentration limit extends to greater than 1 milligram per liter without dilution by calibrating the analog stage of the detector.

[2] Method detection limit for boron is limited by reagent blank concentration.

boron, lithium, selenium, and strontium concentrations less than or equal to 200 µg/L is negligible when using the sample introduction described in Garbarino and Struzeski (1998). However, thallium and vanadium did not recover to reagent-blank intensity levels within the rinse period; thallium and vanadium intensities were 10 and 2 times greater than reagent-blank levels, respectively. Consequently, the analyst must review all analytical results to ensure that errors from carryover are minimized.

Sample matrix composition could also affect the bias and variability of ICP–MS determinations. The use of internal standardization compensates for most matrix effects, however, some matrix interferences remain problematic. Matrix composition can suppress the ionization efficiency of the plasma and result in negatively biased elemental concentrations. Aluminum sulfate, calcium sulfate, iron sulfate, manganese sulfate, sodium sulfate, and sodium chloride were evaluated for their matrix interference potential. A solution containing about 25 µg/L of arsenic, boron, lithium, selenium, strontium, thallium, and vanadium was prepared in increasing concentrations of each compound.

The effects of increasing concomitant concentration are shown in figures 1 through 7. For example, the graphs in figure 1 show the effects of increasing concentrations of cations (aluminum, calcium, iron, manganese, and sodium) and anions (sulfate

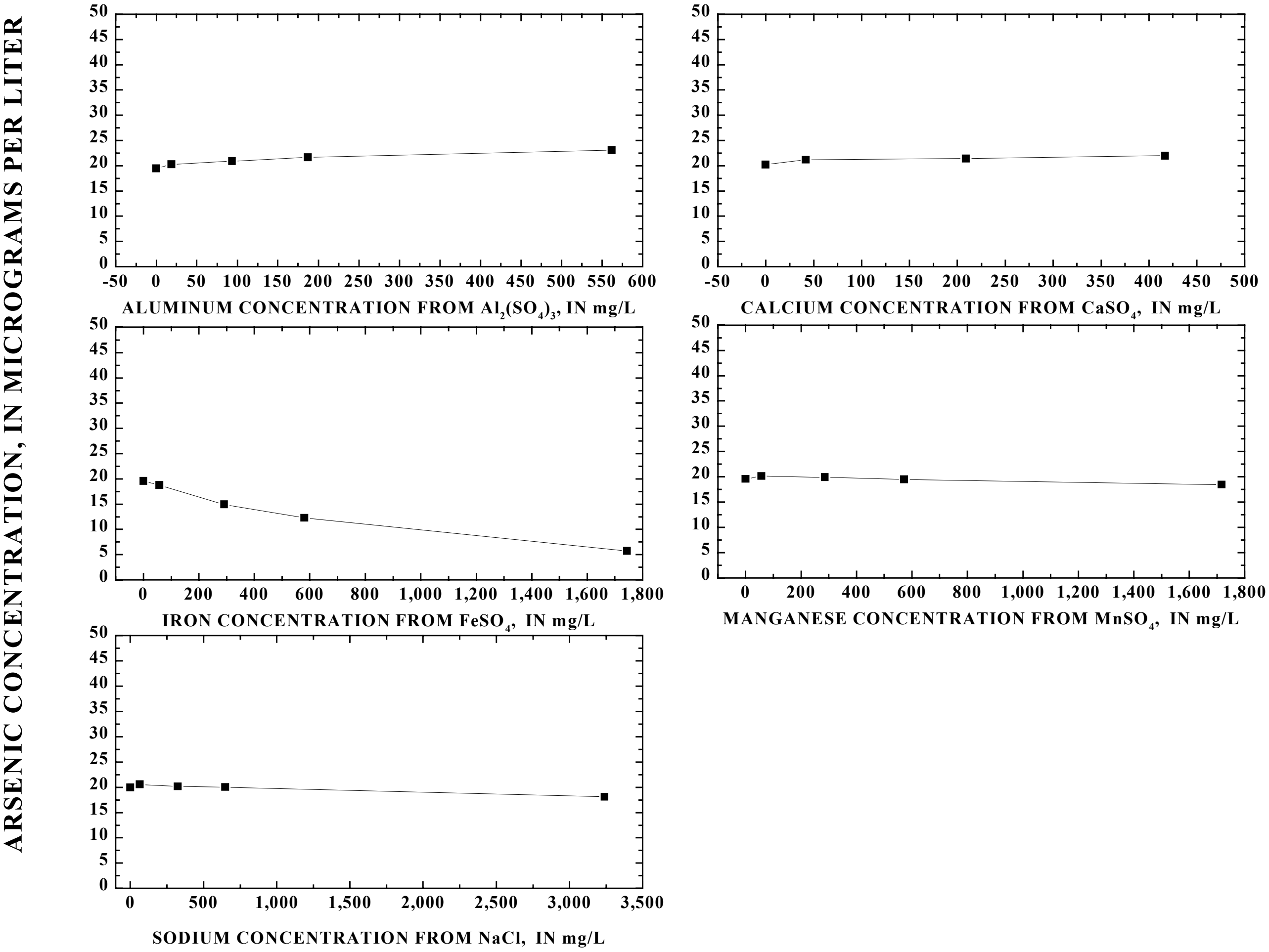


Figure 1. Relations among selected cations and anions and **arsenic** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

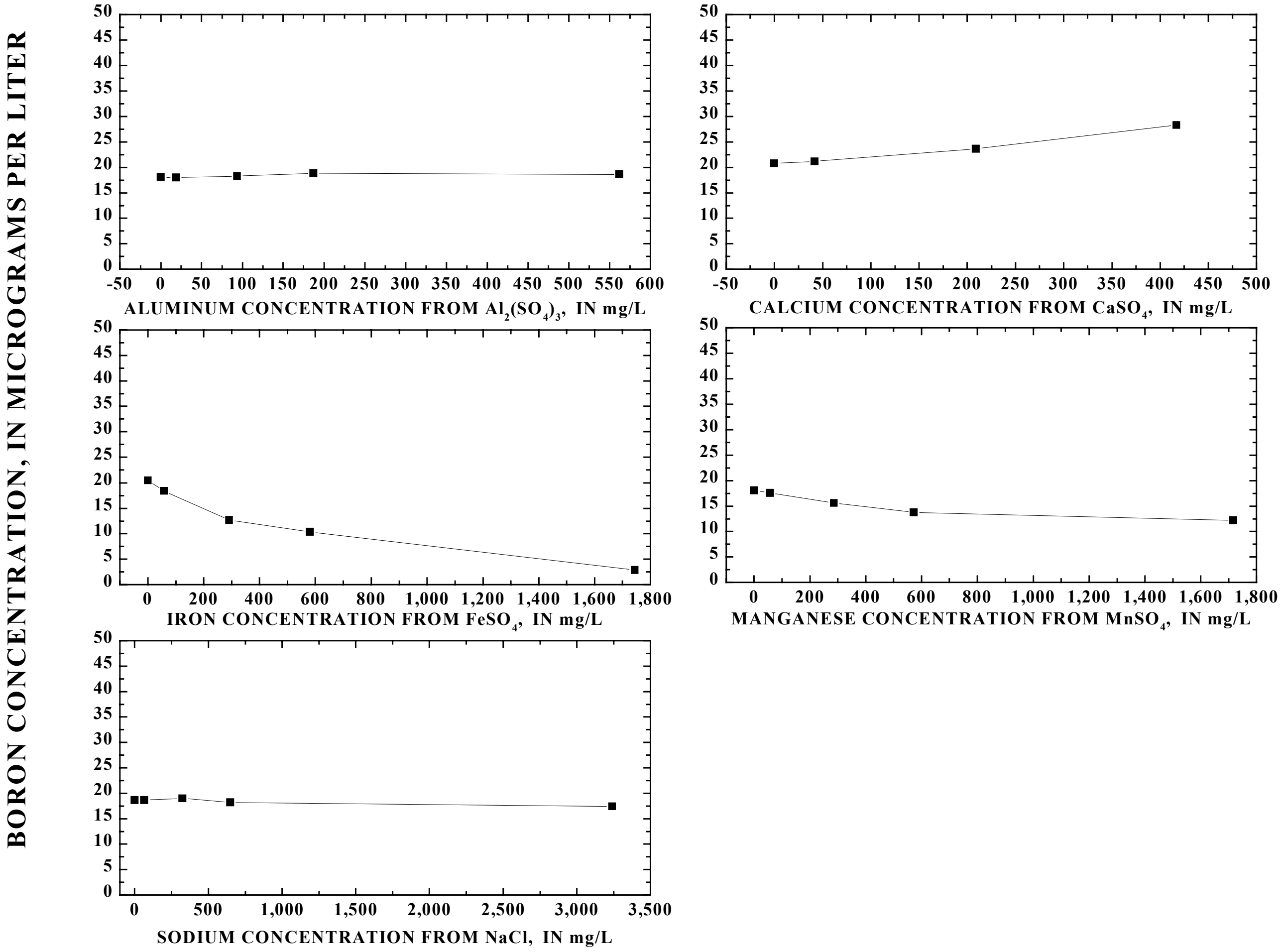


Figure 2. Relations among selected cations and anions and **boron** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

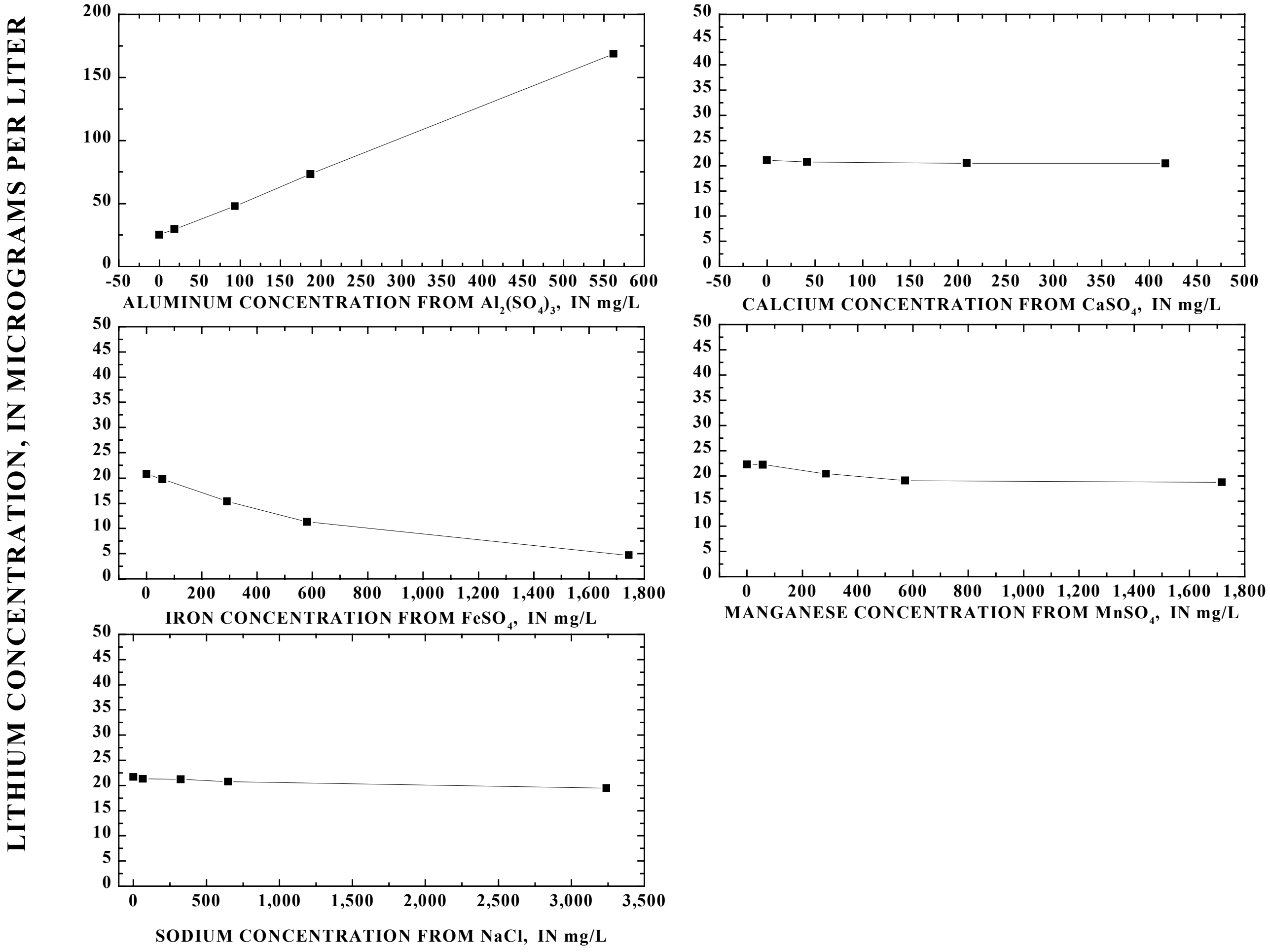


Figure 3. Relations among selected cations and anions and **lithium** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

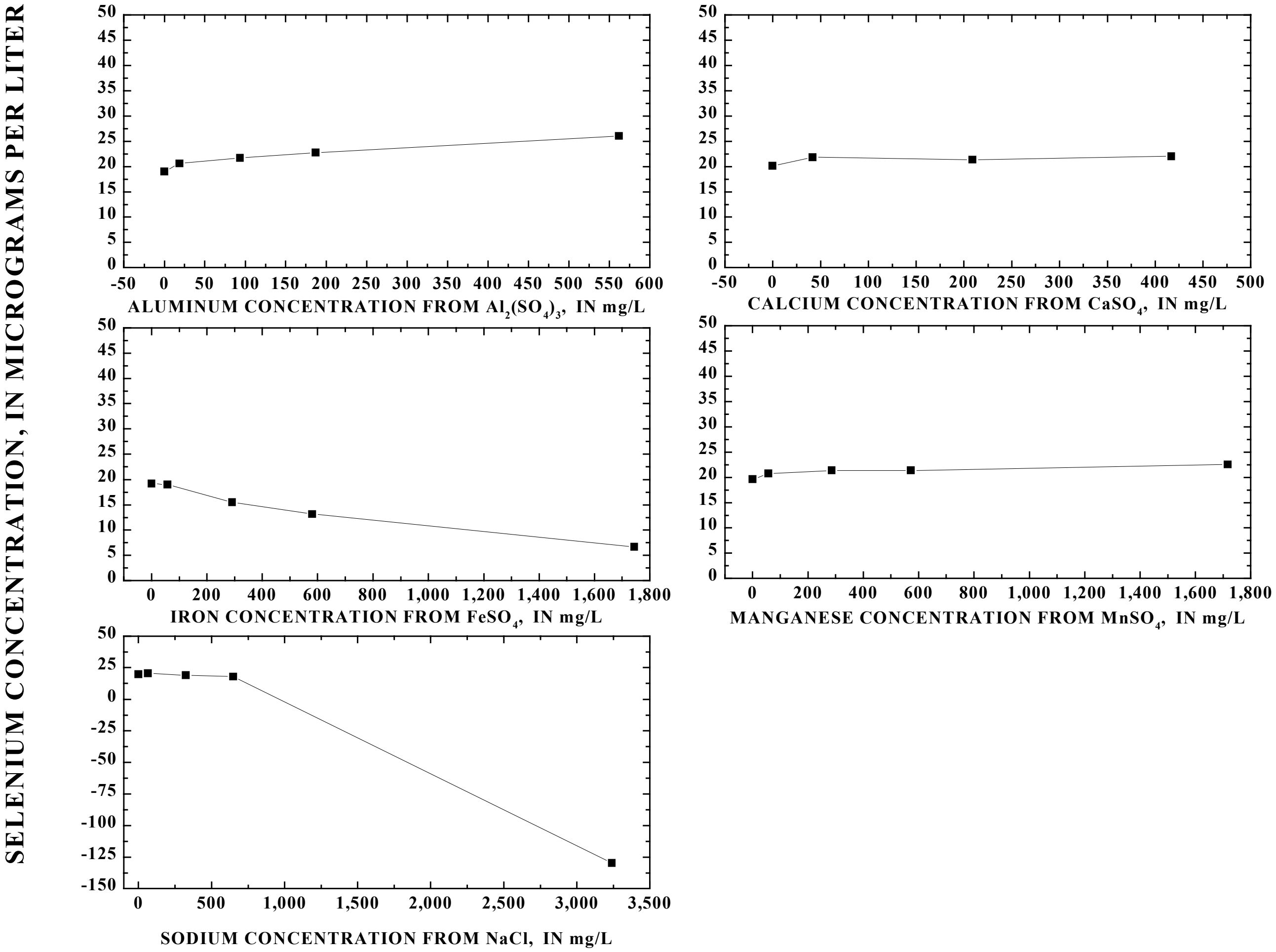


Figure 4. Relations among selected cations and anions and **selenium** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

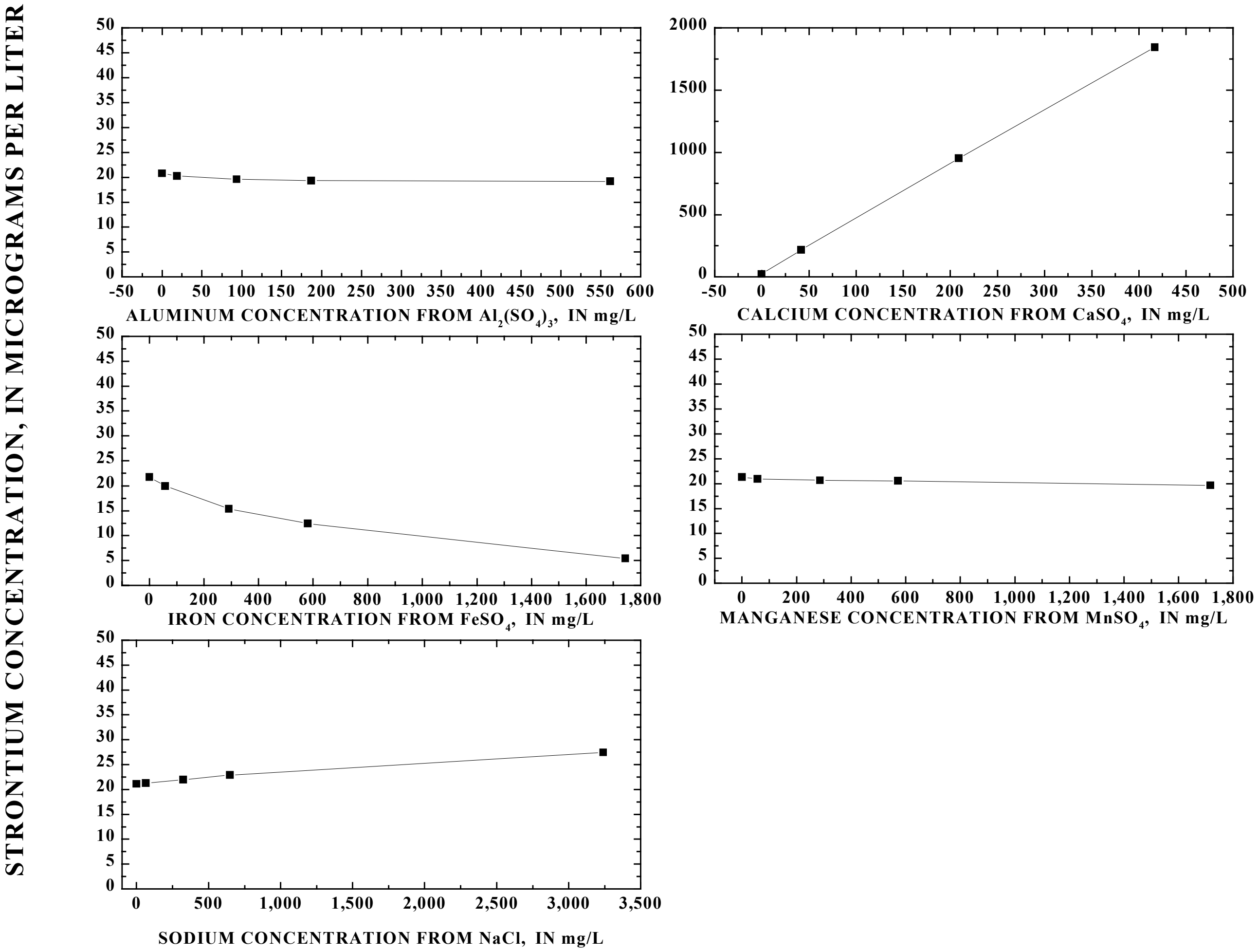


Figure 5. Relations among selected cations and anions and **strontium** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

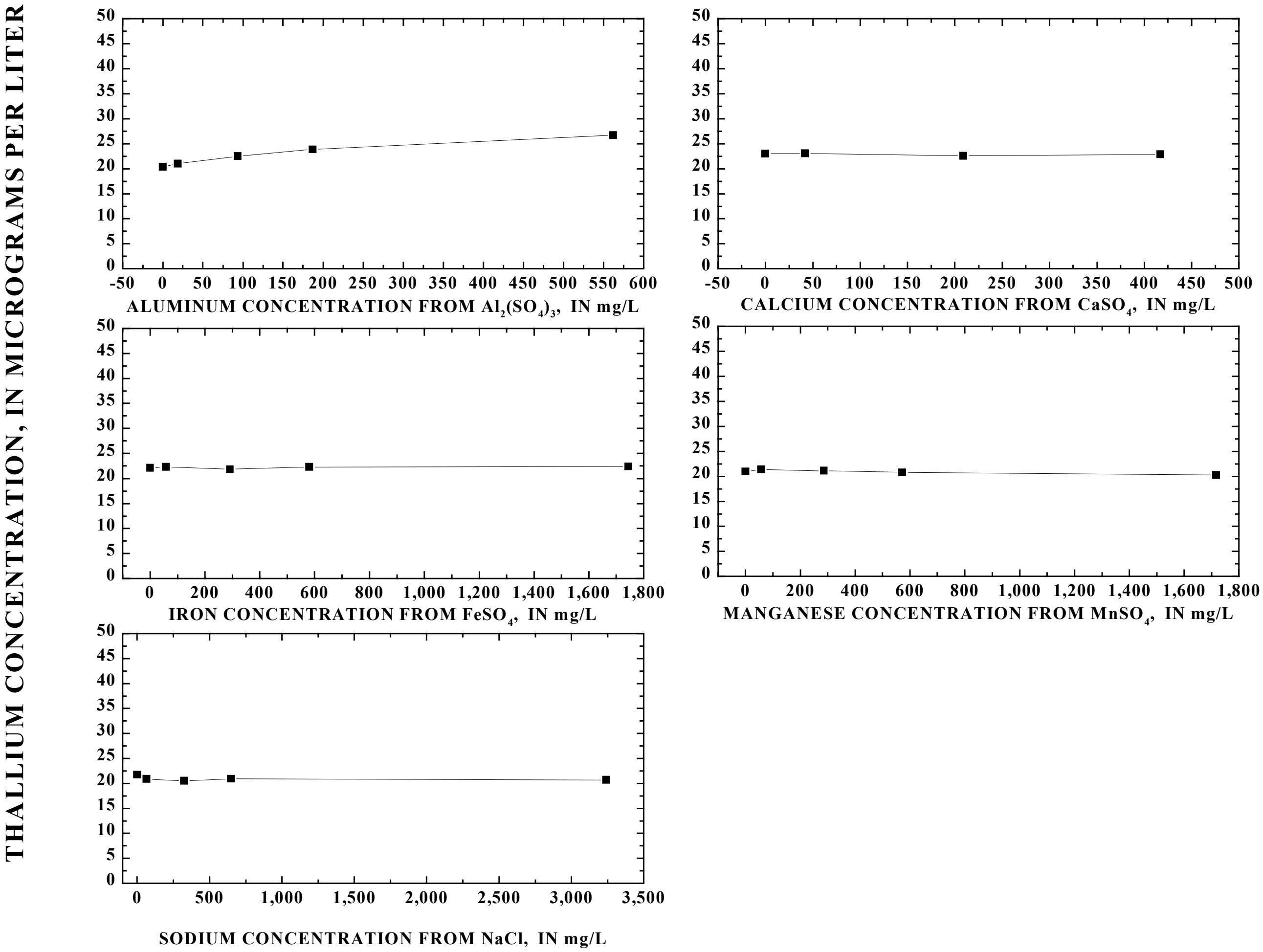


Figure 6. Relations among selected cations and anions and **thallium** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

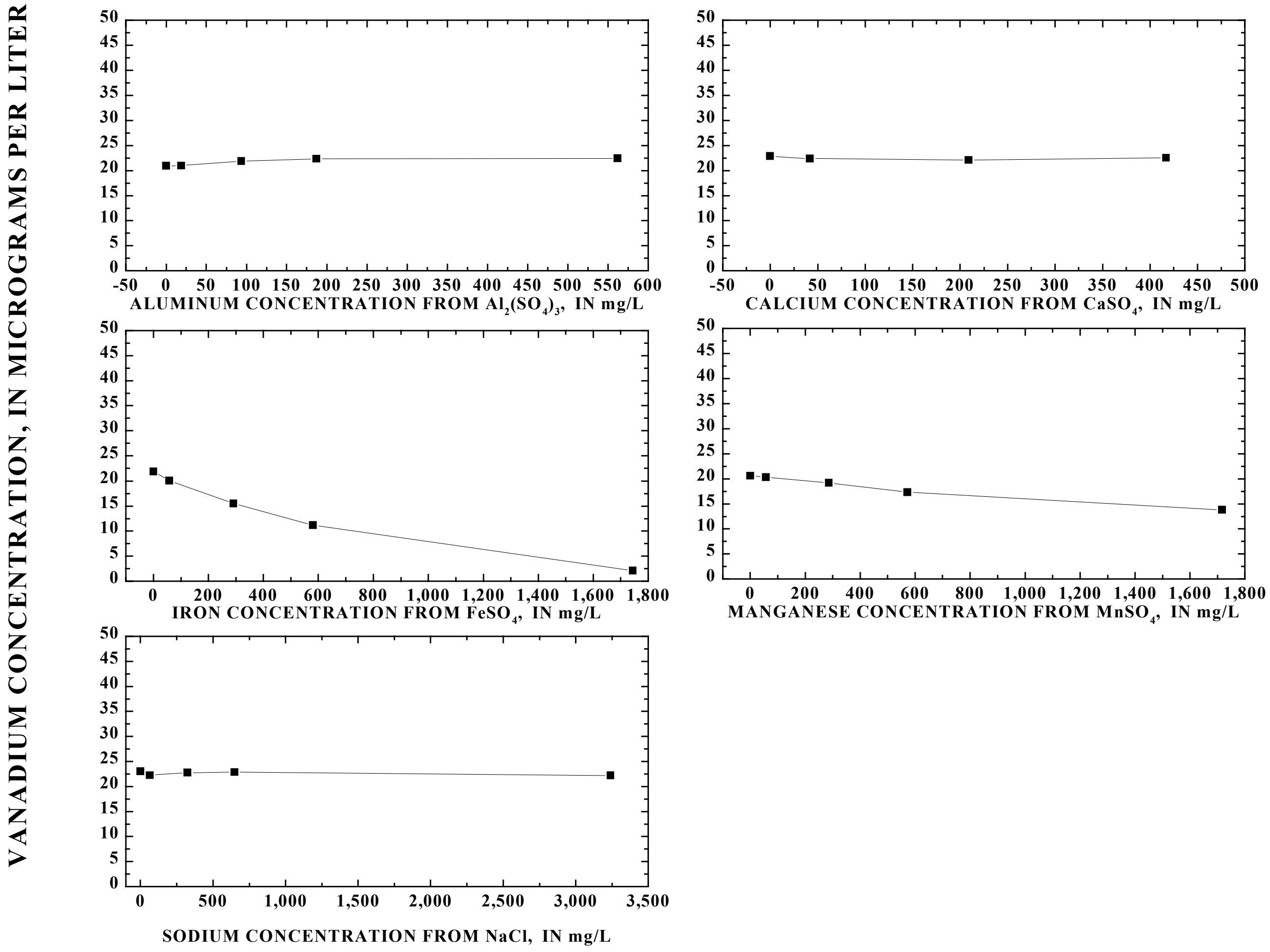


Figure 7. Relations among selected cations and anions and **vanadium** determined by inductively coupled plasma–mass spectrometry (mg/L, milligrams per liter).

and chloride) on the determination of arsenic. A relation with a slope equal to zero indicates no interference. A slope greater than zero suggests a positive interference or contamination; a slope of less than zero indicates signal suppression. Some elemental concentrations, for example, boron in calcium sulfate (fig. 2), lithium in aluminum sulfate (fig. 3), and strontium in calcium sulfate (fig. 5), increased with concomitant concentration. Such increases are from contamination (confirmed by using ICP–AES). Signal suppressions greater than 20 percent are indicated for some elements, depending on the nature of the concomitant. The results indicate that the suppression is not from sulfate or chloride but rather from the accompanying metal cation. Sulfur and chloride have low degrees of ionization, 14 and 0.9 percent, respectively, and therefore, they should not significantly induce signal suppression (Douglas, 1992).

In contrast, all the metal cations tested have degrees of ionization exceeding 90 percent. High iron concentration significantly suppressed all elements except for thallium. The response function was similar for each suppressed element, reaching a maximum of 75-percent suppression at about 1,700 mg/L iron. Lighter elements (less than 80 amu) were affected to a higher degree than heavier elements; for example, thallium was not affected. Manganese suppressed boron and vanadium in a similar manner, although to a lesser degree than iron. Selenium is severely suppressed in the presence of 3,200 mg/L sodium; the suppression is enhanced by selenium's 33-percent degree of ionization. In general, light elements are affected more severely than heavy elements, and heavier concomitant cations cause more severe suppression (Horlick and Shao, 1992). Concomitant concentrations that produce more than a 20-percent suppression are summarized in table 2. For most concomitant elements, 99 percent of the samples submitted for analysis at NWQL have concentrations that are much less than the concentrations listed in table 3. Nevertheless, the analyst must be aware of possible suppression whenever any element is present in a sample at unusually high concentrations; the sample can be diluted to eliminate the suppression.

3.2 *Spectral interferences.* Whenever possible, the isotope used for quantitation either has no spectral interferences or has a small number of potential spectral interferences. Spectral interferences can originate from isobaric ions, molecular ions, or doubly charged ions. The analyst must be aware of these potential spectral interferences when reviewing analytical results. Known spectral interferences for elements being added to the ICP–MS method are listed in the following sections.

3.3 *Isobaric interferences.* The only isobaric interference that affects the new elements is krypton on $^{82}Se^+$and $^{78}Se^+$. Krypton can be a minor contaminant found in argon gas that is used to support the plasma, however, its concentration will remain constant for the standards and samples, and, therefore, usually does not require correction.

3.4 *Molecular-ion interferences.* There are several known molecular-ion interferences associated with arsenic, selenium, and vanadium. Chloride-associated molecular-ion interferences have been documented on arsenic ($^{75}As^+$) and vanadium ($^{51}V^+$) (see Horlick and Shao, 1992; Garbarino and Taylor, 1994). The molecular ions $^{40}Ar^{35}Cl^+$ and $^{35}Cl^{16}O$ interfere with $^{75}As^+$ and $^{51}V^+$, respectively. The $^{81}BrH^+$ ion interferes with the determination of selenium at 82 amu.

Table 3. Concomitant concentrations that result in more than a 20-percent ionization suppression on new elements determined by ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry; mg/L, milligrams per liter; NWQL 99th percentile, the elemental concentration that is greater than 99 percent of the samples submitted to the National Water Quality Laboratory (NWQL); >, the greater than symbol signifies that the concentration causing 20-percent ionization suppression is greater than the stated concentration; nd, not determined because concomitant solution was contaminated with element]

Element	Aluminum, mg/L	Calcium, mg/L	Iron, mg/L	Manganese, mg/L	Sodium, mg/L
NWQL 99th percentile	*55*	*570*	*19*	*11*	*1,800*
Arsenic	>500	>400	300	>1,700	>3,200
Boron	>500	nd	300	300	>3,200
Lithium	nd	>400	300	300	>3,200
Selenium	nd	>400	300	>1,700	600
Strontium	>500	nd	300	>1,700	nd
Thallium	nd	>400	>1,700	>1,700	>3,200
Vanadium	>500	>400	300	300	>3,200

Because arsenic is monoisotopic, and vanadium has only one isotope with suitable natural abundance, no other interference-free isotopes are available for measurement. Equation 2 can be used to correct chloride interference on $^{75}\text{As}^+$; it is derived as follows:

$$^{75}\text{As}^+_{corr} = {}^{75}\text{As}^+ - [{}^{40}\text{Ar}^{35}\text{Cl}^+/{}^{40}\text{Ar}^{37}\text{Cl}^+] \times \{{}^{40}\text{Ar}^{37}\text{Cl}^+ - [{}^{77}\text{Se}/{}^{82}\text{Se}] \times {}^{82}\text{Se}^+\}. \quad (1)$$

The portion of the signal at 75 amu from the $^{40}\text{Ar}^{35}\text{Cl}^+$ interference is calculated by converting the signal at 77 amu from $^{40}\text{Ar}^{37}\text{Cl}^+$ (by measuring $^{77}\text{Se}^+$) after subtracting the contribution from $^{77}\text{Se}^+$ (by measuring $^{82}\text{Se}^+$) to its proportion at 75 amu. All the terms identified by *corr* are the corrected isotope intensities, and the terms in square brackets are the natural abundance isotope ratios; all other terms represent isotope intensities. After substituting constant terms that are based on natural abundance, equation 1 simplifies to

$$^{75}\text{As}^+_{corr} = {}^{75}\text{As}^+ - 3.127 \times \{{}^{77}\text{Se}^+ - [0.874] \times {}^{82}\text{Se}^+\}. \quad (2)$$

However, if bromide is also present in a sample, using equation 2 will give positively biased results because of the $^{81}\text{BrH}^+$ interference at $^{82}\text{Se}^+$. Therefore, whenever bromide is present, the correction must use $^{78}\text{Se}^+$ as shown in equation 3.

$$^{75}\text{As}^+_{corr} = {}^{75}\text{As}^+ - 3.127 \times \{{}^{77}\text{Se}^+ - [0.322] \times {}^{78}\text{Se}^+\}. \quad (3)$$

The positive bias in arsenic results when using equation 2 in the presence of bromide is shown in figure 8. The arsenic concentration will be 40 percent greater than is actually present with only 200 μg/L bromide in a sample. When using equation 3, such bias is not indicated. Nevertheless, in the absense of bromide, equation 2 is accurate as shown in figure 1 for up to 5,000 mg/L chloride.

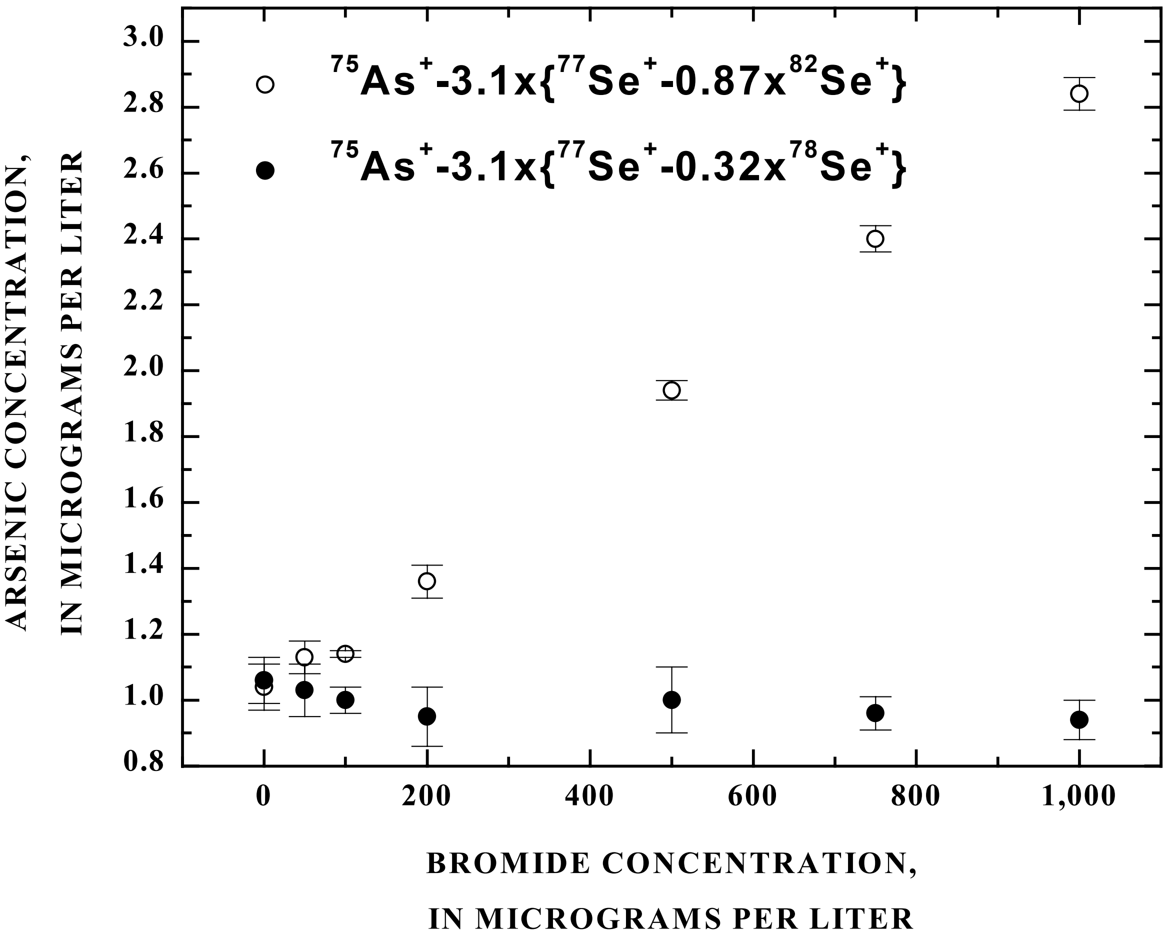


Figure 8. Accuracy of inductively coupled plasma–mass spectrometric arsenic determinations in the presence of bromide using different correction equations. The error bars correspond to one standard deviation based on three instrumental measurements.

Equation 5 must be used to correct chloride interference on $^{51}V^+$; it is derived as follows:

$$^{51}V^+_{corr} = {}^{51}V^+ - [^{35}Cl^{16}O/^{37}Cl^{16}O] \times \{^{37}Cl^{16}O - [^{53}Cr/^{52}Cr] \times {}^{52}Cr^+\}. \quad (4)$$

The portion of the signal at 51 amu from the $^{35}Cl^{16}O^+$ interference is calculated by converting the signal at 53 amu from $^{37}Cl^{16}O^+$ (by measuring $^{53}Cr^+$) after subtracting the contribution from $^{53}Cr^+$ (by measuring $^{52}Cr^+$) to its proportion at 51 amu. After substituting constant terms that are based on natural abundance, equation 4 simplifies to

$$^{51}V^+_{corr} = {}^{51}V^+ - 3.127 \times \{^{53}Cr^+ - [0.113] \times {}^{52}Cr^+\}. \quad (5)$$

The accuracy of using equation 5 is shown in figure 7 for chloride concentrations less than 5,000 mg/L.

Masses at 52 and 53 amu are effected by interference from $^{40}Ar^{12}C^+$ and $^{40}Ar^{13}C^+$, respectively, that arise from any carbon present in the sample. The interference correction is based on the linear relation of the response at 52 amu from $^{40}Ar^{12}C^+$ to the concentration of carbon as shown in figure 9 (a similar linear relation is used for $^{53}Cr^+$). A water-soluble carbon compound such as sodium carbonate can be used to determine the relation (see Krushevska and others, 1998). The corrections are based on equations 6 and 7.

$$^{52}Cr^+_{corr} = {}^{52}Cr^+ - (^{52}Cr^+ / {}^{13}C^+) \times {}^{13}C^+. \quad (6)$$

$$^{53}Cr^+_{corr} = {}^{53}Cr^+ - (^{53}Cr^+ / {}^{13}C^+) \times {}^{13}C^+. \quad (7)$$

The terms ($^{52}Cr^+ / {}^{13}C^+$) and ($^{53}Cr^+ / {}^{13}C^+$) are variables that equal about 0.2 and 0.002, respectively. These variables depend on the instrument operating conditions and must be determined before every calibration. When using equation 6, figure 10 shows that the carbon interference can be eliminated. Such a correction is accurate at carbon concentrations to 1,000 mg/L. The $^{40}Ar^{13}C^+$ interference at $^{53}Cr^+$ is less severe than the corresponding interference at $^{52}Cr^+$ because of the lower natural abundance of ^{13}C. Nevertheless, the accuracy of using equation 7 is comparable to that shown in figure 10 for $^{52}Cr^+$.

3.5 *Doubly charged ion interferences.* A doubly charged ion is created in the plasma for any element that has a second ionization potential less than the ionization potential of argon. Strontium is the only new element that is potentially affected by doubly charged ion interferences. However, lutetium and ytterbium rarely are found in environmental samples at significant concentrations, and their interfering isotopes ($^{176}Lu^{2+}$ and $^{176}Yb^{2+}$) have low natural abundance.

4. Apparatus, Instrumentation, and Operating Conditions

4.1 *Labware.* Use clean Type A glass volumetric flasks to prepare all solutions. Store solutions in fluorinated ethylene propylene (FEP Teflon) bottles to maintain stable elemental concentrations. Regularly verify the accuracy of all pipets and volumetric flasks for preparing standard solutions by using either an analytical balance or an automatic calibrating spectrophotometer.

4.2 *Instrumentation.* Instrumentation previously described in methods by Faires (1993) and Garbarino and Taylor (1994) has been replaced by a Perkin-Elmer Elan 6000 ICP–MS. The Elan 6000 operates under the same general principles as earlier instrumentation but has higher sensitivity and lower MDLs. The standard Perkin-Elmer cross-flow nebulizer and spray chamber is used to introduce samples. The cross-flow nebulizer resists clogging (≤ 0.5 percent total dissolved solids) and is chemically inert.

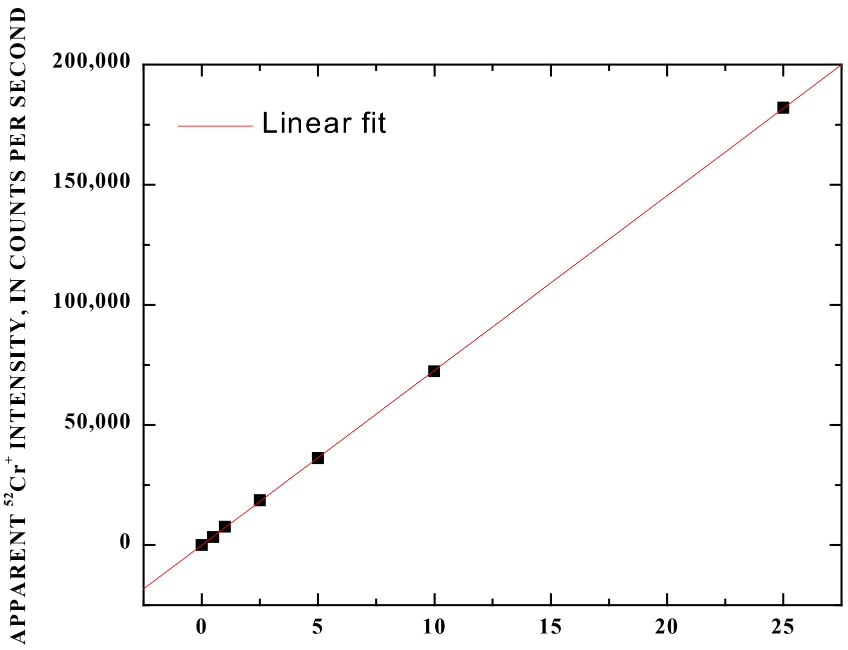


Figure 9. Relation of apparent chromium-52 signal from $^{40}Ar^{12}C^{+}$ as a function of increasing concentrations of carbon.

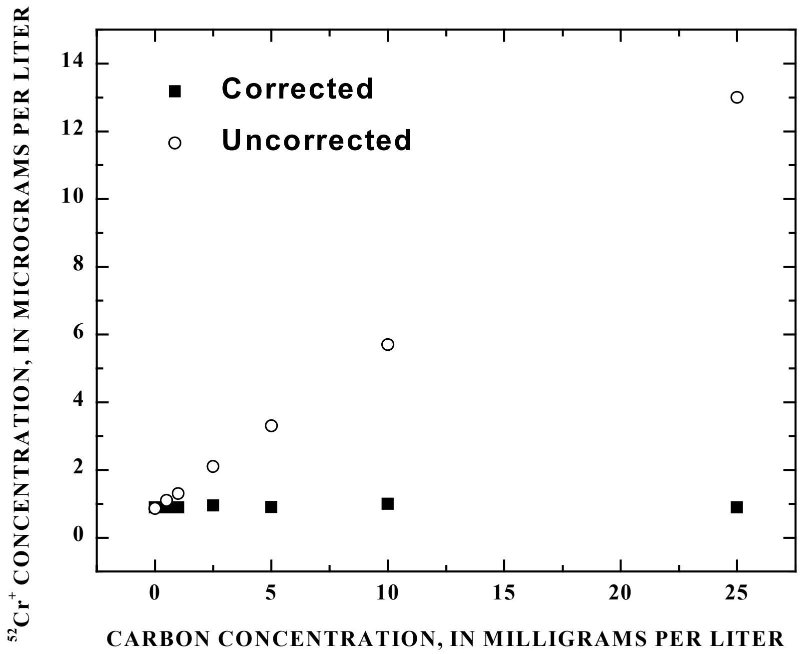


Figure 10. The accuracy of inductively coupled plasma–mass spectrometric chromium-52 determinations in the presence of carbon.

Other nebulizer designs can be used but must be resistant to clogging and capable of providing MDLs that are within a factor of two of those listed in table 1. Details of instrument operation are fully documented in the NWQL Standard Operating Procedure IM0011.1 (T.M. Struzeski, U.S. Geological Survey, written commun., 1998) and in the Perkin-Elmer (1997a and 1997b) software and hardware manuals.

Primary isotopes used to determine dissolved concentrations for the new elements are as follows:

Arsenic	75 amu	Boron	11 amu
Lithium	7 amu	Selenium	78 & 82 amu
Strontium	88 amu	Thallium	205 amu
Vanadium	51 amu		

5. Reagents and Calibration Standards

Earlier reports (Faires, 1993; Garbarino and Taylor, 1994) describe the preparation of calibration standards, internal standard solution, performance check solution, and tuning solution. New elements are calibrated by including them in the multielement standards described in method I-2477-92 at the same concentrations. Multielement standards are prepared in a matrix that is matched to the acid concentration of the samples being analyzed. Arsenic, selenium, and vanadium must not be included in a multielement standard that contains bromide or chloride. The interference solution has been added to verify the accuracy of interference corrections on arsenic and vanadium.

ASTM Type I reagent water (American Society for Testing and Materials, 1995, p. 122–124), spectroscopic grade commercial standards, and ultrapure acids must be used to prepare all solutions. All percentages represent volume-to-volume ratios. All concentrated acids and commercial standards must be verified to contain concentrations of concomitant elements that are less than the MDLs after the prescribed dilution. Every solution must be stored in a designated FEP Teflon bottle.

5.1 *Nitric acid* (HNO_3): Concentrated, specific gravity 1.41.

5.2 *Calibration blank*: Reagent water acidified to 0.4 percent HNO_3.

5.3 *Commercial single-element standard solutions*, 1.00 mL = 10 mg preserved in HNO_3 for each of the following: As, B (in water), Li, Se, Sr, Tl, and V.

5.4 *Commercial standard solutions*, chloride: 1.00 mL = 100 mg in water and bromide: 1.00 mL = 1.0 mg in water.

5.5 *Carbon standard solution,* 1.00 mL = 10 mg of carbon. Weigh 88.3 g dry Na_2CO_3 and transfer quantitatively into a 1-L volumetric flask; dissolve salt using 1,000 mL of reagent water.

5.6 *Multielement stock solution I*, 1.00 mL = 0.010 mg of As, B, Li, Se, Sr, Tl, and V: Dilute 1.0 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent HNO_3.

5.7 5.7 *Multielement calibration standard I,* 1.00 mL = 0.025 µg of As, B, Li, Se, Sr, Tl, and V: Include new elements in an existing calibration standard by diluting 0.250 mL of multielement stock solution I in a 100-mL volumetric flask with the calibration blank.

5.8 *Multielement calibration standard II,* 1.00 mL = 0.100 µg of As, B, Li, Se, Sr, Tl, and V: Include new elements in an existing calibration standard by diluting 1.0 mL of multielement stock solution I in a 100-mL volumetric flask with the calibration blank.

5.9 *Multielement calibration standard III*, 1.00 mL = 0.200 µg of As, B, Li, Se, Sr, Tl, and V: Include new elements in an existing calibration standard by diluting 2.0 mL of multielement stock solution I in a 100-mL volumetric flask with the calibration blank.

5.10 *Interference check standard*, 1.00 mL = 0.500 mg Cl, 0.0005 mg Br, 0.025 mg C, and 0.005 µg As and V: Dilute 5.0 mL of the commercial chloride standard solution, 0.50 mL of commercial bromide standard solution, 2.5 mL of carbon standard solution, and 0.50 mL of multielement stock solution I in a 1,000-mL volumetric flask with the calibration blank.

6. Sample Preparation

Filtered, acidified natural-water samples analyzed by ICP–MS for dissolved arsenic, boron, lithium, selenium, strontium, thallium, and zinc and other elements do not require additional processing.

7. Analytical Procedure

Refer to Perkin-Elmer (1997a, 1997b) and NWQL Standard Operating Procedure IM0011.1 (T.M. Struzeski, U.S. Geological Survey, written commun., 1998) for details of the analytical procedure. In addition, the accuracy of interference-correction equations must be determined by analyzing the interference check standard (see section 5.10) with every batch of samples. The Elan software automatically verifies that the results meet acceptance criteria.

8. Calculations

No additional calculations are required in this method.

9. Reporting Results

The number of significant figures reported varies with element and is a function of concentration. Whenever the concentration is less than the MDL for an element, the result is reported as less than the MDL (< MDL). All other elemental results should be reported using the criteria listed below. These criteria are based on the uncertainty suggested in the following Discussion of Results section. Alternatively, the variability in the mean concentration could be used to establish the appropriate number of significant figures to report for each individual sample matrix. The use of such a procedure would provide the most accurate estimate of the uncertainty associated with each sample.

For arsenic, lithium, and vanadium—

- If the concentration is greater than the MDL, but less than 10 µg/L, report result to two decimal places.

- If the concentration is greater than 10 µg/L, but less than 100 µg/L, report result to one decimal place.

- If the concentration is greater than 100 µg/L, report result to three significant figures.

For strontium and thallium—

- If the concentration is greater than the MDL, but less than 0.5 µg/L, report result to three decimal places.
- If the concentration is greater than 0.5 µg/L, but less than 10 µg/L, report result to two decimal places.
- If the concentration is greater than 10 µg/L, but less than 100 µg/L, report result to one decimal place.
- If the concentration is greater than 100 µg/L, report result to three significant figures.

For boron—

- If the concentration is greater than or equal to the MDL, but less than 100 µg/L, report result to one decimal place.
- If the concentration is greater than 100 µg/L, report result to three significant figures.

DISCUSSION OF RESULTS

The bias of the ICP–MS method for the determination of dissolved concentrations is established by comparing results to former USGS methods of analysis. ICP–MS method variability was determined from replicate analyses over a range of elemental concentrations prepared in a calibration-blank matrix. Results from the analysis of standard reference material, spiked samples, and up to 64 filtered natural-water samples are used to verify that dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium can be determined accurately by using ICP–MS. All former methods are USGS-approved methods (Fishman and Friedman, 1989; Fishman, 1993).

Results for Standard Reference Material

U.S. Geological Survey SRWS T145 was analyzed repetitively for 3 weeks to determine the long-term bias and variability of the ICP–MS method (see table 4). Results for all elements are within one standard deviation of the most probable value (MPV). The average long-term variability is 4±2 percent for elemental concentrations ranging from 10 to 200 µg/L. The paired Student *t*-Test was used to test the null hypothesis that the ICP–MS method yields mean elemental concentrations that are not significantly different from the MPVs. The p-values were calculated for each element to provide a level of confidence in accepting the null hypothesis. The larger the p-value (the level of significance) the greater the confidence in accepting the null hypothesis. When the p-value exceeds 0.05, the null hypothesis is acceptable at the 95-percent confidence level. The Student *t*-Test indicated that only the boron and lithium experimental results are not significantly different from the MPV. Nevertheless, the differences between the MPV and the experimental mean for arsenic, selenium, strontium, thallium, and vanadium are analytically insignificant.

The short-term variability of ICP–MS over an extended concentration range is shown in table 5. The variability is based on three replicate determinations (an acquisition time of about 1 minute) at each elemental concentration in the calibration blank matrix. The short-term variability was less than or equal to 5 percent at 0.5 µg /L for all elements except for boron which was 5 percent at 1 µg/L.

Table 4. Statistical analysis of long-term ICP–MS results for U.S. Geological Survey Standard Reference Water Sample T145

[ICP–MS, inductively coupled plasma–mass spectrometry; elemental results are in micrograms per liter; MPV, the most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation in the experimental mean column; n, number of replicates used to calculate the experimental mean; p-value, level of significance; <, less than]

Element	MPV	Experimental mean, n=12	*t*-Test statistic	p-value
Arsenic	10 ± 1	10.3 ± 0.2	9.00	<0.0001
Boron	46 ± 6	45 ± 3	-0.23	0.8253
Lithium	27 ± 2	28 ± 1	1.54	0.1528
Selenium	10 ± 1	11.2 ± 0.2	18.63	<0.0001
Strontium	203 ± 9	208 ± 4	3.93	0.0024
Thallium	15 ± 3	14 ± 1	-3.12	0.0098
Vanadium	12 ± 2	10.6 ± 0.5	-7.86	<0.0001

Spike Recoveries in Natural-Water Samples

Spike recovery percentages listed in table 6 were determined for the new elements in matrices that are representative of reagent water, surface water, and ground water. Seven replicate recoveries at 5 to 10 times the MDL (the low-level spike) and 75 µg/L (the high-level spike) were determined in each matrix over a period of about 1 week. Average recoveries in the reagent-water matrix ranged from 93 to 105 percent for all elements except boron, whose low-level spike recovery was 77 percent. Recovery variability for the low-level spike ranged from 4 to 11 percent, depending on the element and matrix.

Recoveries of the high-level spike in the surface-water matrix were similar to those of the reagent-water matrix. Ambient concentrations of lithium, strontium, thallium, and vanadium in the surface water, however, hindered the recovery of the low-level spike. Recovery of low-level arsenic, boron, and selenium ranged from 88 to 126 percent. The variability in the recovery of 1 µg/L boron in the presence of 40 µg/L boron was 52 percent; the variability for arsenic and selenium was less than 6 percent at about the same spike concentration.

The ground-water matrix used for spike recoveries was selected to examine the effects of interferent species on elemental determinations. The ground water had high iron (340 mg/L) and sulfate (2,300 mg/L) concentrations, which exceed the level found in most samples analyzed by NWQL. Ambient concentrations of boron, lithium, and strontium precluded the recovery of the low-level spike, however, recoveries for arsenic, selenium, thallium, and vanadium averaged 70 percent. High-level spike recoveries averaged 70±4 percent, excluding thallium, which had 97 percent. The low percent recoveries for the lighter elements confirm the effects from ionization suppression (see section 3.1). Only thallium recovery, a heavier element, was not affected.

Table 5. Short-term analytical variability as a function of elemental concentration for ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry, the percent relative standard deviations are based on three sequential determinations in a 0.4-percent solution of concentrated nitric acid in deionized water; µg/L, micrograms per liter; <MDL, less than the method detection limit; nd, not determined]

Elemental concentration, in µg/L	Percent relative standard deviation							
	0.05	0.1	0.5	1.0	10	50	100	250
Arsenic	<MDL	30	3	4	2	nd	1	0.6
Boron	nd	10	nd	5	2	0.4	0.2	nd
Lithium	0.9	8	2	2	0.7	nd	0.7	0.6
Selenium	<MDL	60	5	3	2	nd	2	0.7
Strontium	0.4	2	2	0.8	0.3	nd	0.7	0.6
Thallium	2	2	0.2	0.9	2	nd	0.8	1
Vanadium	8	10	2	0.6	0.7	nd	0.5	0.5

Table 6. Average percent spike recoveries in reagent-water, surface-water and ground-water matrices by inductively coupled plasma–mass spectrometry

[µg/L, micrograms per liter; number following the plus or minus symbol (±) is the standard deviation on the basis of seven determinations accrued on separate days; high spike, 75 µg/L for all elements; na, not applicable because the difference between the spike concentration and ambient concentration was greater than a factor of 10; <MDL, concentration is less than the method detection limit; %, percent]

Element	Low-spike, in µg/L	Reagent-water matrix			Surface-water matrix		
		Ambient concentration, in µg/L	Low-spike recovery, in %	High-spike recovery, in %	Ambient concentration, in µg/L	Low-spike recovery, in %	High-spike recovery, in %
Arsenic	0.5	<MDL	102±4	101±1	1	112±6	105±2
Boron	1	<MDL	77±9	103±2	40	88±52	102±4
Lithium	0.2	<MDL	94±8	105±3	30	na	99±7
Selenium	0.9	<MDL	110±10	99±2	2	126±7	104±3
Strontium	0.2	<MDL	93±4	104±3	390	na	114±8
Thallium	0.05	<MDL	97±11	100±6	60	na	103±5
Vanadium	0.6	<MDL	98±4	105±4	60	na	104±4
		Ground-water matrix					
Arsenic	0.5	1	75±8	68±4			
Boron	1	350	na	70±20			
Lithium	0.2	220	na	72±12			
Selenium	0.9	1	80±10	73±4			
Strontium	0.2	6,000	na	na			
Thallium	0.05	<MDL	60±20	97±5			
Vanadium	0.6	<MDL	64±20	64±10			

Comparison of Inductively Coupled Plasma–Mass Spectrometry to Former Methods of Analysis

The ICP–MS results are compared to former methods of analysis such as hydride generation–atomic absorption spectrophotometry (HG–AAS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES). Up to 64 filtered, acidified natural-water samples were selected from the population of such samples submitted to the NWQL. The samples have a wide range of elemental concentrations and specific conductance. Surface-water and ground-water samples are included in the sample set; the number of each type is about proportional to its fraction of the total submitted for analysis during an average year. Other chemical characteristics that often influence the performance of analytical methods, such as sulfate and chloride concentrations, were also considered in the selection process (see table 7 for the chemical characteristics of the samples).

Results were evaluated by using several different approaches. Because the data extend over a wide concentration range, it is inappropriate to use the paired Student *t*-test to evaluate the null hypothesis because errors, whether random or systematic, are independent of the concentration. Consequently, linear regression analysis is used to calculate the slope, *y*-intercept, and coefficient of determination (R^2) for the equation that describes the relation between ICP–MS and a former USGS method. A slope coefficient of one and a *y*-intercept of zero indicate exact correlation. The corresponding p-values indicate the degree of confidence in each coefficient. Box plots are also provided to show the distribution of the results from each method. The non-parametric Wilcoxon Signed Rank Test is used as another test to determine whether there is a significant difference between results from the ICP–MS and former USGS methods. Data that were less than the highest MDL or MRL were omitted from the data set prior to statistical analysis. Statistical analysis results are summarized in the following paragraphs and are listed in table 8. Illustrations for the statistical tests are provided in figures 11 through 16.

Table 7. Chemical characteristics of natural-water samples used to evaluate ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry; µg/L, microgram per liter; mg/L, milligram per liter; <MDL, less than the method detection limit; SC, specific conductance]

Element, in µg/L	25th percentile	Median	75th percentile	Maximum
Arsenic	1.7	2.9	7.4	104
Boron	52	120	210	1,700
Lithium	22	39	69	1,600
Selenium	2.9	4.5	8.2	34
Strontium	350	630	1,900	20,800
Thallium	All results were <MDL for former methods			
Vanadium	1.8	4.7	9.7	1,530
Constituent				
Chloride, in mg/L	9.8	68	501	9,176
SC, in µS/cm[1]	455	944	2,490	52,600
Sulfate, in mg/L	108	309	1,306	16,832

[1] Specific conductance in microsiemens per centimeter at 25 °C (µS/cm).

Results of the linear regression analyses show that there is strong correlation between ICP–MS and former USGS methods for the analysis of filtered, acidified natural water. The slope coefficients range from 0.90 to 1.1 (see table 8). The corresponding p-values indicate with 95-percent confidence that all the slopes are not significantly different from 1.0. Thallium concentrations were less than the GF–AAS and ICP–MS method detection limits in all samples. With the exception of lithium and vanadium, the p-values for the y-intercepts indicate a significant nonzero intercept that might result from differences in sensitivity or from the wide range of sample concentrations. For example, boron and strontium concentrations range from the MDLs to about 1,700 and 21,000 µg/L, respectively (see table 7).

The p-values of the Wilcoxon Signed Rank Test indicate with 95-percent confidence that there is no significant difference between ICP–MS and ICP–AES results for dissolved boron and vanadium. In general, the descriptive statistics and figures 11 through 16 indicate that differences among results for the other elements are analytically insignificant considering the range of sample concentrations in the data set.

Table 8. Statistical analysis summary of inductively coupled plasma–mass spectrometry and former methods of analysis

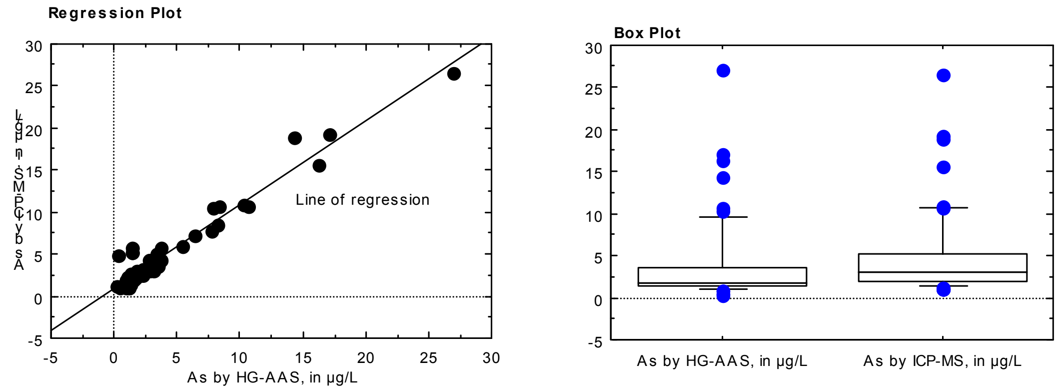
[Coef., either the slope or the y-intercept regression coefficient; p-value, level of significance; R^2, coefficient of determination; HG–AAS, hydride generation–atomic absorption spectrophotometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; GF–AAS, stabilized temperature graphite furnace–atomic absorption spectrophotometry; nd, not detected; <, less than. All thallium results were less than the method detection limit]

Element	Former method	Slope		*y*-intercept		R^2	Wilcoxon signed rank test p-value[c]
		Coef.	p-value[a]	Coef.	p-value[b]		
Arsenic	HG–AAS	1.0	<0.0001	0.95	<0.0001	0.945	<0.0001
Boron	ICP–AES	0.90	<0.0001	13	0.0002	0.995	0.3714
Lithium	ICP–AES	0.92	<0.0001	1.0	0.2197	0.999	<0.0001
Selenium	HG–AAS	1.1	<0.0001	1.7	0.0002	0.864	<0.0001
Strontium	ICP–AES	0.94	<0.0001	96	0.0044	0.996	0.0030
Thallium	GF–AAS	nd	nd	nd	nd	nd	nd
Vanadium	ICP–AES	0.96	<0.0001	0.10	0.9242	0.919	0.1340

[a] The null hypothesis: slope is not equal to one.

[b] The null hypothesis: y-intercept is equal to zero.

[c] The null hypothesis: the difference in concentration between the new inductively coupled plasma–mass spectrometric method and the former USGS method is equal to zero.



Descriptive Statistics

	As by HG-AAS, in µg/L	As by ICP-MS, in µg/L
Mean	3.82	4.76
Std. Dev.	4.87	4.99
Std. Error	0.63	0.65
Count	59	59
Minimum	0.20	0.93
Maximum	27.00	26.48
# Missing	0	0

Wilcoxon Signed Rank Test for As by HG-AAS, in µg/L, As by ICP-MS, in µg/L

# 0 Differences	0
# Ties	1
Z-Value	-6.01
P-Value	<0.0001
Tied Z-Value	-6.01
Tied P-Value	<0.0001

Wilcoxon Rank Info for As by HG-AAS, in µg/L, As by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	53	1681.50	31.73
# Ranks > 0	6	88.50	14.75

EXPLANATION

Hydride generation-atomic absorption spectrophotometry (HG-AAS); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

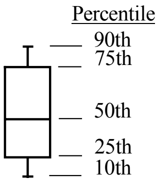
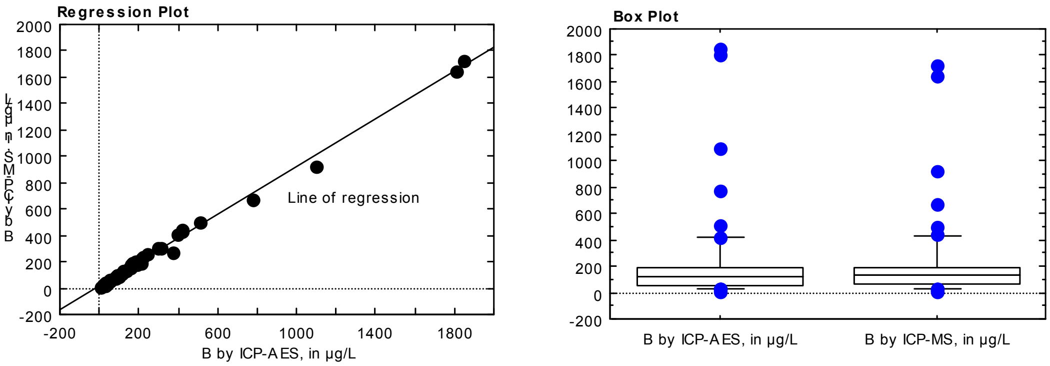


Figure 11. Statistical analysis of **arsenic (As)** results for 59 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and hydride generation–atomic absorption spectrophotometry.



Descriptive Statistics

	B by ICP-AES, in µg/L	B by ICP-MS, in µg/L
Mean	218.74	210.77
Std. Dev.	347.35	315.04
Std. Error	44.11	40.01
Count	62	62
Minimum	9.15	10.31
Maximum	1849.43	1721.82
# Missing	0	0

Wilcoxon Signed Rank Test for B by ICP-AES, in µg/L, B by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-0.89
P-Value	0.3714
Tied Z-Value	-0.89
Tied P-Value	0.3714

Wilcoxon Rank Info for B by ICP-AES, in µg/L, B by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	34	1104.00	32.47
# Ranks > 0	28	849.00	30.32

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

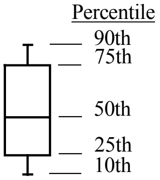
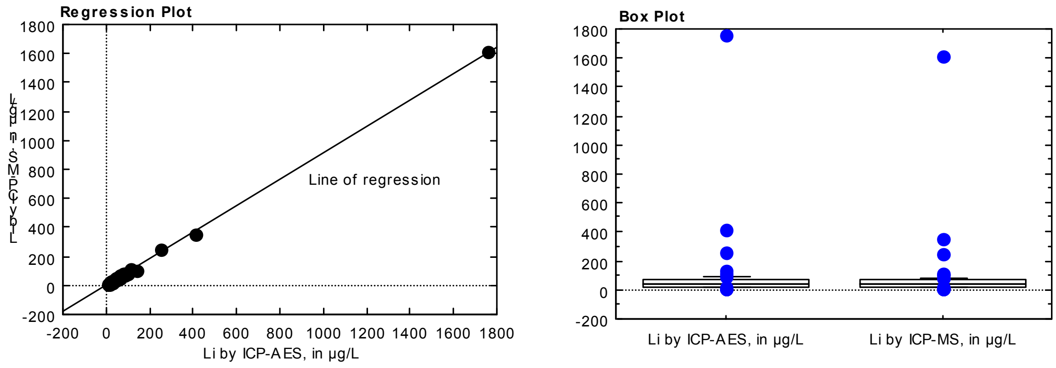


Figure 12. Statistical analysis of **boron (B)** results for 62 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrophotometry.



Descriptive Statistics

	Li by ICP-AES, in µg/L	Li by ICP-MS, in µg/L
Mean	81.33	75.39
Std. Dev.	223.15	204.17
Std. Error	28.11	25.72
Count	63	63
Minimum	5.20	4.01
Maximum	1760.38	1615.30
# Missing	0	0

Wilcoxon Signed Rank Test for Li by ICP-AES, in µg/L, Li by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-3.90
P-Value	<0.0001
Tied Z-Value	-3.90
Tied P-Value	<0.0001

Wilcoxon Rank Info for Li by ICP-AES, in µg/L, Li by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	19	439.00	23.11
# Ranks > 0	44	1577.00	35.84

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

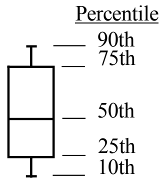
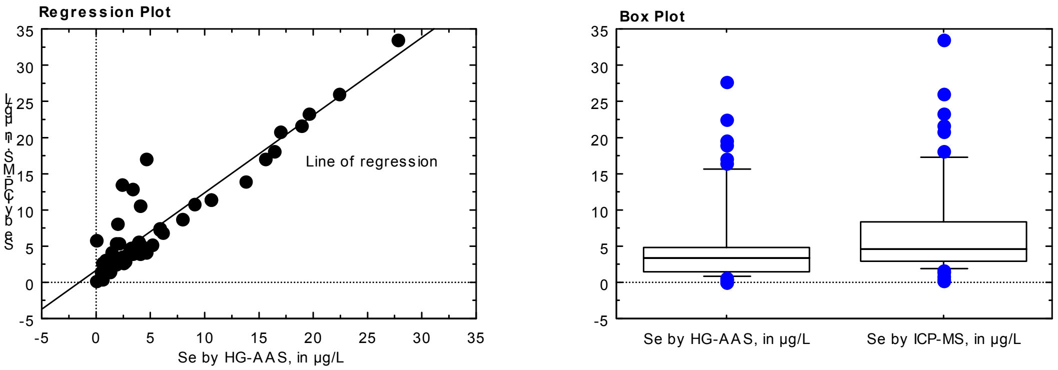


Figure 13. Statistical analysis of **lithium (Li)** results for 63 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrophotometry.



Descriptive Statistics

	Se by HG-AAS, in µg/L	Se by ICP-MS, in µg/L
Mean	5.07	7.09
Std. Dev.	5.91	6.80
Std. Error	0.74	0.85
Count	64	64
Minimum	0	0.22
Maximum	27.80	33.62
# Missing	0	0

Wilcoxon Signed Rank Test for Se by HG-AAS, in µg/L, Se by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-6.86
P-Value	<0.0001
Tied Z-Value	-6.86
Tied P-Value	<0.0001

Wilcoxon Rank Info for Se by HG-AAS, in µg/L, Se by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	62	2066.00	33.32
# Ranks > 0	2	14.00	7.00

EXPLANATION

Hydride generation-atomic absorption spectrophotometry (HG-AAS); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

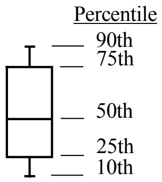
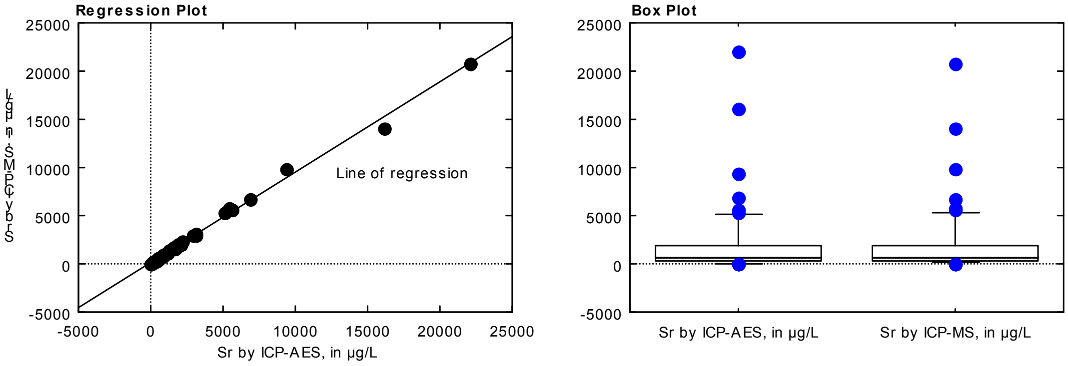


Figure 14. Statistical analysis of **selenium (Se)** results for 64 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and hydride generation–atomic absorption spectrophotometry.



Descriptive Statistics

	Sr by ICP-AES, in µg/L	Sr by ICP-MS, in µg/L
Mean	1891.95	1870.69
Std. Dev.	3644.10	3425.62
Std. Error	459.11	431.59
Count	63	63
Minimum	31.02	30.53
Maximum	22068.32	20823.39
# Missing	1	1

Wilcoxon Signed Rank Test for Sr by ICP-AES, in µg/L, Sr by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-2.96
P-Value	0.0030
Tied Z-Value	-2.96
Tied P-Value	0.0030

One case w as omitted due to missing values.

Wilcoxon Rank Info for Sr by ICP-AES, in µg/L, Sr by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	43	1441.00	33.51
# Ranks > 0	20	575.00	28.75

One case w as omitted due to missing values.

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

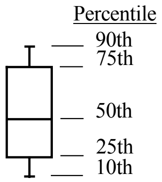
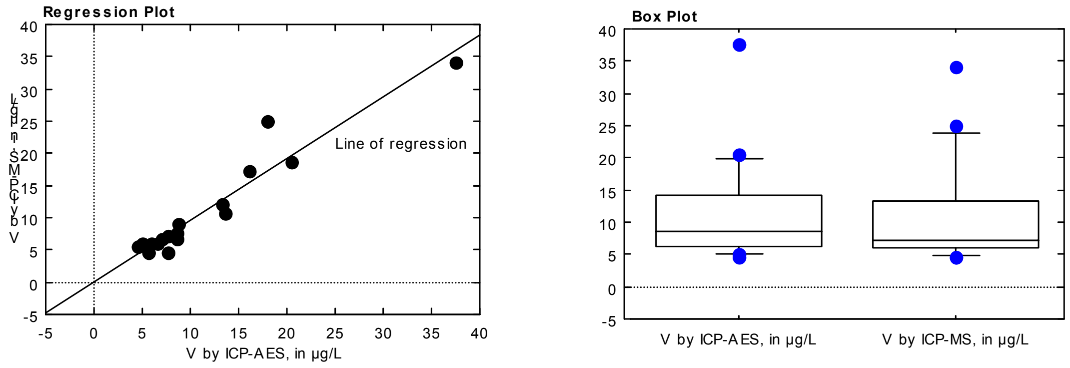


Figure 15. Statistical analysis of **strontium (Sr)** results for 63 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrophotometry.



Descriptive Statistics

	V by ICP-AES, in µg/L	V by ICP-MS, in µg/L
Mean	11.46	11.06
Std. Dev.	8.23	8.21
Std. Error	2.00	1.99
Count	17	17
Minimum	4.60	4.64
Maximum	37.54	34.10
# Missing	0	0

Wilcoxon Signed Rank Test for V by ICP-AES, in µg/L, V by ICP-MS, in µg/L

# 0 Differences	0
# Ties	0
Z-Value	-1.49
P-Value	0.1359
Tied Z-Value	-1.49
Tied P-Value	0.1359

Wilcoxon Rank Info for V by ICP-AES, in µg/L, V by ICP-MS, in µg/L

	Count	Sum Ranks	Mean Rank
# Ranks < 0	6	45.00	7.50
# Ranks > 0	11	108.00	9.82

EXPLANATION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES); Inductively coupled plasma-mass spectrometry (ICP-MS); micrograms per liter (µg/L); Std. Dev., standard deviation; Std. Error, standard error; <, less than; >, greater than; #, number

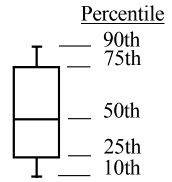


Figure 16. Statistical analysis of **vanadium (V)** results for 17 filtered, acidified, natural-water samples from inductively coupled plasma–mass spectrometry and inductively coupled plasma–atomic emission spectrophotometry.

CONCLUSIONS

Results from reference material, spike recoveries, and the analysis of natural-water samples were used to evaluate the overall bias and variability of the determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium by inductively coupled plasma–mass spectrometry (ICP–MS). All test results provide an accurate estimate of the expected analytical performance. The following list outlines the major conclusions of this report. In addition to analytical performance comparisons, suggestions are provided for selecting appropriate methodology and the potential effects of the use of ICP–MS on long-term trend analysis in water-quality studies.

- Method detection limits (MDLs) for ICP–MS are between about 10 and 200 times lower than hydride generation–atomic absorption spectrophotometry (HG–AAS) and inductively coupled plasma–atomic emission spectrometry (ICP–AES) methods.

- The short- and long-term accuracy for the determination of the new elements by ICP–MS were acceptable; all the elements were within one standard deviation of the most probable value.

- Data from up to 64 surface- and ground-water samples indicated that there was no significant method bias for the determination of dissolved arsenic, boron, lithium, selenium, strontium, and vanadium by ICP–MS.

- Determination of dissolved arsenic and selenium by ICP–MS does not require any digestion procedure as does the HG–AAS method.

- Matrix interferences from high concentrations of concomitant metals can affect the determination of lighter elements (< 60 amu). The concomitant concentrations that cause significant interference, however, are generally above the 99th percentile of elemental concentrations in samples submitted to the National Water Quality Laboratory (NWQL).

- ICP–MS is a state-of-the-art multielement technique that is more efficient and cost effective than former USGS single-element methods, such as HG–AAS. ICP–MS is the method of choice whenever multiple elements must be determined or whenever elemental concentrations are less than 10 μg/L.

- Use of the ICP–MS method for the determination of arsenic and selenium reduces the amount of chemical reagents and chemical waste when compared to HG–AAS.

- Data from ICP–MS will affect long-term trends in water-quality studies because of the reduced bias and variability at elemental concentrations less than 10 μg/L.

REFERENCES CITED

American Society for Testing and Materials, 1995, Annual book of ASTM standards, Section 11, Water (D1193, Standard specification for reagent water): Philadelphia, v. 11.01, p. 122–124.

Douglas, D.J., 1992, Fundamental aspects on inductively coupled plasma–mass spectrometry *in* Montaser, Akbar, and Golightly, D.W., eds., Inductively coupled plasmas in analytical atomic spectrometry (2d ed.): New York, VCH Publishers, Inc., p. 614.

Faires, L.M., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of metals in water by inductively coupled plasma–mass spectrometry: U.S. Geological Survey Open-File Report 92-634, 28 p.

Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma–optical emission spectrometry and inductively coupled plasma–mass spectrometry: U.S. Geological Survey Open-File Report 98-165, 101 p.

Garbarino, J.R., and Taylor, H.E., 1994, Inductively coupled plasma–mass spectrometric determination of dissolved trace elements in natural water: U.S. Geological Survey Open-File Report 94-358, 28 p.

Horlick, Gary, and Shao, Youbin, 1992, Inductively coupled plasma–mass spectrometry for elemental analysis *in* Montaser, Akbar, and Golightly, D.W., eds., Inductively coupled plasmas in analytical atomic spectrometry (2d ed.): New York, VCH Publishers, Inc., p. 551.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Krushevska, Antoaneta, Waheed, Shahida, Nóbrega, Joaquim, Amarisiriwardena, Dulasiri, and Barnes, R.M., 1998, Reducing polyatomic interferences in the ICP–MS determination of chromium and vanadium in biofluids and tissues: Applied Spectroscopy, v. 52, no. 2, p. 205–211.

Perkin-Elmer, 1997a, Elan 6000 inductively coupled plasma–mass spectrometer software guide: Norwalk, Connecticut, Perkin-Elmer part number 0993-8968 Rev. F.

_______1997b, Elan 6000 inductively coupled plasma–mass spectrometer hardware guide: Norwalk, Connecticut, Perkin-Elmer part number 0993-8969 Rev. E.

U.S. Environmental Protection Agency, 1997, Guidelines for establishing test procedures for the analysis of pollutants (Part 136, Appendix B. Definition and procedure for the determination of the method detection limit—Revision 1.11): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 1997, p. 265–267.

Printed on recycled paper