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

By John R. Garbarino and Tedmund M. Struzeski

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

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director

For addtional information write to:

U.S. Gelogical Survey
Chief, National Water Quality Laboratory
Box 25046, Mail Stop 407
Federal Center
Denver, CO 80225-0425

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286, Mail Stop 417
Denver Federal Center
Denver, CO 80225-0046

Contents

CONTENTS—Continued

FIGURES

1. Schematics showing:

2–30. Graphs showing:

FIGURES—Continued

FIGURES—Continued

FIGURES—Continued

FIGURES—Continued

FIGURES—Continued

TABLES

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

Multiply	By	To obtain
liter (L)	2.64×10^{-1}	gallon
meter (m)	3.94×10^{1}	inch
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
millibar	1.93×10^{-2}	pounds per square inch
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon
millimeter (mm)	3.94×10^{-2}	inch
nanometer (nm)	3.94×10^{-8}	inch

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

$$^{o}F = 9/5\ (^{o}C) + 32$$

Abbreviated water-quality units used in this report:

L/min	liter per minute
mL/min	milliliters per minute
mg/L	milligram per liter
mg/mL	milligram per milliliter
µg/L	microgram per liter
µL	microliter
µS/cm	microsiemens per centimeter at 25°C

Other abbreviations used in this report:

amu	atomic mass unit
ASTM	American Society for Testing and Materials
CAS	Chemical Abstract Service
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
ICP–MS	inductively coupled plasma–mass spectrometry
ICP–OES	inductively coupled plasma–optical emission spectrometry, also known as inductively coupled plasma–atomic emission spectrometry (ICP–AES)
kW	kilowatt
lb/in^2	pound per square inch

MDL(s)	method detection limit(s)
MHz	megahertz
MPV(s)	most probable value(s)
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
QA/QC	quality assurance/quality control
SRWS(s)	U.S. Geological Survey Standard Reference Water Sample(s)
SOP	standard operating procedure
W	watt
~	approximate
>	greater than
<	less than
±	plus or minus

Glossary

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 elemental 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, 1994).
MPV	The most probable value (MPV) is equal to the mean value for numerous interlaboratory analyses using multiple analytical methods.
Spectrum shifter step	One step equals about 0.008 nm.

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ABSTRACT

Inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) can be used to determine 26 elements in whole-water digests. Both methods have distinct advantages and disadvantages—ICP–OES is capable of analyzing samples with higher elemental concentrations without dilution, however, ICP–MS is more sensitive and capable of determining much lower elemental concentrations. Both techniques gave accurate results for spike recoveries, digested standard reference-water samples, and whole-water digests. Average spike recoveries in whole-water digests were 100±10 percent, although recoveries for digests with high dissolved-solid concentrations were lower for selected elements by ICP–MS. Results for standard reference-water samples were generally within 1 standard deviation of the most probable values. Statistical analysis of the results from 43 whole-water digests indicated that there was no significant difference among ICP–OES, ICP–MS, and former official methods of analysis for 24 of the 26 elements evaluated.

INTRODUCTION

Elements associated with water-suspended particulate material are an important fraction of the total elemental composition of natural water. Elements adsorbed to the surface of the particulate material are solubilized by using a mineral acid medium at low temperature and filtered to produce the whole-water digest (Hoffman and others, 1996). The U.S. Geological Survey's National Water Quality Laboratory (NWQL) offers several methods for the determination of elements in whole-water digests. Former methods use single-element quantification that is based on either atomic absorption or atomic emission spectrophotometry. Alternative methods by use of inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) technology provide simultaneous multielement determinations that reduce analytical costs while maintaining or exceeding the analytical performance of earlier methods. The elements determined by ICP–OES and ICP–MS methods are listed as follows:

Element	ICP–OES	ICP–MS	Element	ICP–OES	ICP–MS
Aluminum	✓	✓	Magnesium	✓	
Antimony		✓	Manganese	✓	✓
Barium	✓	✓	Molybdenum	✓	✓
Beryllium	✓	✓	Nickel	✓	✓
Boron	✓		Selenium		✓
Cadmium	✓	✓	Silicon	✓	
Calcium	✓		Silver	✓	✓
Chromium		✓	Sodium	✓	
Cobalt	✓	✓	Strontium	✓	✓
Copper	✓	✓	Thallium		✓
Iron	✓		Uranium		✓
Lead	✓	✓	Vanadium	✓	
Lithium	✓	✓	Zinc	✓	✓

The objectives of this report are to:

- Provide a detailed description of new ICP–OES and ICP–MS methods for whole-water digest analysis. Detailed descriptions of operating conditions and procedures are concisely outlined in sections 1A-8A and 1B-8B, respectively.
- Compare the accuracy of ICP–OES and ICP–MS methods to former methods of analysis. Multiple strategies are used in the statistical analysis of the experimental data to provide a practical estimate of the expected accuracy.
- Compare the variability of ICP–OES and ICP–MS methods to former methods of analysis.
- Compare the analytical performance of ICP–OES and ICP–MS methods.
- Estimate potential effects on long-term water-quality studies.
- Provide guidance for selecting the most appropriate method of analysis.

Whole-water recoverable elements at present determined by flame–atomic absorption spectrophotometry and by direct current plasma–atomic emission spectrometry will be determined by ICP–OES effective December 1, 1998. The ICP–MS method described in this report will be implemented at a date to be announced. The methods were developed by the U.S. Geological Survey (USGS) for use at the NWQL. These methods supplement other methods of the USGS that are described by Fishman and Friedman (1989) and by Fishman (1993).

ANALYTICAL METHODS

Inorganic Constituents and Parameter Codes: Metals, Acid Digestion, Whole-Water Recoverable, I-4471-97

Inductively coupled plasma–optical emission spectrometry

Parameter	Lab code	Parameter	Lab code	Parameter	Lab code
Aluminum, µg/L	2351	Copper, µg/L	2358	Nickel, µg/L	2365
Barium, µg/L	2352	Iron, µg/L	2359	Silica (SiO_2), mg/L	2366
Beryllium, µg/L	2353	Lead, µg/L	2360	Silver, µg/L	2367
Boron, µg/L	2354	Lithium, µg/L	2361	Sodium, mg/L	2368
Cadmium, µg/L	2355	Magnesium, mg/L	2362	Strontium, µg/L	2369
Calcium, mg/L	2356	Manganese, µg/L	2363	Vanadium, µg/L	2370
Cobalt, µg/L	2357	Molybdenum, µg/L	2364	Zinc, µg/L	2371

Inductively coupled plasma–mass spectrometry

Parameter	Lab code	Parameter	Lab code	Parameter	Lab code
Aluminum, µg/L	2372	Copper, µg/L	2379	Silver, µg/L	2386
Antimony, µg/L	2373	Lead, µg/L	2380	Strontium, µg/L	2387
Barium, µg/L	2374	Lithium, µg/L	2381	Thallium, µg/L	2388
Beryllium, µg/L	2375	Manganese, µg/L	2382	Uranium, µg/L	2389
Cadmium, µg/L	2376	Molybdenum, µg/L	2383	Zinc, µg/L	2390
Chromium, µg/L	2377	Nickel, µg/L	2384		
Cobalt, µg/L	2378	Selenium, µg/L	2385		

Inductively Coupled Plasma–Optical Emission Spectrometry

1A. Application

This method is used to determine aluminum, barium, beryllium, boron, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, silicon (reported as silica, SiO_2), silver, sodium, strontium, vanadium, and zinc in natural whole-water digested by using the in-bottle procedure described by Hoffman and others (1996). The method detection limits (MDLs) and analytical concentration ranges are listed in table 1. MDLs were calculated by using U.S. Environmental Protection Agency's (1994) definition and represent pooled averages on the basis of four MDLs determined on different days over several weeks.

2A. Summary of Method

Whole-water recoverable elements are determined simultaneously on a single sample using inductively coupled plasma–optical emission spectrometry. Sample solution is pumped into a high dissolved-solids tolerant nebulizer to produce an aerosol. The aerosol is subsequently transported by argon gas through a spray chamber and torch assembly into an inductively coupled plasma source where the

Table 1. Former methods, ICP–OES, and ICP–MS method detection limits and calibration limits for elements determined in whole-water digests

[All results are in micrograms per liter; MDL, method detection limit; ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; DCP–AES, direct current plasma–atomic emission spectrometry; GF–AAS, stabilized temperature graphite furnace–atomic absorption spectrophotometry; F–AAS, flame–atomic absorption spectrophotometry; na, not available; nd, not determined]

	Former methods			ICP–OES		ICP–MS	
Element	**Technique**	**MDL**	**Upper limit (without dilution)**	**MDL**	**Upper limit (without dilution)**	**MDL**	**Upper limit (without dilution)**
Aluminum	DCP–AES	[1] 10	10,000	14	500,000	1	1,000
Antimony	GF–AAS	0.8	25	nd	nd	0.7	500
Barium	F–AAS	[1] 100	5,000	0.5	10,000	0.08	1,000
Beryllium	F–AAS	[1] 10	200	2	10,000	0.07	500
Boron	DCP–AES	[1] 10	10,000	13	10,000	nd	nd
Cadmium	GF–AAS	0.06	5	5	10,000	0.05	500
Calcium	F–AAS	[1] 100	60,000	5	1,000,000	nd	nd
Chromium	GF–AAS	0.3	20	nd	nd	2	500
Cobalt	GF–AAS	0.4	25	7	10,000	0.04	500
Copper	GF–AAS	0.4	25	5	10,000	0.3	500
Iron	F–AAS	8	1,000	6	200,000	nd	nd
Lead	GF–AAS	0.4	25	60	10,000	0.05	500
Lithium	F–AAS	5	1,000	8	10,000	0.04	500
Magnesium	F–AAS	[1] 100	10,000	3	500,000	nd	nd
Manganese	F–AAS	4	1,000	2	25,000	0.06	1,000
Molybdenum	GF–AAS	0.9	50	34	10,000	0.4	500
Nickel	GF–AAS	0.5	25	35	10,000	0.3	500
Selenium	GF–AAS	0.8	50	nd	nd	2	500
Silicon (as SiO_2)	na	na	na	70	100,000	nd	nd
Silver	GF–AAS	0.1	10	4	1,000	0.7	25
Sodium	F–AAS	[1] 100	80,000	70	500,000	nd	nd
Strontium	F–AAS	[1] 10	5,000	0.5	10,000	0.04	500
Thallium	na	na	na	nd	nd	0.3	500
Uranium	na	na	na	nd	nd	0.2	500
Vanadium	na	na	na	5	10,000	nd	nd
Zinc	F–AAS	6	500	20	25,000	0.5	1,000

[1] Method reporting level, no method detection limit has been established.

sample is desolvated, atomized, and the resultant atoms or ions excited. The intensity of light emission that results when the excited-state atoms or ions relax to their ground state is directly proportional to the concentration of the emitting species in solution. Mean concentrations of elements are reported from three replicate determinations.

3A. Interferences

Corrective action must be taken to minimize interferences that might lead to inaccuracies in ICP–OES results, including physical and spectral interferences.

3A.1 *Physical interferences:* Physical interferences are generally considered to be effects associated with sample transport and nebulization processes. Sample matrices that are significantly different than the calibration standards, such as those having high dissolved-solid concentrations (or high specific conductance), might cause changes in the transport and nebulization process leading to significant inaccuracy in the final result. Physical interference effects can be overcome by using dilution or internal standards, or both. Simple dilution reduces the viscosity of the sample solution and the concentration of matrix salts. Addition of a surfactant to the samples and calibration standards also tends to stabilize sample transport.

The use of an internal standard can reduce the effects associated with changing sample transport properties as well as instrument drift. Yttrium (371.029 nm) is commonly used as an internal standard for ICP–OES analyses. The accuracy of internal standardization relies on the absence of yttrium in the sample. If yttrium is present, results will be negatively biased. Therefore, it is important to verify the absence of yttrium in the samples being analyzed. There are several methods that can be used by the analyst to verify its absence. The best procedure requires a rapid spectral scan of each sample to determine if yttrium is present. An alternate method would be to monitor the yttrium intensity in each sample during the analyses. Whenever the yttrium intensity is 10 percent greater than the yttrium intensity for a preceding yttrium-free Standard Reference Water Sample (SRWS), an unacceptable level of yttrium is indicated. In such cases, a different internal standard element must be used.

3A.2 *Spectral interferences:* Spectral interferences occur when constituents in a sample emit radiation at wavelengths close to the analytical wavelength being measured. Unresolved spectral emission at the analytical wavelength can result in significant positive bias in the results. In some instances, the high concentration of an interferent can suppress the emission from an element and result in a negative bias. Relating the apparent elemental concentration to the concentration of the interfering element (see table 2) is used to minimize this type of interference. This relation is a linear function of concentration that must be calibrated daily. Other spectral interferences can result from stray light, molecular broadband emission, and spectral-line broadening that contribute to the background or offset in the element signal. By measuring the background emission at one or two positions adjacent to the analytical wavelength, this offset can be subtracted from the signal (see table 3 for background measurement positions).

Experiments were conducted to evaluate spectral interferences by measuring element responses from 10- to 100-mg/L concentrations of numerous inorganic constituents, including major cations (calcium, magnesium, potassium, silica, and sodium), major anions (carbonate, chloride, nitrate, phosphate, and sulfate), and other minor elements. Elements that have significant spectral interferences are listed in table 2 with the interferent and the approximate degree of the interference.

Specific conductance is used to identify filtered, acidified samples that can exhibit physical interference effects because of high dissolved-solid concentrations. Since the specific conductance for a whole-water digest is inherently high but generally unknown, a nebulizer that can tolerate high dissolved solids must be used. A Noordemeer V-groove maximum dissolved-solids nebulizer was used to obtain the data presented in this report. Other nebulizer designs can be used, but they must be resistant to clogging and capable of providing

Table 2. Spectral interferences that affect elements determined by ICP–OES in natural whole-water digests

[ICP–OES, inductively coupled plasma–optical emission spectrometry; nm, nanometer; µg/L, microgram per liter]

Affected element	Affected elements' analytical wavelength [1] (nm)	Interferent	Interferent concentration (µg/L)	Apparent concentration of affected element (µg/L)
Aluminum [2]	167.081	Iron	100,000	250
Boron [2]	249.773	Iron	100,000	20
Beryllium	313.042	Vanadium	10,000	70
Cadmium	214.438	Iron	100,000	20
Cadmium	214.438	Aluminum	100,000	15
Cobalt	238.892	Iron	5,000	350
Copper	324.754	Manganese	25,000	-8
Iron	259.940	Manganese	25,000	10
Iron	259.940	Sodium	500,000	35
Lead	220.353	Aluminum	100,000	75
Manganese	257.610	Aluminum	100,000	-30
Manganese	257.610	Iron	100,000	-30
Manganese	257.610	Magnesium	500,000	15
Sodium	330.223	Zinc	25,000	-60
Vanadium	292.402	Iron	100,000	-10
Vanadium	292.402	Molybdenum	500	-8
Zinc [2]	206.200	Iron	100,000	20

[1] Interferent effects are wavelength specific.

[2] Wavelength is second order.

method detection limits within a factor of two of those listed in table 1.

4A. Apparatus, Instrumentation, and Operating Conditions

4A.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 accuracy of all pipets and volumetric flasks used to prepare standard solutions with either an analytical balance or an automatic calibrating spectrophotometer.

4A.2 *Instrumentation:* A Thermo Jarrell-Ash (TJA) argon or nitrogen purged spectrometer with a 0.75-m focal length and spectrum shifter background correction was used in this method. The argon plasma was generated using 27.12 MHz energy. Accessories included a TJA Model AS300 autosampler, Gilson peristaltic pump, TJA internal standards kit (Part #13670800), and computer data system. A Noordemeer V-groove nebulizer was used because of its ability to resist clogging when analyzing samples with high dissolved-solid concentrations.

Table 3. Analytical wavelengths and background correction points used for the determination of elements in whole-water digests by ICP–OES

[ICP–OES, inductively coupled plasma–optical emission spectrometry; nm, nanometer; one spectrum shifter step equals about 0.008 nm]

Element	Wavelength [1] (nm)	Background correction point [3] (spectrum shifter steps)
Aluminum (1) [2]	167.081	12
Aluminum (2)	308.215	12
Barium	455.403	-11
Beryllium	313.042	-11
Boron [2]	249.773	12
Cadmium	214.438	-11
Calcium (1)	396.847	-11
Calcium (2)	315.887	12
Chromium	267.716	-11
Cobalt	238.892	12
Copper	324.754	12
Iron	259.940	12
Lead	220.353	-11
Lithium	670.784	none
Magnesium (1)	279.553	12
Magnesium (2)	383.231	-11
Manganese	257.610	-11
Molybdenum	203.844	12
Nickel [2]	231.604	-11
Silicon, as SiO_2	288.158	12
Silver	328.068	-11
Sodium (1)	588.995	none
Sodium (2)	330.223	-11
Strontium	421.552	-11
Vanadium	292.402	-11
Yttrium	371.029	-11
Zinc [2]	206.200	12

[1] Wavelengths are instrument and method specific.

[2] Wavelength is second order.

[3] Shift relative to indicated wavelength; a shift to a lower wavelength is identified by the minus sign.

The wavelengths used to measure elemental concentrations are listed in table 3. Two analytical wavelengths are listed for aluminum, calcium, magnesium, and sodium. These wavelengths are listed in order of the emission intensity; therefore, the first wavelength is the more sensitive. There is some overlap in the calibration curves for the two wavelengths; hence a range of concentrations can be quantified with either wavelength. Upper and lower concentration limits for both wavelengths are determined by the linearity of their response. These concentration limits and overlap regions are listed in table 4. The analyst or data system determines which emission line results should be reported on the basis of elemental concentration, quality-control results, and the presence of interferences.

Table 4. Upper and lower concentration limit and concentration overlap region for ICP–OES elements having dual emission wavelengths

[ICP–OES, inductively coupled plasma–optical emission spectrometry; all concentrations are in milligrams per liter, except for aluminum, which is in micrograms per liter; the overlap region is the concentration range where results from either emission wavelength can be reported; MDL, method detection limit (see table 1)]

Element [1]	Concentration limits		
	Lower	Upper	Overlap region (use wavelength 1 or 2)
Aluminum (1)	MDL	75,000	
Aluminum (2)	300	500,000	300 to 75,000
Calcium (1)	MDL	25	
Calcium (2)	6	1,000	6 to 25
Magnesium (1)	MDL	100	
Magnesium (2)	6	500	6 to 100
Sodium (1)	MDL	125	
Sodium (2)	50	500	50 to 125

[1] Corresponding wavelengths are listed in table 3.

4A.3 *Operating conditions:*

- *Inductively coupled plasma operating conditions—*

Optimized operating conditions are listed as follows. These settings are based on experiments that maximize the signal to noise ratio for several atomic emission and ionic emission wavelengths that have different ionization potentials as a function of incident power, horizontal observation position, and sample delivery rate.

Incident radio frequency power	~ 0.95 kW
Reflected radio frequency power	~ 0 W
Torch gas flow rate	~ 14 L/min (high)
Auxiliary flow rate	~ 1.0 L/min
Nebulizer pressure	~ 45 lb/in^2 (~3.2 kilograms/square centimeter)
Sample flow rate (to nebulizer)	~ 2.9 mL/min
Horizontal observation position	~ 15 mm above load coil
Vertical observation position	Center

- *Internal standard manifold—*

Yttrium is used as the internal standard. Other elements may be substituted if needed; however, the choices are limited to the elemental wavelengths present on the instrument. The internal standard introduction system is based on a modified TJA internal standard kit (TJA item # 13670800). The peristaltic pump tubing provided in the kit was modified to achieve the overall lowest possible MDLs using the Noordemeer V-groove nebulizer. The manifold system is shown in figure 1a (see Appendix).

- *Data acquisition—*

Two measurements are made for every element, one at the analytical wavelength maximum and one adjacent to the analytical wavelength (background correction). Both measurements consist of three 5-second integrations.

- *Interelement correction factors—*

Interelement correction factors are used to adjust for apparent increases or decreases in a signal because of unresolved spectral interferences (see section 3A.2 and table 2).

- *Background correction protocol—*

The background adjacent to the analytical wavelengths is measured to minimize spectral background interferences. Background correction points are listed in table 3.

- *Optimization of primary refractor plate position (profile)—*

Instrument profile is adjusted to within 0.1 spectrum shifter steps of the maximum peak intensity for mercury at 435.835 nm.

- *Autosampler cycles—*

Specified cycle times have been shown to minimize memory effects from samples containing all elements up to the upper calibration standard (see table 1) and boron up to 5,000 µg/L. The length of the cycle times is dependent on the sample introduction system being used. If the sample introduction system described in this method is modified, these times likely will require adjustment.

Rinse cycle	~ 25 seconds
Flush cycle	~ 90 seconds

5A. Reagents and Calibration Standards

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 clean FEP Teflon bottle; solutions that contain silver must be stored in a designated clean opaque FEP Teflon bottle.

5A.1 *Nitric acid* (HNO_3): Concentrated, specific gravity 1.41.

5A.2 *Hydrochloric acid* (HCl): Concentrated, specific gravity 1.196.

5A.3 *Calibration blank and rinse solution*, ASTM Type I reagent water acidified to 0.4 percent nitric acid and 2 percent hydrochloric acid.

5A.4 *Commercial single-element standard solutions*, 1.00 mL = 10 mg preserved in nitric acid for each of the following: Al, Ag, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sr, and Zn.

5A.5 *Commercial single-element standard solution*, 1.00 mL = 5 mg vanadium preserved in nitric acid.

5A.6 *Commercial single-element standard solution*, 1.00 mL = 10 mg molybdenum preserved in hydrochloric acid.

5A.7 *Commercial single-element standard solution*, 1.00 mL = 5 mg boron in water.

5A.8 *Commercial single-element standard solution*, 1.00 mL = 10 mg silicon in water.

5A.9 *Commercial single-element standard solution*, 1.00 mL = 10 mg yttrium preserved in nitric acid.

5A.10 *Brij-35* (CAS 9002-92-0), 30 percent solution of polyoxyethylene lauryl ether.

5A.11 *Multielement calibration standard I*, 1.00 mL = 5.0 µg of Cd, Cr, Pb, and Zn; 1.00 mL = 50.0 µg Fe. Dilute 0.5 mL (except for Fe, use 5.0 mL) of each commercial single-element standard to 1,000 mL in a volumetric flask with calibration blank.

5A.12 *Multielement calibration standard II*, 1.00 mL = 5.0 µg of Ba, Be, Co, Cu, Ni, Sr, and V. Dilute 0.5 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with calibration blank.

5A.13 *Multielement calibration standard III*, 1.00 mL = 4.0 µg of Ag; 1.00 mL = 5.0 µg of Li and Mo; 1.00 mL = 10.0 µg of Ca. Dilute 0.4 mL of the commercial Ag standard, 0.5 mL of the commercial Li and Mo standard, and 1.0 mL of the commercial Ca standard to 1,000 mL in a volumetric flask with calibration blank.

5A.14 *Multielement calibration standard IV*, 1.00 mL = 5.0 µg of Mn; 1.00 mL = 50 µg of Ca and Na. Dilute 5.0 mL (except for Mn, use 0.5 mL) of each commercial single-element standard to 1,000 mL in a volumetric flask with calibration blank.

5A.15 *Multielement calibration standard V*, 1.00 mL = 10.0 µg of Mg and Na; 1.00 mL = 50.0 µg of Al. Dilute 1.0 mL of the commercial single-element standard (except for Al, use 5.0 mL) to 1,000 mL in a volumetric flask with calibration blank.

5A.16 *Multielement calibration standard VI*, 1.00 mL = 5.0 µg of B and Si. Dilute 0.5 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with calibration blank.

5A.17 *Performance check solution*, 1.00 mL = 5.0 µg of Ag, Al, B, Ba, Be, Ca, Cd, Co, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sr, V, and Zn. Dilute 0.5 mL of each commercial single-element standard, except dilute B and V using 1.0 mL, to 1,000 mL in a volumetric flask with calibration blank.

5A.18 *Spectral interference check solution I*, 1.00 mL = 100 µg of Fe. Dilute 10.0 mL of the commercial single-element standard to 1,000 mL in a volumetric flask with calibration blank.

5A.19 *Spectral interference check solution II*, 1.00 mL = 5.0 µg of Fe and V; 1.00 mL = 500 µg of Mg. Dilute 0.5 mL of the commercial Fe standard, 50 mL of the commercial Mg standard, and 1.0 mL of the commercial V standard to 1,000 mL in a volumetric flask with calibration blank.

5A.20 *Spectral interference check solution III*, 1.00 mL = 500 µg of Al and Na; 1.00 mL = 5.0 µg of Mo. Dilute 50 mL of each commercial single-element standard (except for Mo, use 0.5 mL) to 1,000 mL in a volumetric flask with calibration blank.

5A.21 *Spectral interference check solution IV*, 1.00 mL = 25 µg of Mn; 1.00 mL = 5.0 µg of Zn. Dilute 2.5 mL of the commercial Mn standard and 0.5 mL of the commercial Zn standard to 1,000 mL in a volumetric flask with calibration blank.

5A.22 *Internal standard working solution*, 1 mL = 5 µg Y. Dilute 0.5 mL of commercial single-element standard for Y and 200 µL Brij-35 solution to 1,000 mL in a volumetric flask with calibration blank.

6A. Analytical Procedure

Refer to Thermo Jarrell-Ash (1991) for details of procedures outlined in the following paragraphs.

6A.1 Set up the instrument using the operating conditions described in section 4A.3

and ignite the plasma. Allow the instrument to warm up for at least 30 minutes prior to optimization.

6A.2 Start the ThermoSPEC software.

6A.3 Edit an autosampler table with the unknown sample identifiers. Load the autosampler with calibration blank, multielement calibration standards, quality assurance/quality control (QA/QC) samples, and unknown samples.

6A.4 Turn on the instrument-mounted mercury pen lamp, move it in front of the entrance slit, and execute the profile option in the ThermoSPEC software. Adjust the mercury profile until the peak position is within ± 0.1 spectrum shifter steps. Start calibrating the instrument.

6A.5 Verify the accuracy of the calibration by using the results from the instrument performance check solution (see section 5A.17) and calibration blank. Instrument performance check solution concentrations must not deviate from the theoretical concentrations by more than ±5 percent, and the relative standard deviation of the replicate integrations must be less than 4 percent. If the error exceeds ±5 percent, reanalyze the instrument performance check solution. If error still exceeds the criterion, the instrument must be recalibrated. Relative standard deviations greater than 4 percent for the instrument performance check solution most likely indicate problems with sample introduction. Whenever the variability is poor, the nebulizer, peristaltic pump, and transmission tubing must be checked and the instrument re-calibrated.

Calibration blank concentrations must be within ±12 percent of the current MDLs. If any result is outside this limit, reanalyze the calibration blank. If a result is still outside the limit, use another calibration blank solution and recalibrate the instrument.

6A.6 Verify that interelement correction factors are accurate by using results from the spectral interference check solutions (see sections 5A.18–21). If the concentration for any element that is affected by spectral interference deviates by more than ±12 percent from the current MDLs, a new interelement correction factor for that element must be established before continuing sample analyses. A "U-DELETE" (unable to analyze) code will be reported instead of cobalt concentrations for samples that have iron concentration greater than or equal to 2,000 μg/L because of the large spectral interference from iron emission on the cobalt analytical wavelength. Whenever iron concentrations exceed 2,000 μg/L, the accuracy of the interelement correction becomes unacceptable.

6A.7 The QA/QC plan requires analysis of at least one of the following solutions at a frequency of at least 1 in every 10 unknown samples: SRWS, calibration blank, duplicate sample, diluted sample, or matrix spike. If SRWSs are used, the analyst must ensure that results fall within the established quality-control limits. Selection of a suitable SRWS should be based on the expected sample concentration range.

6A.8 If all data-acceptance criteria are satisfied, then the analytical results are acceptable. If any one criterion is not satisfied, then the analyst must reanalyze the sample in question. If the results remain outside the criteria, the instrument must be recalibrated and all samples following the last acceptable QA/QC check reanalyzed. For selected elements, the upper calibration limit does not represent the endpoint of the linear range but rather a concentration limit more appropriate for the majority of samples analyzed. Nevertheless, if an elemental result is greater than the upper calibration limit, the sample must be diluted (with the calibration blank), so that the elemental result will be less than the upper calibration limit, and reanalyzed.

7A. Calculations

7A.1 Concentrations are automatically calculated by the instrument's computer software. Headings identify the results.

7A.2 If samples were diluted, multiply results by appropriate dilution factor using the computer software.

7A.3 Formulas used to calculate percent spike recovery for the matrix spike and percent difference for duplicates are provided in the standard operating procedure (SOP; T.M. Struzeski, U.S. Geological Survey, written commun., 1998).

8A. Reporting of Results

The number of significant figures reported in the results varies with element and is a function of concentration. Whenever the elemental concentration is less than the MDL, the result is reported as less than the MDL (< MDL). All other elemental results for whole-water digests are reported by use of the criteria listed below. These criteria are based on the uncertainty indicated in table 17. Alternatively, the variability associated with the mean concentration (reported with the mean by each instrument) measured in each sample could be used to establish the appropriate number of significant figures to report. The use of such a procedure would provide the most accurate estimate of the uncertainty associated with each unique sample matrix.

For barium and strontium—

- If the concentration is greater than or equal to the MDL, but less than 100 µg/L, then report result to the nearest 0.1 µg/L.

- If the concentration is greater than 100 µg/L, but less than 1,000 µg/L, then report result to the nearest 1 µg/L.

- If the concentration is greater than 1,000 µg/L, then report result to the nearest 10 µg/L.

For aluminum, beryllium, boron, cadmium, cobalt, copper, lithium, manganese, molybdenum, nickel, silver, vanadium, and zinc—

- If the concentration is greater than or equal to the MDL, but less than 100 µg/L, then report result to the nearest 1 µg/L.

- If the concentration is greater than 100 µg/L, then report result to the nearest 10 µg/L.

NOTE: Whenever the concentration of iron is greater than or equal to 2,000 µg/L, an "U-DELETE" (unable to analyze) code will be reported for cobalt (see section 6A.6).

For lead—

- If the concentration is greater than or equal to the MDL, then report result to the nearest 10 µg/L.

For calcium, iron, magnesium, and sodium—

- If the concentration is greater than or equal to the MDL, but less than 1 mg/L, then report result to the nearest 0.001 mg/L.

- If the concentration is greater than or equal to 1 mg/L, but less than 10 mg/L, then report result to the nearest 0.01 mg/L.

- If the concentration is greater than or equal to 10 mg/L, but less than 100 mg/L, then report result to the nearest 0.1 mg/L.

- If the concentration is greater than or equal to 100 mg/L, then report result to the nearest 1 mg/L.

For silicon (reported as SiO_2)—

- If the concentration is greater than or equal to the MDL, but less than 1 mg/L, then report result to the nearest 0.01 mg/L.

- If the concentration is greater than or equal to 1 mg/L, but less than 10 mg/L, then report result to the nearest 0.1 mg/L.

- If the concentration is greater than or equal to 10 mg/L, but less than 100 mg/L, then report result to the nearest 1 mg/L.

Inductively Coupled Plasma–Mass Spectrometry

1B. Application

This method is used to determine recoverable aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, lithium, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, and zinc in natural whole-water samples digested by using the in-bottle procedure that is described by Hoffman and others (1996). The MDLs and analytical concentration ranges are listed in table 1. The method calibration ranges were optimized for elemental concentrations normally found in natural water, however, the dynamic range for ICP-MS is linear to a maximum of about 1 mg/L for elements that are monoisotopic, and somewhat greater than 1 mg/L for elements that have multiple isotopes. MDLs were calculated by using U.S. Environmental Protection Agency's (1994) definition and represent pooled averages on the basis of four MDLs that were determined on different days over several weeks.

2B. Summary of Method

Whole-water recoverable elements are determined simultaneously on a single sample by using inductively coupled plasma–mass spectrometry. An aerosol of the sample solution is produced by using a high dissolved-solids tolerant nebulizer. The aerosol is introduced into the argon plasma where it undergoes desolvation, atomization, and ionization. Ions are sampled through multiple orifices into the quadrupole mass spectrometer where they are separated on the basis of their mass-to-charge ratios. An electron multiplier detects the ions by generating an electrical current that is directly proportional to the concentration of the element present in the sample. A more detailed description of ICP–MS theory and application is described in Montaser and Golightly (1992) and Boumans (1987a and 1987b).

3B. Interferences

Several types of physical and spectral interference are recognized and documented for ICP–MS techniques. 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 interferences. Data from multiple isotopes can indicate the presence and magnitude of interferences. The analyst must be conscious of these interferences because they might occur with certain types of sample matrices.

3B.1 *Physical interferences:* The effects of sample transport, instrumental drift, and matrix-induced fluctuations in plasma characteristics are reduced by using the ratio of elemental ion intensity to the internal standard element ion intensity for calibration. Accurate results depend on having a constant internal standard ion intensity throughout the analysis of all standards and samples. Constant internal standard ion intensity requires that any interferences associated with the internal standard element can be corrected and that the internal standard element is not naturally present in the samples being analyzed.

Three isotopes that extend the mass range from 6 to 240 atomic mass units (amu) are used as internal standards—in this method $^{45}Sc^+$, $^{115}In^+$, and $^{209}Bi^+$ are routinely used. Alternative isotopes may be substituted after ensuring that there are no spectral interferences associated with the new selections. Analytical isotopes less than 45 amu are normalized to $^{45}Sc^+$, and those greater than 209 amu are normalized to $^{209}Bi^+$. Analytical isotopes between 45 and 115 amu are normalized by using a response obtained from the linear interpolation of the responses for $^{45}Sc^+$ and $^{115}In^+$. Similarly, isotopes between 115 and 209 amu are normalized by using an interpolated response based on $^{115}In^+$ and $^{209}Bi^+$.

Memory effects that are related to sample transport are negligible for most elements normally present in natural whole-water digests. Carryover from samples that have elemental concentrations less than 1,000 µg/L is negligible for all elements except antimony. Antimony concentrations greater than 50 µg/L can produce substantial carryover in subsequent samples. Analyses following samples that have elemental concentrations greater than 1,000 µg/L must be reanalyzed to verify that carryover was negligible.

3B.2 *Spectral interferences:* Whenever possible, the isotope used for quantitation has no spectral interferences or has a small number of potential spectral interferences that is unlikely to occur in whole-water digests or can easily be corrected. 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. Spectral overlap contributions caused by insufficient abundance sensitivity are negligible and can be minimized by measuring each isotope at three points that transect the peak maximum, which is centered at the nominal mass. The known interferences for the elements that are determined in this method are listed below.

3B.2.1 *Isobaric interferences:* There are only three isobaric interferences for isotopes measured in this method—$^{82}Kr^+$ on $^{82}Se^+$, $^{114}Sn^+$ on $^{114}Cd^+$, and $^{115}Sn^+$ on $^{115}In^+$. Krypton can be a minor contaminant found in argon gas used to support the plasma, however, its concentration will remain constant for both the standards and samples, and, therefore, usually does not require correction.

The most abundant cadmium isotope $^{114}Cd^+$ is used as a secondary isotope and is subject to isobaric overlap from $^{114}Sn^+$. The following equation must be used to calculate the ion intensity corresponding to only $^{114}Cd^+$:

$$^{114}Cd^+ = I114 - [I118 \times (^{114}Sn/^{118}Sn)] \qquad (1)$$

or

$$^{114}Cd^+ = I114 - (I118 \times 0.02707)\ , \qquad (2)$$

where I114 and I118 are the ion intensities measured at 114 and 118 amu, respectively, and $^{114}Sn/^{118}Sn$ is the ratio of the natural abundance of the two tin isotopes (this ratio is based on the assumption of natural abundance). This isobaric correction is acceptable for tin concentrations less than or equal to 2 mg/L. If tin concentrations exceed 2 mg/L, then only $^{111}Cd^+$ results can be considered.

Indium is routinely used as an internal standard. Whenever tin is present in a sample, its isobaric interference on $^{115}In^+$ isotope is eliminated by using the following equation:

$$^{115}In^+ = I115 - [I118 \times (^{115}Sn/^{118}Sn)] \quad (3)$$

or

$$^{115}In^+ = I115 - (I118 \times 0.01416) \ , \quad (4)$$

where I115 and I118 are the ion intensities measured at 115 and 118 amu, respectively, and $^{115}Sn/^{118}Sn$ is the ratio of the natural abundance for the given tin isotopes. This isobaric correction is acceptable for tin concentrations less than or equal to 2 mg/L. If tin concentrations exceed 2 mg/L, an alternate internal standard element, such as rhodium ($^{103}Rh^+$), can be used.

3B.2.2 *Molecular ion interferences:* There are several known molecular ion interferences associated with elements determined in this method. Molecular ions, for example, CeO^+, ClO^+, and $NaAr^+$, are produced within the expansion zone behind the interface. Molecular ion spectral interferences are listed in table 5 as apparent elemental concentrations corresponding to a given concentration of interferent with the ionic species responsible for the interference.

Molecular ion interferences on $^{52}Cr^+$ and $^{53}Cr^+$ from $^{40}Ar^{12}C^+$ and $^{40}Ar^{13}C^+$, respectively, have been found to be negligible. The interference on $^{53}Cr^+$ from $^{38}Ar^{15}N^+$ also is negligible because of the low natural abundance of the argon and nitrogen isotopes. Interferences on chromium that are associated with chloro-oxygen species are minimized by matrix-matching the calibration standards to the same percentage of hydrochloric acid as the in-bottle digests, however, the matrix matching must be accurate.

Sulfur and oxygen isotopes form molecular ions of S_2^+, SO^+, and SO_2^+ that interfere with chromium, copper, selenium, and zinc determinations. Sulfur molecular ions arise from sulfide, sulfite, or sulfate, although in whole-water digests, sulfate is the primary form. The interference on selenium and chromium is negligible for sulfate concentrations less than 1,000 mg/L. However, sulfur molecular ion interferences can significantly affect copper and zinc results. Errors associated with these interferences are corrected by calibrating the apparent copper and zinc concentrations to sulfate concentration. Apparent $^{65}Cu^+$ and $^{66}Zn^+$ concentrations are linear through 1,000 mg/L sulfate based on the instrument response at $^{32}S^{16}O^+$ (see figs. 2a–b in Appendix). Instrument response at $^{32}S^{16}O^+$ as a function of sulfate concentration is represented best by a polynomial equation for concentrations less than 1,000 mg/L (see fig. 3 in Appendix), however, the response is linear at less than 600 mg/L. Using $^{32}S^{16}O^+$ to quantitate sulfate interferences requires correction for unresolved contributions from $^{48}Ca^+$ (0.19 percent abundance) and $^{48}Ti^+$ (73.8 percent abundance). These contributions are determined by measuring $^{43}Ca^+$ and $^{47}Ti^+$ and calculating the corresponding effect at 48 amu using the following equations:

$$^{48}Ca^+ = I43 \times (^{48}Ca/^{43}Ca) = I43 \times 1.36 \quad (5)$$

$$^{48}Ti^+ = I47 \times (^{48}Ti/^{47}Ti) = I47 \times 10.1 \quad (6)$$

$$^{32}S^{16}O^+ = I48 - {}^{48}Ca^+ - {}^{48}Ti^+ \ , \quad (7)$$

where I43, I47, and I48 are the ion intensities measured at 43, 47, and 48 amu, respectively, and $^{48}Ca/^{43}Ca$ and $^{48}Ti/^{47}Ti$ are the ratios of the natural abundance for the given isotopes. This correction method is problematic because calcium concentration can be relatively high in whole-water digests. In the absence of calcium or titanium, subtracting the apparent concentration from the original concentration (25 µg/L copper and zinc) gives a corrected concentration of acceptable accuracy (see figs. 4a–b in Appendix).

Table 5. Molecular ion interferences for elements determined in whole-water digests by ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry; µg/L, microgram per liter; mg/L, milligram per liter; ~, approximate; <, less than; MDL, method detection limit; >, greater than]

Isotope [1]	Primary interferent	Interferent ion or ions	Interferent concentration	Approximate apparent element concentration (µg/L)
$^{52}\mathrm{Cr}$	Chloride	$^{35}\mathrm{Cl}^{16}\mathrm{OH}^+$	100 mg/L Cl	~0.2
$^{52}\mathrm{Cr}$	Sulfate	$^{36}\mathrm{S}^{16}\mathrm{O}^+$	1,000 mg/L SO_4^2	~2
$^{53}\mathit{Cr}$	Chloride	$^{37}\mathrm{Cl}^{16}\mathrm{O}^+$, $^{35}\mathrm{Cl}^{18}\mathrm{O}^+$	100 mg/L Cl	~0.2
$^{53}\mathit{Cr}$	Sulfate	$^{36}\mathrm{S}^{16}\mathrm{O}^+$	1,000 mg/L SO_4^2	~2
$^{59}\mathrm{Co}$	Calcium	$^{43}\mathrm{Ca}^{16}\mathrm{O}^+$, $^{42}\mathrm{Ca}^{16}\mathrm{OH}^+$	250 mg/L Ca	<MDL
$^{60}\mathrm{Ni}$	Silicon as SiO_2	$^{28}\mathrm{Si}^{16}\mathrm{O}_2^+$	40 mg/L SiO_2	~0.2
$^{60}\mathrm{Ni}$	Calcium	$^{44}\mathrm{Ca}^{16}\mathrm{O}^+$	250 mg/L Ca	<MDL
$^{63}\mathit{Cu}$	Sodium	$^{40}\mathrm{Ar}^{23}\mathrm{Na}^+$	500 mg/L Na	~10
$^{65}\mathrm{Cu}$	Titanium	$^{49}\mathrm{Ti}^{16}\mathrm{O}^+$	1 mg/L Ti	~0.5
$^{65}\mathrm{Cu}$	Sulfate	$^{33}\mathrm{S}^{16}\mathrm{O}_2^+$, $^{32,33}\mathrm{S}_2^+$	1,000 mg/L SO_4^2	~20
$^{66}\mathrm{Zn}$	Barium	$^{132}\mathrm{Ba}^{2+}$	100 mg/L Ba	~5
$^{66}\mathrm{Zn}$	Chromium	$^{50}\mathrm{Cr}^{16}\mathrm{O}^+$	1 mg/L Cr	~0.1
$^{66}\mathrm{Zn}$	Sulfate	$^{34}\mathrm{S}^{16}\mathrm{O}_2^+$, $^{32,34}\mathrm{S}_2^+$, $^{33}\mathrm{S}_2^+$	1,000 mg/L SO_4^2	~10
$^{66}\mathrm{Zn}$	Titanium	$^{50}\mathrm{Ti}^{16}\mathrm{O}^+$	1 mg/L Ti	~0.3
$^{66}\mathrm{Zn}$	Vanadium	$^{50}\mathrm{V}^{16}\mathrm{O}^+$	1 mg/L V	~0.1
$^{67}\mathit{Zn}$	Barium	$^{134}\mathrm{Ba}^{2+}$, $^{135}\mathrm{Ba}^{2+}$	100 mg/L Ba	>50
$^{82}\mathrm{Se}$	Sulfate	$^{34}\mathrm{S}^{16}\mathrm{O}_3^+$	1,000 mg/L SO_4^2	~9
$^{107}\mathrm{Ag}$	Zirconium	$^{91}\mathrm{Zr}^{16}\mathrm{O}^+$	1 mg/L Zr	~1
$^{109}\mathit{Ag}$	Niobium	$^{93}\mathrm{Nb}^{16}\mathrm{O}^+$	not determined	not determined
$^{111}\mathrm{Cd}$	Molybdenum	$^{95}\mathrm{Mo}^{16}\mathrm{O}^+$	1 mg/L Mo	~0.4
$^{114}\mathit{Cd}$	Molybdenum	$^{98}\mathrm{Mo}^{16}\mathrm{O}^+$	1 mg/L Mo	~0.6

[1] Isotopes that are routinely used as secondary isotopes are listed in italic.

Errors ranged from 0.5 to 1 µg/L copper or zinc for sulfate concentrations from 0 to 1,000 mg/L.

An alternative correction method determines the linear regression equations for apparent $^{65}\mathrm{Cu}^+$ and $^{66}\mathrm{Zn}^+$ as a function of sulfate concentration by analyzing two sulfate standards (see sections 5B.21 and 22) with each batch of samples. After the analyses have been completed, these equations and the sulfate concentrations obtained for each sample by using another analytical method are used to determine the fraction of $^{65}\mathrm{Cu}$ and $^{66}\mathrm{Zn}$ concentrations that result from sulfate. The regression equations and interference corrections are calculated by using a software program that is executed following the analyses. The accuracy of this method of interference correction is equivalent to the method described in the preceding paragraph, however, it is likely to be more accurate as calcium concentrations increase.

Oxides of chromium, molybdenum, niobium, silicon, titanium, vanadium, and zirconium generally are negligible because of the low ambient concentration levels for these elements in whole-water digests. Interferences on $^{111}Cd^+$ (from $^{95}Mo^{16}O^+$) and $^{66}Zn^+$ (from $^{50}Cr^{16}O^+$) are not routinely determined because the interferences are negligible at molybdenum and chromium concentrations that are usually present in natural whole-water digests. Comparing results for primary and secondary isotopes may identify other possible oxide interferences. For example, comparing $^{107}Ag^+$ to $^{109}Ag^+$ results could indicate the degree of zirconium or niobium interference on silver.

If concentration levels of interferent-causing elements exceed those listed in tables 5 and 6, the sample must be diluted by an appropriate factor and reanalyzed. Dilution must be made by using the calibration blank (see section 5B.3).

3B.2.3 *Doubly charged ion interferences:* A doubly charged ion is created in the plasma for any element that has a second ionization potential that is less than the ionization potential for argon. Under normal operating conditions, the ICP–MS generates less than 0.2 percent doubly charged barium ion (see table 6). Apparent copper and zinc concentrations will exceed MDL concentration levels whenever barium concentrations exceed 1,000 µg/L. Lutetium and ytterbium (176 amu) doubly charged ions will interfere with strontium. Similarly, dysprosium, europium, and holmium (163, 164, and 165 amu) doubly charged ions interfere with selenium. These rare earth isotopes, however, are usually found at negligible concentrations in whole-water digests.

Table 6. Doubly charged ion interferences for elements determined in whole-water digests by ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry; µg/L, microgram per liter; mg/L, milligram per liter; ~, approximate]

Isotope	Interferent	Interferent ion	Interferent concentration	Apparent element concentration (µg/L)
^{65}Cu	Barium	$^{130}Ba^{2+}$	1 mg/L Ba	~0.1
^{66}Zn	Barium	$^{132}Ba^{2+}$	1 mg/L Ba	~0.4
^{67}Zn	Barium	$^{134}Ba^{2+}$	1 mg/L Ba	~10

4B. Apparatus, Instrumentation, and Operating Conditions

4B.1 *Labware:* See section 4A.1

4B.2 *Instrumentation:* VG Elemental PlasmaQuad I ICP–MS system, which consists of a Gilson 222 automatic sampler, high-solids pneumatic nebulizer, Gilson peristaltic pump, internal standard introduction manifold, computer system, and printer. The high-solids nebulizer used for sample introduction was a parallel-path design that was entirely constructed of tetrafluoroethylene monomer (CPI Inc., Model 50, P/N 4060-69). This nebulizer design resists clogging and is chemically inert. Other nebulizer designs can be used, however, they must be resistant to clogging and capable of providing MDLs that are within a factor of two of those listed in table 1. More state-of-the-art (circa 1997) ICP–MS instruments will provide MDLs that are a factor of 4–50 times lower than levels reported in this study. Instrument software must be capable of providing automatic interference correction (for example, PQVision Version 4.1.2).

4B.3 *Operating conditions:*

- *Isotopes—*

Isotopes used to quantify elements, which are determined in whole-water digests by inductively coupled plasma–mass spectrometry, are listed in table 7. Secondary isotopes are in italic. In addition, the use of the sum of all four lead isotopes for quantitation is highly recommended because the lead isotopic abundance in a sample may deviate from natural abundance.

- *Internal standards—*

^{45}Sc, ^{115}In, and ^{208}Bi are used as internal standards in the interpolated mode. Other interference-free isotopes may be substituted if needed.

- *Inductively coupled plasma—*

Incident radio frequency power:	~ 1.3 kW
Reflected radio frequency power	< 5 W
Coolant flow rate	~ 13 L/min
Auxiliary flow rate	~ 0.5 L/min
Nebulizer flow rate	~ 0.7 L/min

- Vacuum system, in millibar—

Section	Static pressure	Operating pressure
Analyzer	~ 1 X 10^{-8}	~ 5 X 10^{-6}
Intermediate	~ 10^{-4}	~ 10^{-4}
Expansion	atmosphere	~ 1.5

- *Ion sampling position—*

Signal response on the rate meter for ^{115}In is maximized while adjusting the x, y, and z positioning on the torch box.

Table 7. Isotopes used to quantify elements determined in whole-water digests by ICP–MS

[ICP–MS, inductively coupled plasma–mass spectrometry]

Element	Isotope [1]	Element	Isotope [1]	Element	Isotope [1]
Aluminum	27	Copper	65, *63*	Silver	107, *109*
Antimony	121	Lead [2]	208	Strontium	88
Barium	137	Lithium	7	Thallium	203
Beryllium	9	Manganese	55	Uranium	238
Cadmium	111, *114*	Molybdenum	95	Zinc	66, *67*
Chromium [3]	52	Nickel	60		
Cobalt	59	Selenium	82		

[1] Secondary isotopes are shown in italic.

[2] The sum of all lead isotopes (204, 206, 207, and 208) for quantitation is highly recommended (see section 4B.3).

[3] Quantification can be problematic because of molecular ion interferences.

- *Ion optics—*

The potentials applied to the ion optics are optimized to give the maximum reading on the rate meter for ^{115}In. Nominal vernier settings for each ion lens are listed below.

Lens	Vernier setting	Lens	Vernier setting
Collector	~ 8	L4	~ 2
Extraction	~ 0.5	Differential aperture	~ 1
L1	~ 8	Front plate	~ 5
L2	~ 6	Pole bias	~ 5
L3	~ 5	Prefilter	~ 4

- *Peristaltic pump—*

Pump rate is adjusted to approximately 1 mL/min.

- *Internal standard manifold—*

The internal standard introduction system uses a 12-turn microbore mixing coil (Alpkem 303-0310), microbore double injection fitting (Alpkem 303-107-00), microbore debubbler (Alpkem 303-0103-00), and the peristaltic pump tubing that is listed in figure 1b (see Appendix).

- *Detector potential—*

The potential applied to the electron multiplier must be optimized by using manufacturer's guidelines (Galileo Electro-Optic Corporation, 1991). This potential will increase over the life of the multiplier.

- *Data acquisition—*

Data are acquired using the peak-hopping mode to collect three points per peak per isotope. Three 40-second integrations are averaged for the reported result.

- *Mass calibration and resolution—*

Mass calibration is verified at 4 to 6 masses that extend throughout the full mass range. The calibration must be within 0.1 amu of the theoretical value for each mass.

The valleys between Mg and Pb isotopes must be about 10 percent of the maximum peak height.

- *Oxide molecular ion and doubly charged ion levels—*

Oxide and doubly charged ion intensities should be less than the following upper limits:

BaO^+ / Ba^+	< 0.5 percent
Ba^{2+} / Ba^+	< 3 percent

- *Autosampler cycles—*

Autosampler cycle times listed below minimize carryover in the sample introduction configuration shown in figure 1b (see Appendix).

Rinse cycle	~ 60 seconds
Flush cycle	~ 75 seconds

5B. Reagents and Calibration Standards

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 clean FEP Teflon bottle; solutions that contain silver must be stored in a designated clean opaque FEP Teflon bottle.

5B.1 *Nitric acid* (HNO_3): Concentrated, specific gravity 1.41.

5B.2 *Hydrochloric acid* (HCl): Concentrated, specific gravity 1.196.

5B.3 *Calibration blank*: Reagent water acidified to 0.4 percent nitric acid and 2 percent hydrochloric acid.

5B.4 *Commercial single-element standard solutions*, 1.00 mL = 10 mg preserved in nitric acid for each of the following: Al, Ag, Ba, Bi, Be, Cd, Co, Cr, Cu, In, Li, Mn, Mo, Ni, Pb, Se, Sb, Sc, Sn (may include a low percentage of hydrofluoric acid), Sr, Tl, U, and Zn.

5B.5 *Commercial sulfate standard*, 1.00 mL = 10 mg sulfate in water (from sodium sulfate).

5B.6 *Multielement stock solution I*, 1.00 mL = 0.010 mg of Be, Cd, Co, Cr, Cu, Mo, Ni, and Pb: Dilute 1.0 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.7 *Multielement stock solution II*, 1.00 mL = 0.010 mg of Se, Sb, Sr, Tl, and U: Dilute 1.0 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.8 *Multielement stock solution III*, 1.00 mL = 0.010 mg of Al, Ba, Mn, and Zn: Dilute 1.0 mL of each commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.9 *Lithium stock solution IV*, 1.00 mL =0.010 mg of Li: Dilute 1.0 mL lithium commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.10 *Silver stock solution V*, 1.00 mL = 0.010 mg of Ag: Dilute 1.0 mL silver commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.11 *Multielement calibration standard I*, 1.00 mL = 0.025 µg Al, Ag, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Se, Sb, Sr, Tl, U, and Zn: Dilute 0.250 mL of multielement stock solutions I, II, and III, lithium stock solution IV and silver stock solution V to 100 mL in a volumetric flask with calibration blank.

5B.12 *Multielement calibration standard II*, 1.00 mL = 0.100 µg Al, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Se, Sb, Sr, Tl, U, and Zn: Dilute 1.0 mL of multielement stock solutions I, II, and III and lithium stock solution IV to 100 mL in a volumetric flask with calibration blank.

5B.13 *Multielement calibration standard III*, 1.00 mL = 0.500 µg Be, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Se, Sb, Sr, Tl, and U: Dilute 5.0 mL of multielement stock solutions I, II, and III and lithium stock solution IV to 100 mL in a volumetric flask with calibration blank.

5B.14 *Multielement calibration standard IV*, 1.00 mL = 1.00 µg Al, Ba, Mn, and Zn: Dilute 1.0 mL of multielement stock solution III to 100 mL in a volumetric flask with calibration blank.

5B.15 *Internal standard stock solution*, 1 mL = 0.1 mg Sc, In, and Bi: Dilute about 10 mL of each commercial single-element standard for Sc, In, and Bi and 10 mL ultrapure nitric acid to 1,000 mL in a volumetric flask with reagent water.

5B.16 *Brij-35* (CAS 9002-92-0), 30 percent solution of polyoxyethylene lauryl ether.

5B.17 *Internal standard working solution*, 1 mL = 0.5 µg Sc, In, and Bi: Dilute 5 mL of internal standard stock solution and 100 µL of Brij-35 solution to 1,000 mL in a volumetric flask with calibration blank.

5B.18 *Performance check standard*, 1.00 mL = 0.010 µg of Ag, Al, Ba, Be, Cd, Cr, Co, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, Tl, U, and Zn. Dilute 4.0 mL of multielement calibration standard I to 10 mL with calibration blank.

5B.19 *Interference check stock solution*, 1.00 mL = 0.010 mg Sn: Dilute 1.0 mL of the tin commercial single-element standard to 1,000 mL in a volumetric flask with 1 percent nitric acid.

5B.20 *Interference check standard*, 1.00 mL = 0.100 µg of Sn. Dilute 1.0 mL of interference check stock solution to 100 mL in a volumetric flask with calibration blank.

5B.21 *Sulfate interference calibration standard I*, 1 mL = 100 µg of sulfate. Dilute 0.1 mL of sulfate standard to 10 mL with calibration blank.

5B.22 *Sulfate interference calibration standard II*, 1 mL = 500 µg of sulfate. Dilute 0.5 mL of sulfate standard to 10 mL with calibration blank.

5B.23 *Tuning solution*, 1 mL = 0.1 µg Be, Co, In, Mg, Pb, U: Dilute about 10 µL of each commercial single-element standard for Be, Co, In, Mg, Pb, and U and 10 mL reagent grade nitric acid to 1,000 mL in a volumetric flask with reagent water.

6B. Analytical Procedure

Refer to VG Elemental (1988, 1994) and NWQL Standard Operating Procedure IM0011.0 (J.R. Garbarino and M.R. Hill, U.S. Geological Survey, written commun., 1994) for details of procedures outlined in the following paragraphs.

6B.1. Ignite plasma. Ensure that inductively coupled plasma and vacuum conditions are set correctly (see section 4B.3). Allow at least 30 minutes prior to optimization. Use the tuning solution (see section 5B.23) for procedures outlined in sections 6B.2–4.

6B.2. Optimize plasma-sampling position and ion optics.

6B.3. Adjust the electron multiplier voltage to provide about 2,000 counts per second for 1 µg/L ^{115}In.

6B.4. Verify mass resolution and mass calibration.

6B.5. Assemble an analytical procedure having the calibration blank, multielement calibration standards, QA/QC samples, and unknown samples. In addition, include sulfate interference calibration solutions if external calibration is being used.

6B.6 Load the autosampler with calibration blank, multielement calibration standards, QA/QC samples, and unknown samples. Execute the analytical procedure.

6B.7 Verify the accuracy of the calibration using the results from the performance check solution. Concentrations must not deviate from the theoretical concentrations by more than ±5 percent (except for selenium at ±30 percent). Elemental relative standard deviations for the performance check solution must be within

±0.5 percent of the variability listed in table 17 for 12.5 µg/L. The instrument must be recalibrated for failure in either criterion for any element.

6B.8 Verify the accuracy of interference correction equations by analyzing the interference check standard (see section 5B.20). If either the indium intensity exceeds that of the calibration blank by more than 5 percent, or the secondary cadmium isotope (^{114}Cd) concentration exceeds the MDL, then the instrument must be recalibrated or the interference equations must be reestablished before continuing sample analyses.

6B.9 The QA/QC plan requires analysis of at least one of the following at a frequency of at least 1 in every 10 unknown samples: SRWS, calibration blank, duplicate sample, diluted sample, or matrix spike. If SRWSs are used, the analyst must ensure that results fall within the established quality-control limits. Selection of a suitable SRWS should be based on the expected sample concentration range.

6B.10 Acceptance criteria for duplicates, dilutions, and matrix spikes are fully outlined in the SOP. If all data-acceptance criteria are met, then the analytical results are acceptable. If any one criterion is not satisfied, then the analyst must reanalyze the sample in question. If the results remain outside the criteria, the instrument must be recalibrated and all samples following the last acceptable QA/QC check reanalyzed. The upper calibration limits do not represent the endpoint of the linear analytical range but rather a concentration limit more appropriate for the majority of samples analyzed. Nevertheless, if an elemental result is greater than the upper calibration limit, the sample must be diluted (with the calibration blank) and reanalyzed so that the concentration will be less than the upper calibration limit.

7B. Calculations

Correct the copper and zinc results from sulfate interference after the analyses have been completed if external sulfate calibration was used. This operation can easily be done by using a spreadsheet program. All other calculations are performed automatically by the operating system. If a sample was diluted, the appropriate dilution factor must be included in the analytical procedure before the automatic calculation is performed. Linear regression coefficients and standard and sample concentrations for every element are printed out immediately after the analyses. VG Elemental (1994) describes the formulas that are used in the calculations.

8B. Reporting of Results

The number of significant figures reported in the results 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 for whole-water digests are reported by using the criteria listed below. These criteria are based on the uncertainty indicated in table 17. Alternatively, the variability that is associated with the mean concentration (reported with the mean by each instrument) measured in each sample could be used to establish the appropriate number of significant figures to report. The use of such a procedure would provide the most accurate estimate of the uncertainty that is associated with each unique sample matrix.

For antimony, barium, beryllium, cadmium, copper, lithium, manganese, molybdenum, nickel, and zinc—

- If the concentration is greater than or equal to the MDL, but less than 100 µg/L, then report result to the nearest 0.1 µg/L.

- If the concentration is greater than 100 µg/L, but less than 500 µg/L, then report result to the nearest 1 µg/L.

- If the concentration is greater than 500 µg/L, then report result to the nearest 10 µg/L.

For cobalt, lead, silver, strontium, thallium, and uranium—

- If the concentration is greater than or equal to the MDL, but less than 10 µg/L, then report result to the nearest 0.01 µg/L.

- If the concentration is greater than 100 µg/L, but less than 500 µg/L, then report result to the nearest 1 µg/L.

- If the concentration is greater than 500 µg/L, then report result to the nearest 10 µg/L.

For aluminum, chromium, and selenium—

- If the concentration is greater than or equal to the MDL, but less than 500 µg/L, then report result to the nearest 1 µg/L.

- If the concentration is greater than 500 µg/L, then report result to the nearest 10 µg/L.

DISCUSSION OF RESULTS

Accuracy and Variability

The accuracy and variability for the analysis of whole-water digests are evaluated by comparing results obtained by ICP–OES and ICP–MS to results obtained by former USGS methods of analysis. Results from the analysis of digested SRWS, spiked natural whole-water digests, and 43 natural whole-water digests are used to identify elements that can be determined by using ICP–OES or ICP–MS, while maintaining or exceeding the performance of the former methods. Former USGS methods include U.S. Geological Survey approved methods (Fishman and Friedman, 1989; Fishman, 1993) and U.S. Environmental Protection Agency methods of analysis (U.S. Environmental Protection Agency, 1992) that have been adapted for use at the NWQL.

It is either not practical or instrumentally impossible to determine all elements by both ICP–OES and ICP–MS. Antimony is not determined by ICP–OES because the instrument currently (1998) does not support it, and the determination of selenium is not feasible because of poor sensitivity. Calcium, iron, magnesium, silicon, sodium, and vanadium are not determined by ICP–MS either because the concentration level normally present in whole-water digests exceeds the working range of the technique or because substantial molecular ion interferences are present.

Results for Digested Standard Reference Water Samples

U.S. Geological Survey SRWS T107, T119, T133, T135, and WW-1 were analyzed to determine the accuracy and variability of the ICP–OES and ICP–MS methods. Only WW-1 approximates a natural whole-water sample that has suspended sediment, although the amount of sediment exceeds the level routinely present in such samples that are submitted to the NWQL. Other SRWSs are filtered, acidified natural-water matrices. SRWS T135 was only analyzed by ICP–OES because selected elements are present at concentrations better suited to evaluate the accuracy for less sensitive elements (for example, lead and molybdenum). Ten bottles of SRWS T107, T119, T133, and T135 and five bottles of WW-1 were digested on different days by using the in-bottle digestion procedure (Hoffman and others, 1996).

In general, results for SRWS digests from ICP–OES and ICP–MS were obtained within different time domains. Data for SRWS T107, T119, T133, and T135 by ICP–OES represent short-term (about 1-hour) results obtained by analyzing each of 10 in-bottle SRWS digests within a single calibration period. In contrast, all the SRWS data from ICP–MS correspond to long-term results obtained by analyzing all the standard solutions over a 2-week period using different calibrations. However, long-term accuracy and variability of the two methods are directly comparable using results from SRWS WW-1. All five bottles of SRWS WW-1 were analyzed four times over a 2-week period.

The analytical variability of the two techniques is compared by using the variance from determinations of standards that have a wide range of concentrations. Three determinations were performed sequentially on a single aliquot in less than 1 minute. A WW-1 digest, or another SRWS that has more suitable concentration levels for ICP–OES, and a series of standards are used for comparing the data.

The accuracy of the SRWS results is examined by comparing the experimental mean to the published most probable value (MPV) by use of two methods. First, the experimental mean is compared to the 1σ (68 percent) confidence interval about the published MPV. Then the Student *t*-Test or the Wilcoxon Signed Rank Test, depending on whether the data set was normally distributed and showed equal variance, is used to test whether the experimental mean is significantly different from the MPV at the 95-percent confidence level (a p-value less than 0.05). Frequently the p-value indicates that the experimental mean is significantly different from the MPV, even though the result is within the confidence interval of the MPV. In most of these cases, failure is related to the variability in the experimental data, and the difference between the experimental mean and the MPV is analytically insignificant.

Short-term ICP–OES results for SRWS T107, T119, T133, and T135 are listed in tables 8 through 11. The confidence intervals about the MPV and the experimental ICP–OES mean are shown in figures 5a, 6a, and 7a and in figure 8 (see Appendix). The experimental means for elements determined by ICP–OES were inside the 1σ-confidence interval of the MPV for all SRWS except for calcium, magnesium, manganese, nickel, silver, vanadium, and zinc. Calcium, magnesium, manganese, and vanadium means, however, are within the 1.5σ-confidence interval that is acceptable by the NWQL. Silver is only slightly outside the interval in SRWS T135. All zinc data are acceptable except for T133, which is negatively biased. Nickel results are outside the 1σ-confidence interval in 75 percent of the SRWSs and greater than 1.5σ for T107 and T119.

All long-term experimental means for SRWS T107, T119, and T133 by ICP–MS (see tables 12 through 14 and figures 5a, 6b, and 7b in Appendix) are within the 1σ-confidence interval of the MPV except for beryllium, boron, chromium, lithium, and silver. The mean beryllium and lithium concentrations measured in T107 are outside the 1.5σ-confidence interval of the MPV. Boron and chromium results for T107 and silver in T119 are inside the 1.5σ-confidence interval for the MPV.

The 1σ-confidence interval about the MPV, the long-term experimental mean and standard deviation, the statistical test used, the test statistic value, and the p-value for SRWS WW-1 are listed in table 15. The MPV confidence interval and the experimental results from ICP–OES and ICP–MS are shown in figure 9 (see Appendix). Elemental results from both methods are within the 1σ-confidence interval of the MPV except for ICP–OES cadmium and nickel results; however, both elements are well within the 1.5σ-confidence interval, so the data are acceptable. For selected elements, one method can be seen to have greater long-term accuracy and variability than the other. For example, the experimental mean for beryllium, cadmium, and nickel by ICP–MS are somewhat more accurate than for ICP–OES; results for the other elements are equivalent. Less variability is indicated in the ICP–OES data for some of the lighter elements (those less than 60 amu, for example, beryllium, chromium, lithium, and manganese). Increase in variability for some of the ICP–MS results may be the consequence of shifting spectral background that is not entirely offset by the internal standard. Cadmium, molybdenum, nickel, and silver concentrations are at or less than the ICP–OES MDLs and the aluminum concentration is much greater than the 1,000-µg/L calibration limit for ICP–MS.

The analytical variability in ICP–OES and ICP–MS data from WW-1 (except for aluminum, cobalt, lead, molybdenum, and silver which used other reference standards) is listed in table 16. The analytical variability should represent only the component associated with each method because using a single WW-1 digest eliminates the variability from the in-bottle digestion procedure and the homogeneity of WW-1. SRWS T107 data were used for aluminum (220 µg/L), cobalt (11 µg/L), and silver (12 µg/L) and SRWS T117 was spiked with about 100 µg/L lead and 50 µg/L molybdenum to provide concentration levels measurable by ICP–OES. The median analytical variability for elements common to both methods is about a factor of two to three better by ICP–MS. The variability in elemental results is lower for ICP–MS than for ICP–OES when concentrations are less than 100 µg/L, a decrease most likely a consequence of its higher sensitivity. In contrast, ICP–OES provides lower variability in elemental results for concentrations greater than 100 µg/L (for example, barium, manganese, and strontium).

The analytical variability that can be expected over an extended range of concentrations is listed in table 17. In contrast to the variability presented for WW-1, these data were obtained for a calibration blank matrix and therefore correspond to optimal matrix conditions. The variability (in terms of percent relative standard deviation) generally increases as the concentration approaches the MDL. Elements with similar MDLs for ICP–OES and ICP–MS show about the same variability. Results for ICP–MS show much lower variability for elements, such as chromium, cobalt, lead, molybdenum, nickel, and zinc, because the corresponding MDLs are lower. Nevertheless, the variability of both methods approaches each other as the concentrations increase. As with the WW-1 data, these data indicate that the variability of ICP–OES is somewhat lower for selected elements at higher concentrations (for example, barium and strontium in table 17).

Spike Recoveries in Natural Whole-Water Digests

The percentage of spike recoveries for all elements was determined in six natural whole-water digests. Two ground-water and four surface-water samples that have specific conductance that are representative of the range of whole-water samples submitted to the laboratory for analysis were spiked. The pre-digestion specific conductances for the ground-water samples were 519 and 1,600 µS/cm and 103, 230, 683, and 1,900 µS/cm for the surface-water samples. The spike concentration level was determined individually for each sample and element. First, the original concentration of every element was determined in each sample digest. If the original concentration was found to be less than the MDL, the concentration of the spike was ten times the MDL, otherwise the sample was spiked at two times the original concentration.

Spike recovery results for the whole-water digest samples are listed in table 18. The average percent recovery for the six samples was used as an indicator for the overall accuracy of each method for every element. The average percent recovery is within 100±10 for all elements determined by ICP–OES. All elements determined by ICP–MS were also within this range except for beryllium, cadmium, chromium, manganese, and silver. The average percent recoveries for these elements are only marginally outside the 10-percent interval. Nevertheless, the recoveries are acceptable, considering that beryllium, cadmium, chromium, and silver were spiked at low concentrations. The mean recovery for manganese should have been expected to be within 10 percent, however, the mean recovery was influenced by the spike recovery for one digest. Low spike recoveries in the ground-water sample that have high specific conductance indicate high concentrations of dissolved solids may affect the accuracy of ICP–MS determinations (see table 18, for example, boron, cobalt, copper, lithium, manganese, nickel, and zinc). For this particular sample, the percentage recovery for selected elements was invariably low, however, never by more than 25 percent.

Comparison of Inductively Coupled Plasma–Optical Emission Spectrometry and Inductively Coupled Plasma–Mass Spectrometry to Former Methods in the Analysis of Natural Whole-Water Digests

Forty-three acidified, whole-water samples that had been digested by using the in-bottle procedure were selected from the population of such samples that were submitted to the NWQL. Selected digested whole-water samples have a wide range of element concentrations and specific conductance. Both surface-water and ground-water samples are included in the sample set; the number of each type is approximately 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 concentration, chloride concentration, and alkalinity, were also considered in the selection process (see table 19 for sample characteristics).

Every sample digest was analyzed by ICP–OES, ICP–MS, and one former method. The former method was either stabilized temperature graphite furnace–atomic absorption spectrophotometry (GF–AAS), flame–atomic absorption spectrophotometry (F–AAS), or direct current plasma–atomic emission spectrometry (DCP–AES), depending on the element being determined.

The presence or absence of significant bias (bias relative to the former method as opposed to method analytical bias) in ICP–OES and ICP–MS results was determined using a combination of statistical treatments. ICP–OES and ICP–MS results were compared to former method results by constructing scattergrams and box plots to show the bias and variance of the data set, by determining linear regression coefficients to identify systematic errors, and by using statistical analysis techniques to test whether ICP–OES and ICP–MS results differed significantly from former method results. Before an appropriate method of statistical analysis could be selected, all data sets were tested for normality and equal variance. If the data set was normally distributed with equal variance, a parametric test was used, otherwise, a nonparametric test was used.

A realistic statistical evaluation of the sample results was provided by only comparing results that were greater than the MDLs and within the calibration range of the methods being compared. The only exception to this approach was for comparisons made to GF–AAS. A high percentage of whole-water digests analyzed by GF–AAS required dilution because of its narrow linear calibration range. If these samples were omitted, the data set would have been too small for statistical analysis. In contrast, only a small number of digests required dilution for the other methods. Statistical analysis was impractical for some elements because the number of samples having results greater than the MDL was small. For example, cadmium, cobalt, lead, and molybdenum have only a small number of samples with concentrations greater than the MDLs for ICP–OES, therefore, only ICP–MS results could be compared with GF–AAS results. Aluminum, calcium, magnesium, and sodium concentrations exceed the calibration range for some samples and for some methods. Selected elements could not be determined by both ICP–OES and ICP–MS, hence, only one method was compared to the former method.

Nonparametric test procedures generally were used to compare methods because all the element concentrations extended several orders of magnitude. The Kruskal-Wallis Test was used whenever sufficient sample results were available for all three methods. The test was used to determine if there was any significant difference in the medians from each method at the 95-percent confidence level. Test results include the test statistic, p-value, and mean rank for each method. The mean rank is useful for relating individual methods to one another; the closer the mean ranks are to each other the better the overall correspondence. In all instances, the group-1 mean rank corresponds to ICP–OES data, group-2 corresponds to the ICP–MS, and group-3 corresponds to the former method. For selected elements, ICP–OES and ICP–MS also are compared individually to the former method using the One-sample Sign Test to determine if there is any difference between the medians at the 95-percent confidence level. The One-sample Sign Test was applied whenever one of the three methods was omitted because of its limited data set or whenever only two methods were available for comparison.

Linear regression analysis was used to calculate the slope and *y*-intercept coefficients of the equation describing the relation between ICP–OES or ICP–MS to the former method. The reliability of such a treatment was improved by always using the more precise, or equally precise, method as the independent variable (the x-axis variable). The regression coefficients (the slope, labeled with the former method's acronym and the y-intercept) and their 95-percent confidence intervals are provided (for example, see fig. 10a in Appendix).

The range of element concentrations composing the sample set is listed in table 19. The 25th percentile, 50th percentile (median), 75th percentile, and maximum concentration for every element demonstrate the broad concentration range of the sample set. The fraction of samples having concentrations less than the MDL provides insight into the suitability of each method for the analysis of a representative subset of the whole-water digests submitted to the NWQL. Results of the Kruskal-Wallis Test and One-sample Sign Test for each element are listed in table 20. Scattergrams, box plots, and regression coefficients for the same data set also are provided to augment the statistical results (see figs.10 through 30 in Appendix). There are no U.S. Geological Survey approved methods for the determination of silicon, thallium, uranium, and vanadium in whole-water digests, therefore, no comparisons could be made to ICP–OES and ICP–MS. The conclusions drawn from all statistical treatments are summarized for each of the following elements. Illustrations showing results of the statistical treatments are provided in the Appendix (see figs. 10–30).

Aluminum

Seventeen sample results were omitted from the data set used in the statistical analysis because the upper calibration limit for aluminum by DCP–AES is 10,000 µg/L and by ICP–MS is 1,000 µg/L; ICP–OES has an upper limit of 500,000 µg/L. However, the data set included two samples having the aluminum concentrations greater than 1,000 µg/L that were diluted and analyzed by ICP–MS. Only one sample was omitted because the aluminum concentration was less than an MDL. Using data having aluminum concentrations from 13 to greater than 13,000 µg/L, the Kruskal-Wallis Test indicated that there was no significant difference among results obtained using DCP–AES (the former method), ICP–OES, and ICP–MS (for n=25, the p-value=0.9750, see fig. 10b). Nevertheless, the mean rank for ICP–MS is somewhat closer to the mean rank for DCP–AES than is ICP–OES. The slope of the relation of ICP–OES to DCP–AES (0.88±0.02, see fig. 10a) indicates there is a slight negative bias (about 10 percent) in the ICP–OES results; the large y-intercept is negligible at the 95-percent confidence level (62±108). No systematic errors are indicated by the regression coefficients for ICP–MS in relation to DCP–AES (slope=1.04±0.02, *y*-intercept= –3.8±104).

Antimony

Only nine sample results could be compared because over 70 percent of the samples had antimony concentrations less than the MDL. Antimony concentration in the sample data set ranged from about 0.8 to 5 µg/L. Since the limited data set was normally distributed with equal variance, the Student *t*-Test was used to determine if there was a significant difference between the means from ICP–MS and GF–AAS. A p-value of 0.3061 suggests that any difference between the means is statistically insignificant, however, the scattergram and box plots indicate considerable variation in the results and show that ICP–MS results are negatively biased by about 30 percent (see fig. 11).

Barium

The size of the data set used in the comparison of ICP–OES and ICP–MS to the former F–AAS method was limited because of the high F–AAS method reporting limit of 100 µg/L (no MDL has been established); therefore, only 20 samples were used in the statistical analysis. The scattergrams show that there is considerable nonlinearity between F–AAS and ICP–OES results and between F–AAS and ICP–MS results (see fig. 12a). The box plots show a significantly larger variability in the F–AAS results. Nevertheless, the Kruskal-Wallis Test indicates that there is no significant difference between results for the three methods (p-value=0.3754). The mean ranks for ICP–OES and ICP–MS results were nearly equal although slightly greater than F–AAS, indicating that F–AAS results may be biased low (also shown in the box plots for ICP–OES and ICP–MS in fig. 12b). A comparison of regression analysis coefficients for ICP–MS and ICP–OES results shows close agreement (see fig. 12c showing a slope of 1.13±0.04).

Beryllium

All the samples have beryllium concentrations less than the F–AAS MDL, and only five are greater than the ICP–OES MDL of 0.7 µg/L. ICP–OES and ICP–MS results for these five samples were normally distributed with similar variance, so the Student *t*-Test was used to compare the results. The test indicated that there is no significant difference in the data (p-value=0.0974) and a slope of 1.0±0.1 indicated negligible bias (see fig. 13).

Boron

Fifteen data points (seven samples having boron concentrations less than the MDLs and eight samples having boron concentrations greater than the ICP–MS upper calibration limit of 100 µg/L) were omitted so that the data set would have boron concentrations that ranged from 13 to 82 µg/L. The scattergrams, box plots, and regression coefficients indicate considerable differences among the DCP–AES, ICP–OES, and ICP–MS results, a finding also supported by the Kruskal-Wallis Test (p-value=0.0021, see fig. 14b). The mean rank for ICP–OES was about 30 percent lower than the DCP–AES mean rank; ICP–MS was about 20 percent higher. In treating the methods separately by using the One-sample Sign Test, there is still a significant difference (p-value=0.0288, n=36, see fig. 14c) between DCP–AES and ICP–OES results and between DCP–AES and ICP–MS results (p-value=0.0009, n=28, see fig. 14d). The slope of the regression (2.0±0.7, see fig. 14a) also indicates that ICP–MS results are about two times greater than DCP–AES results. This difference can easily be seen in the box plot (see fig. 14d). However, the slope of 1.00±0.03 for ICP–OES indicates close agreement with DCP–AES (see fig. 14c). In addition, the average difference between DCP–AES and ICP–OES over the entire concentration range of the samples was approximately 8 µg/L, a concentration that is less than the method reporting limit for DCP–AES.

Cadmium

The accuracy of the ICP–OES method could not be determined because only one sample out of 43 had a cadmium concentration greater than its MDL of 6 µg/L. Statistical analysis indicated that there is no significant difference in results from ICP–MS and GF–AAS (p-value=0.0522, n=27, see fig. 15) for samples with cadmium concentrations ranging from less than 0.1 to 6 µg/L. Also, the slope (1.00±0.02) and y-intercept (0.03±0.03) indicate there is no significant bias or method offset.

Calcium

Thirty-two samples have calcium concentrations less than the calibration limit (60 mg/L) of the former method (F–AAS). Statistical analysis of the data set using the One-sample Sign Test indicated a substantial difference between ICP–OES and F–AAS results (p-value=<0.0001, see fig. 16). This difference is based on the fact that 29 out of 32 ICP–OES results were greater than F–AAS; the median difference for the data set is approximately 1 mg/L for samples having from 1 to 60 mg/L calcium. However, the slope coefficient of the regression 1.03±0.03 suggests that the bias between F–AAS and

ICP–OES results is negligible. The box plots (see fig. 16) also support this conclusion.

Chromium

Because the MDLs for ICP–OES (4 μg/L) and ICP–MS (2 μg/L) are greater than GF–AAS, the data set is reduced to only 15 samples having between 6 to 160 μg/L chromium. Using this data set, the Kruskal-Wallis test showed there is a high probability that GF–AAS, ICP–OES, and ICP–MS results are statistically different (p-value=0.0078), an outcome supported by the box plots in figure 17b. When comparing the methods individually to GF–AAS, the One-sample Sign Test indicated significant differences between ICP–OES and GF–AAS (p-value=<0.0001, n=15, see fig. 17c) and between ICP–MS and GF–AAS (p-value=<0.0001, n=26, see fig. 17d). ICP–OES results were always less than GF–AAS (by a median of 13 μg/L) and ICP–MS results were always greater than GF–AAS (by a median of 3 μg/L). The slope of the regression equation for ICP–OES in relation to GF–AAS (0.52±0.05) also shows a 50 percent negative bias in the ICP–OES results (fig. 17a). However, the slope (1.04±0.05) for the regression of ICP–MS in relation to GF–AAS suggests no significant bias, although there is perhaps a slight offset in the results (y-intercept=3±2).

Cobalt

Cobalt concentrations were greater than the relatively high ICP–OES MDL of 10 μg/L in only six samples. ICP–OES gave high results for four of these samples when compared to GF–AAS (see fig. 18a). This inaccuracy is related to the direct spectral overlap from a nearby iron wavelength; the four samples had iron concentrations ranging from 2 to 50 mg/L. The accuracy of the algorithm used to correct iron emission contributions to cobalt is apparently unsatisfactory when iron concentrations exceed 2 mg/L. ICP–MS and GF–AAS results from 31 samples having cobalt concentrations ranging from 0.5 to 86 μg/L showed significant differences (p-value =0.0033, see fig. 18c). The slope of 0.87±0.04 suggests about 14 percent negative bias in the ICP–MS data, however, the median difference between the methods was only about 0.3 μg/L (fig. 18b). When data from three samples having the largest deviation from the former method are omitted, the bias in the ICP–MS data was reduced to about 3 percent.

Copper

Due to the relatively high copper concentrations, 28 samples could be used to compare ICP–OES, ICP–MS, and GF–AAS methods; 15 samples were omitted because copper concentrations were less than the MDL by ICP–OES. Copper concentrations ranged from 3 to 370 μg/L. Statistical analysis of the data set using the Kruskal-Wallis Test indicated that the results from the three methods were not significantly different (p-value=0.5285, see fig. 19b). Scattergrams in figure 19a show a pattern of nonlinearity in GF–AAS for cooper concentrations greater than 100 μg/L that is possibly a result of dilution error. The ICP–OES mean rank of 38 is slightly less than the former method probably because about half the sample concentrations were near the MDL (see fig. 19b). In contrast, the mean rank for ICP–MS equals that of GF–AAS and there is no significant difference indicated by the One-sample Sign Test (p-value=0.6440, n=42, see fig. 19c) for the extended data set.

Iron

Thirty-eight sample results were included in the sample set, two samples with iron concentrations greater than 50,000 μg/L, one sample with iron concentration less than the MDL, and two samples were not analyzed because of the lack of sample. The One-sample Sign Test implies that substantial differences exist between ICP–OES and F–AAS results for the samples having iron concentrations between 40 and 19,000 µg/L (p-value=0.0002, n=38, see fig. 20). Over 80 percent of the ICP–OES results were less than the former method (a median difference of only 80 µg/L) probably because of its lower MDL. The slope of the regression equation (0.87±0.03) shows a negative bias of more than 10 percent in ICP–OES results, a level that is acceptable considering the wide concentration range of the samples analyzed. When the concentration range is narrowed to include samples with concentrations from 440 to 4,500 µg/L iron (the concentration boundaries where 50 percent of the iron results occur), there is no significant difference between the two methods.

Lead

Because of the insensitivity of the lead emission wavelength, only four samples had lead concentrations that are measurable using ICP–OES. Nonetheless, ICP–OES results for these samples were inexact because the concentrations were less than a factor of two greater than the MDL of 50 µg/L. The number of results comparing ICP–MS to GF–AAS was reduced to 31 by eliminating nine samples having lead concentrations less than the GF–AAS MDL and three samples having lead concentrations greater than the upper calibration limit of 100 µg/L for ICP–MS. The One-sample Sign Test suggested that there was no significant difference between ICP–MS and GF–AAS results (p-value =0.2810, see fig. 21). This result is supported by linear regression coefficients that show no systematic errors or offset (slope=0.98±0.06 and y-intercept=0.12±1.3, for n=31).

Lithium

Sixteen samples having lithium concentrations less than 10 µg/L, the method-reporting limit for the former method F–AAS, were omitted from the data set. The differences between analytical results for F–AAS, ICP–OES, and ICP–MS were found to be statistically insignificant using the Kruskal-Wallis Test (p-value=0.9191, see fig. 22b). The scattergram of ICP–OES in relation to F–AAS data indicate slight nonlinearity, however, the slope interval of 0.90±0.09 indicates the negative bias is insignificant (see fig. 22a). The slight positive bias (slope interval 1.1±0.1) between F–AAS and ICP–MS is also negligible.

Magnesium

The upper calibration limit for magnesium by the F–AAS method is 50 mg/L. This limitation reduced the data set to 41 samples for which no statistically significant difference between ICP–OES and F–AAS results was indicated (p-value=0.6440, see fig. 23). Regression analysis indicated only a minor 7 percent negative bias in the ICP–OES results (slope=0.93±0.03) probably because of the lower variability in the ICP–OES data set (see the box plot in fig. 23).

Manganese

The sample set was reduced to 36 by eliminating one sample having manganese concentration less than the reporting limit by F–AAS and six samples having manganese concentrations greater than 1,000 µg/L, the ICP–MS upper calibration limit. Results of the Kruskal-Wallis Test suggest that there are no significant differences among the former F–AAS method, ICP–OES, and ICP–MS (p-value=0.8669, see fig. 24b) for samples having manganese concentrations ranging from 6 to 870 µg/L. However, ICP–OES provided somewhat more accurate results for the sample set when compared to F–AAS, as indicated by its mean rank, than did ICP–MS. Both proposed methods gave marginally lower results than the former F–AAS method. However, the slopes for ICP–OES (0.99±0.04, n=36) and ICP–MS (0.94±0.05, n=36) in relation to F–AAS showed no bias (see fig. 24a).

Molybdenum

All the samples had molybdenum concentrations less than the ICP–OES MDL (about 20 μg/L), therefore, only ICP–MS could be compared to the GF–AAS. Only 28 samples composed the data set; 15 samples had molybdenum concentrations less than either the ICP–MS or GF–AAS MDLs. The One-sample Sign Test suggested that there was no significant difference between ICP–MS and GF–AAS results (p-value=0.5716, see fig. 25) for the sample set having molybdenum concentrations from about 0.4 to 13 μg/L. In addition, no bias was indicated by the regression analysis (slope=1.0±0.2).

Nickel

Eighty percent of the samples have nickel concentrations less than the ICP–OES MDL. Of the seven remaining samples, five were only two times greater than the MDL of 20 μg/L. Two samples having greater than 100 μg/L nickel compared favorably (within 2 to 20 percent) to the ICP–MS and GF–AAS results. The data set used for comparing ICP–MS to GF–AAS was composed of 34 samples; six samples were omitted because the nickel concentration was less than the GF–AAS or ICP–MS MDL and three because the nickel concentration exceeded the upper calibration limit for ICP–MS. Statistical analysis of the data set indicates there is a significant difference between ICP–MS and GF–AAS results (p-value=0.0243, see fig. 26) even though the median difference was only 0.2 μg/L. The slope of the regression suggests that the ICP–MS data are negatively biased by about 10 percent when compared to GF–AAS. This bias would represent from 0.2 to 0.8 μg/L for 50 percent of the samples.

Selenium

Only four samples have selenium concentrations greater than 0.8 μg/L, the MDL for the former method GF–AAS. Using this limited, normally distributed data set, the Student *t*-Test indicated that there were no significant differences between ICP–MS and GF–AAS results (p-value=0.3670). Although not presented in figure 27, the One-sample Sign Test also indicated no significant difference (p-value=0.62). Close examination of the data shows that ICP–MS measured levels up to two times its MDL (2 μg/L) in 4 of the 40 samples in which GF–AAS detected less than 0.8 μg/L. However, this apparent discrepancy is not unusual because of the inherent limitations of measuring samples near the MDL.

Silver

Only one sample had silver at concentration levels greater than the GF–AAS MDL of 0.1 μg/L; all the samples were less than the ICP–OES MDL. The single GF–AAS result (2.0 μg/L) compared favorably to the ICP–MS result of 2.1 μg/L.

Sodium

Significant differences between ICP–OES and F–AAS results (p-value=0.0046, n=33, see fig. 28) are suggested by the One-sample Sign Test. Seventy-five percent of the ICP–OES results were greater than the corresponding F–AAS measurements. The median difference was only about 0.7 mg/L for sodium concentrations ranging from 0.7 to 38 mg/L. A slight positive bias in the ICP–

OES results (slope=1.08±0.02) might be related to differences in calibration standards.

Strontium

Thirty-seven samples composed the data set used to compare the methods; six samples were not analyzed because of the lack of sample volume. Statistical analysis indicated there was no significant difference between the method results (p-value=0.9369, see fig. 29b) and no significant bias was implied in the regression coefficients.

Zinc

Twenty-six samples were not included in the comparison of ICP–OES, ICP–MS, and the former method F–AAS because either the zinc concentration was less than ICP–OES or F–AAS MDLs or the zinc concentration was greater than the upper calibration limit for F–AAS. Statistical analysis of the remaining 17 samples indicated that there were no significant differences in the results obtained by the three methods (p-value=0.8097, see fig. 30b) although the mean rank for ICP–OES is slightly higher than for F–AAS. The One-sample Sign Test suggested that there was no significant difference between ICP–MS and F–AAS (p-value=0.8388, n=26, see fig. 30c) for the extended data set. However, the slopes indicated about a 10-percent negative bias in the ICP–MS results compared to only 4 percent for ICP–OES (fig. 30a).

CONCLUSIONS

Results from SRWS, spike recoveries for six natural whole-water digests, and the analysis of 43 natural whole-water digests were used to evaluate the overall accuracy and variability of ICP–OES and ICP–MS. The conclusions derived from all these test results provide an accurate estimate of the expected analytical performance of the new methods. Summaries of results of the evaluation process are provided separately for ICP–OES and ICP–MS in the following paragraphs. Poor performance in any of the evaluation processes for an element is specifically addressed for each method.

Summary of Test Results for Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES)

Most results from Standard Reference Water Sample (SRWS) analyses, spike recoveries for six natural whole-water digests, and the analysis of 43 natural whole-water digests show that aluminum, barium, beryllium, boron, cadmium, calcium, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, silicon, silver, sodium, strontium, vanadium, and zinc can be accurately determined using ICP–OES. Some calcium, magnesium, manganese, and vanadium SRWS data are outside the 1σ interval about the most probable value (MPV) but within the 1.5σ interval that is acceptable by National Water Quality Laboratory (NWQL) criteria. Zinc and silver concentrations in one SRWS and nickel in two SRWSs are greater than the 1.5σ interval of the MPV. Spike recoveries in two ground-water and four surface-water sample digests ranged from 90 to 110 percent for all elements. Elemental results for a large number of digested natural whole-water samples agree with former methods of analysis for most elements. Evaluation of these results for beryllium, cadmium, lead, molybdenum, nickel, and silver are constrained by a small number of sample results because concentrations are less than the ICP–OES method detection limits (MDLs). All other data indicate that samples having concentrations greater than MDL for these elements can be accurately analyzed. The vanadium and silicon evaluations were based only on SRWS and spike recovery data because former methods are not available at NWQL.

Only chromium and cobalt exhibited unacceptable performance in selected tests. Chromium results for whole-water digests were consistently more than 50 percent lower than the former method results even though the concentrations were greater than the MDL. The suppression of the chromium emission for the whole-water digests is apparently not being adequately controlled by the yttrium internal standard. This suppression is not apparent in the SRWS or spike-recovery data and could possibly be related to the dissolved-solid concentration in the digests or an unidentified spectral interference. Therefore, the determination of chromium by ICP–OES is not recommended without further investigations.

The evaluation of the accuracy of cobalt results for the whole-water digests was difficult because of the limited number of samples; more than 90 percent of the measurements were less than the MDL. The severe direct-spectral overlap, however, prevented accurate cobalt determinations whenever the iron concentration exceeded 2,000 μg/L. Because natural whole-water digests likely contain substantial amounts of iron, the determination of cobalt will always be problematic. Therefore, the determination of cobalt by ICP–OES is recommended only when samples have less than 2,000 μg Fe/L.

Summary of Test Results for Inductively Coupled Plasma–Mass Spectrometry (ICP–MS)

Most results from SRWS analyses, spike recoveries for six natural whole-water digests, and the analysis of 43 natural whole-water digests show that aluminum, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, lithium, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, and zinc can be determined accurately by using ICP–MS. All elemental results were within $\pm 1.5\sigma$ of the MPV for all SRWSs except for beryllium and lithium in one SRWS. Spike recovery results were 100±10 percent except for beryllium, cadmium, chromium, and silver. These elements are only marginally outside the ±10 percent acceptance limit. The spike concentrations, however, were generally less than 10 μg/L except for chromium. Because of the low spike levels and acceptable accuracy for SRWSs and whole-water digests, these four elements can most likely be determined accurately by ICP–MS. The accuracy achieved in the SRWS and spike recovery data for antimony, selenium, and silver is not strongly supported with whole-water digest results because of the small number of samples with detectable concentrations. Nevertheless, the probability is high that accurate determination of these elements can be achieved.

Thallium and uranium accuracy is based only on SRWS and spike recovery data because former methods for determination of these elements in whole-water digests are not available at NWQL. Subsequent to conducting this evaluation, a new SRWS (T139) became available that has MPV for thallium (3.1±0.8 μg/L) and uranium (5.0±0.2 μg/L). ICP–MS results for thallium and uranium are within the 1σ-confidence intervals of the MPVs. These elements also are generally unaffected by spectral interferences because of their high masses.

Whole-water digest results for boron show considerable deviation from the former direct current plasma–atomic emission spectrometry (DCP–AES) method. The slope of the regression indicates that ICP–MS results are consistently two times greater than the former method. Box plots and scattergrams also show considerable variation throughout the concentration range. Even though SRWS and spike recovery data do not indicate any problem for the determination of boron, apparently some form of interference is affecting the accuracy of results. Conse-quently, the determination of boron by ICP–MS is not recommended without additional investigations.

Accurate determination of chromium by ICP–MS has been shown to be acceptable by the data presented here. Correction for chlorine-based molecular ion interference, however, has been based on matrix matching the calibration standards to the in-bottle digests. This method of correction can become problematic. In a small number of instances, the degree of accuracy has been found to be unacceptable.

The bulleted list below provides a succinct outline of the major conclusions of this report. In addition to analytical performance comparisons, suggestions are provided for selecting appropriate methodology and the potential effect of the ICP–OES and ICP–MS methods on long-term trend analysis in water-quality studies.

- MDLs for ICP–MS are between 5 and 1,000 times lower than ICP–OES. ICP–MS MDLs are similar in magnitude to former graphite furnace–atomic absorption spectrophotometry (GF–AAS) methods and MDLs for both ICP–MS and ICP–OES are much lower than former flame–atomic absorption spectrophotometry (F–AAS) methods.

- The short- and long-term accuracy of ICP–OES and ICP–MS was acceptable for the reference materials studied. Greater than 90 percent of the elements were within 1σ of the most probable value.

- For most elements, ICP–MS is the method of choice whenever concentrations are less than 100 µg/L. Conversely, ICP–OES performs better at concentrations greater than 1,000 µg/L.

- The median long-term variability in elemental results from a simulated whole-water sample (SRWS WW-1) was 2 to 3 times lower for ICP–MS than for ICP–OES. Nevertheless, there was somewhat less variability in results from ICP–OES for lighter elements (< 60 amu) and whenever elemental concentrations were greater than 100 µg/L.

- Short-term analytical variability decreased with method sensitivity; therefore, there is less variability in results from ICP–MS, especially at lower concentration levels.

- Matrix interferences affected the determination of lighter elements (< 60 amu) in selected samples by ICP–MS; however, the maximum error was 25 percent.

- Data from 43 surface- and ground-water samples indicated there was no significant method bias for 90 percent of the elements tested. Only chromium (by ICP–OES) and boron (by ICP–MS) results were unacceptably biased.

- Data from ICP–MS will have the highest probability of affecting long-term trends in water-quality studies. For example, more than 50 percent of the whole-water digests analyzed had cadmium, chromium, lead, molybdenum, nickel, and zinc concentrations less than the ICP–OES MDLs. The level of accuracy and variability for concentrations less than 100 µg/L will be substantially different than for most former methods. Data from ICP–OES will have somewhat less of an effect.

- ICP–OES and ICP–MS are state-of-the-art multielement techniques that are more efficient and cost effective than former USGS single-element methods such as F–AAS, GF–AAS, or DCP–AES. For these reasons they are the methods of choice.

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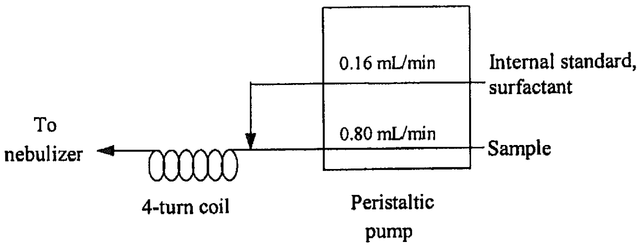
APPENDIX

Figures 1 – 30

Tables 8 – 20

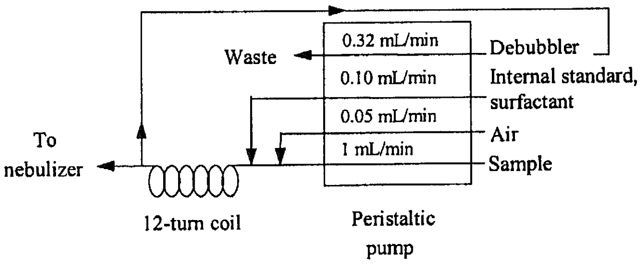


Peristaltic pump tubing color code

0.16 mL/min	orange/yellow
0.80 mL/min	red

mL/min, milliliters per minute

Figure 1a. Sample introduction manifold for inductively coupled plasma–optical emission spectrometric method.



Peristaltic pump tubing color code

0.32 mL/min	black
0.10 mL/min	orange/green
0.05 mL/min	orange/blue
1 mL/min	gray

mL/min, milliliters per minute

Figure 1b. Sample introduction manifold for inductively coupled plasma–mass spectrometric method.

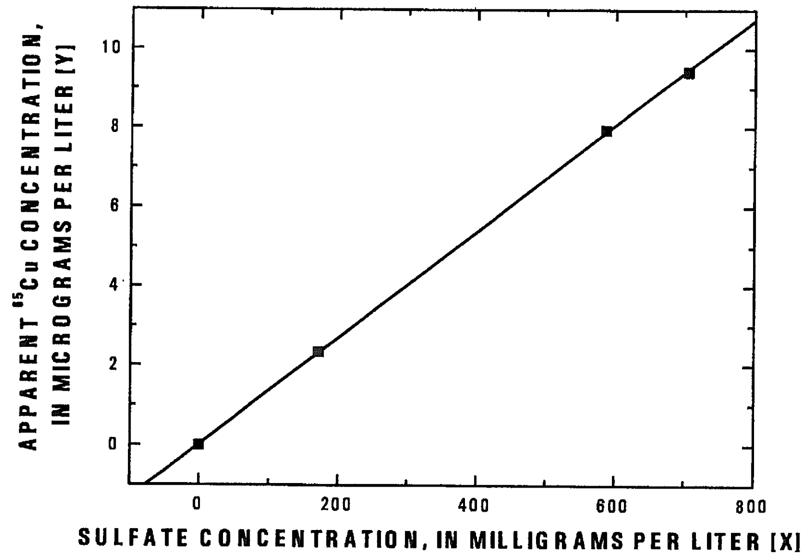


Figure 2a. Sulfate interference on copper determinations by inductively coupled plasma–mass spectrometry. The linear regression equation is $y = 0.021 + 0.013x$ ($R^2 = 0.9999$).

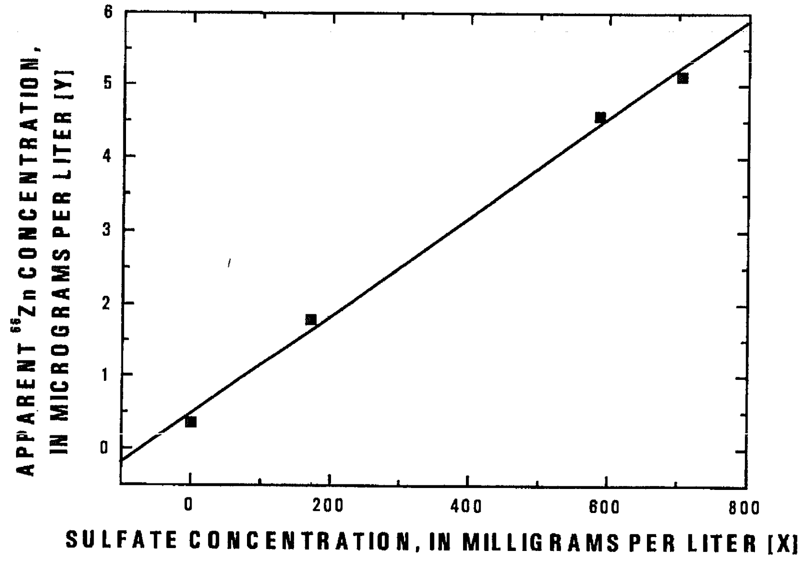


Figure 2b. Sulfate interference on zinc determinations by inductively coupled plasma–mass spectrometry. The linear regression equation is $y = 0.48 + 0.0068x$ ($R^2 = 0.9977$).

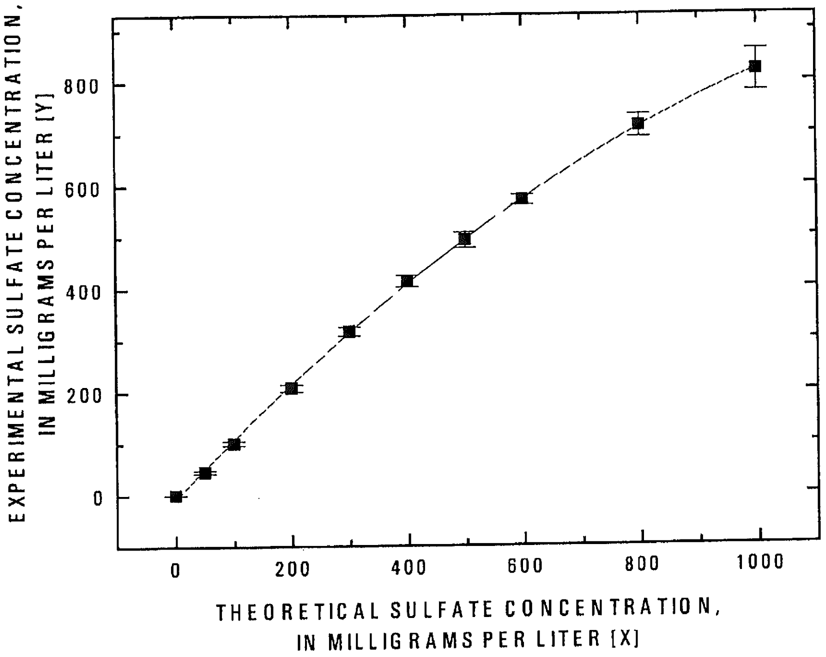


Figure 3. Accuracy of inductively coupled plasma–mass spectrometric sulfate determinations using $^{32}S^{16}O^{+}$ response. The polynomial regression equation is $y = -7.9 + 1.2x - 0.0004x^2$ ($R^2 = 0.9998$). Error bars represent ± 1 standard deviation.

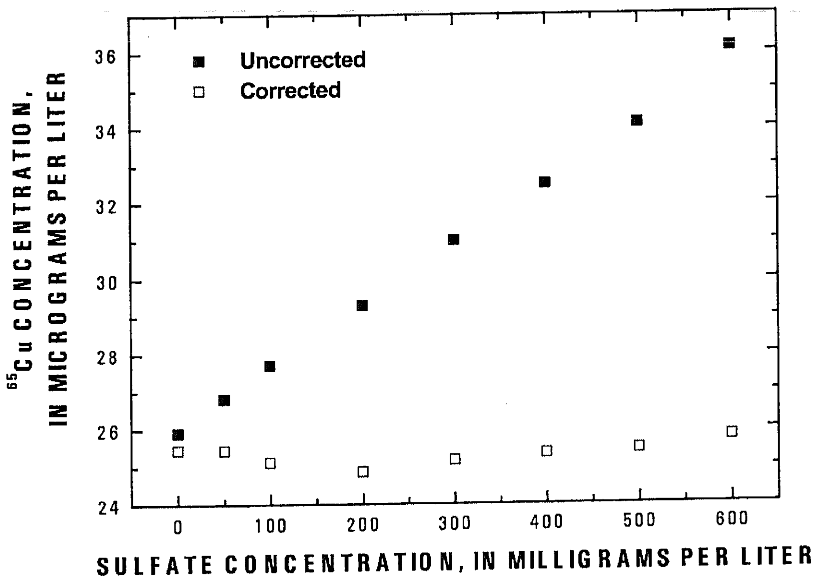


Figure 4a. Accuracy of sulfate interference corrections on copper determinations by inductively coupled plasma–mass spectrometry.

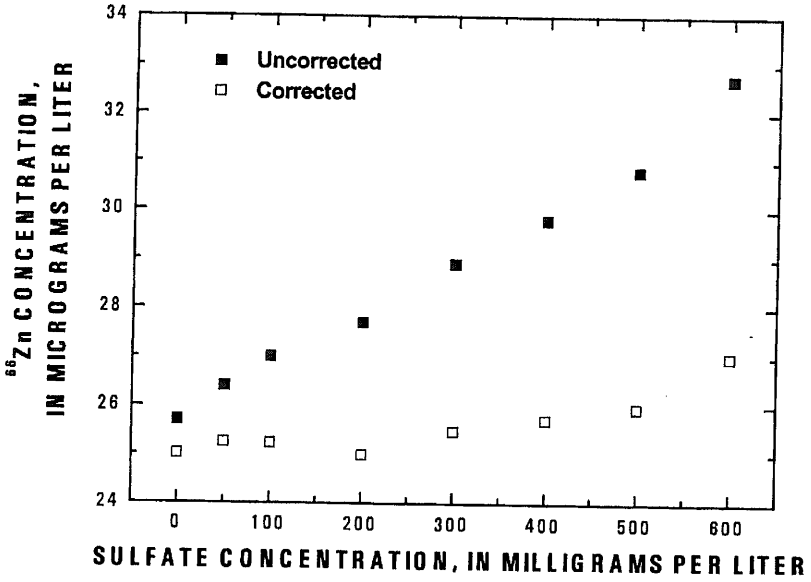


Figure 4b. Accuracy of sulfate interference corrections on zinc determinations by inductively coupled plasma–mass spectrometry.

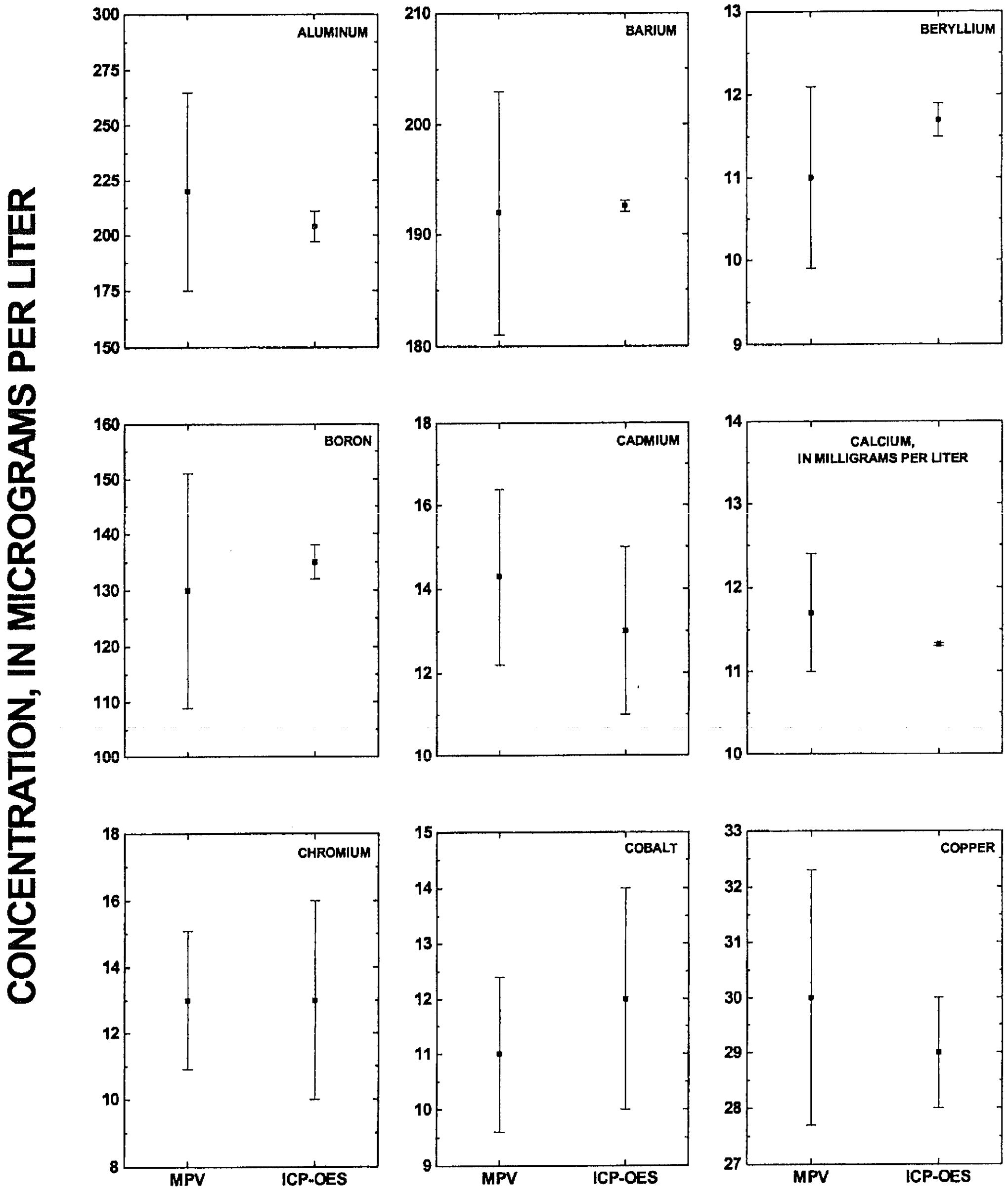


Figure 5a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T107. Error bars represent ± 1 standard deviation from the mean.

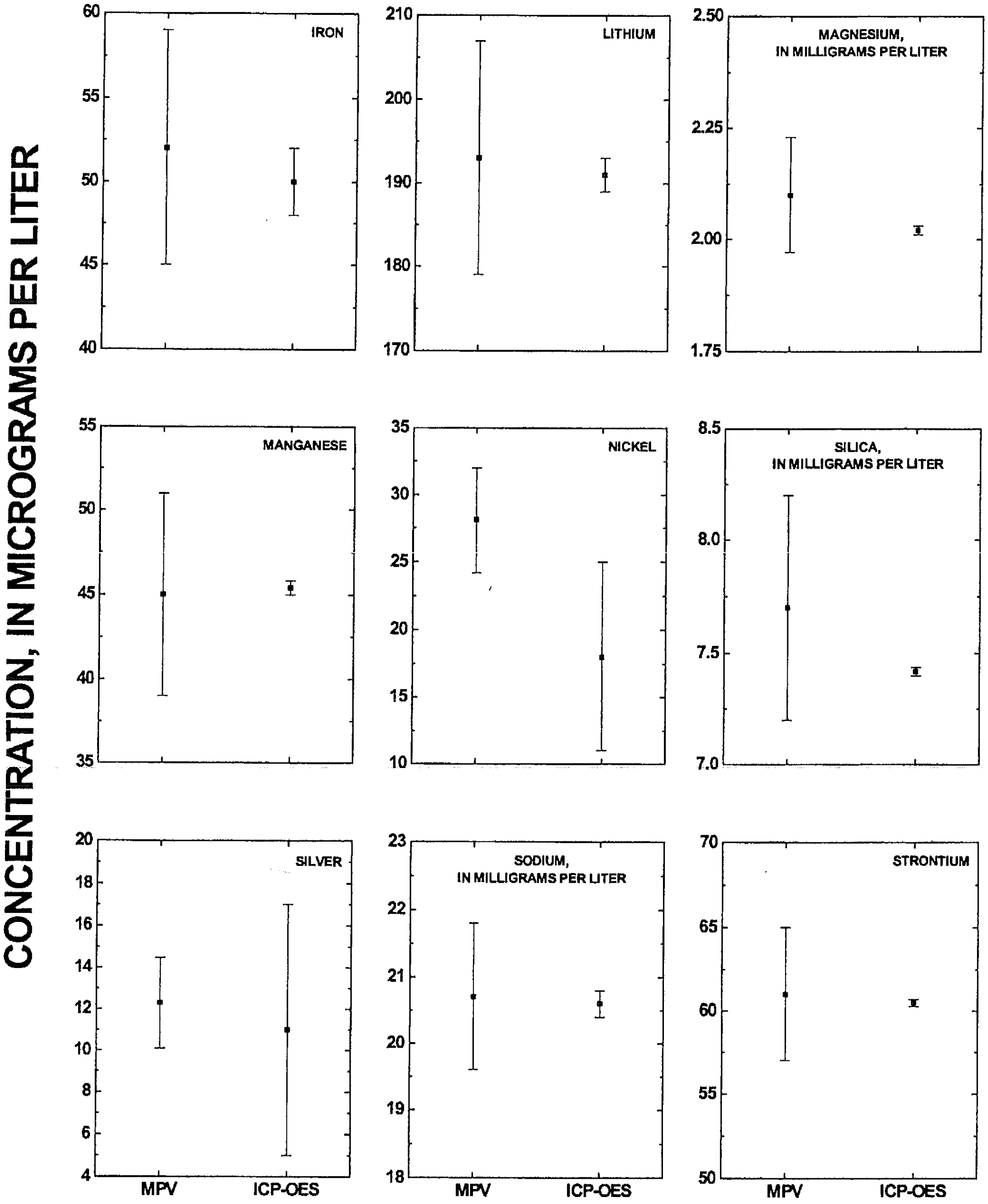


Figure 5a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T107—Continued.

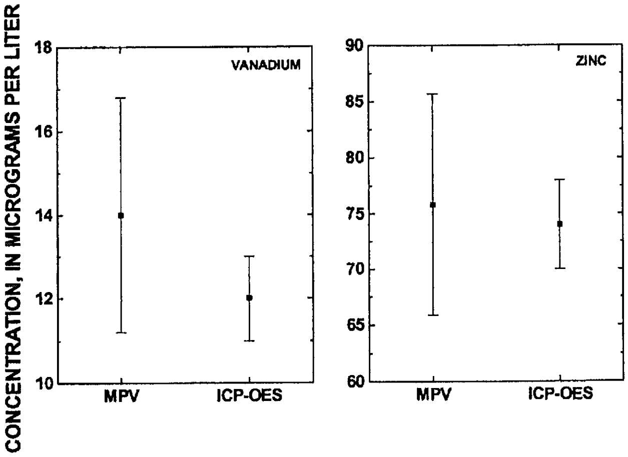


Figure 5a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T107—Continued.

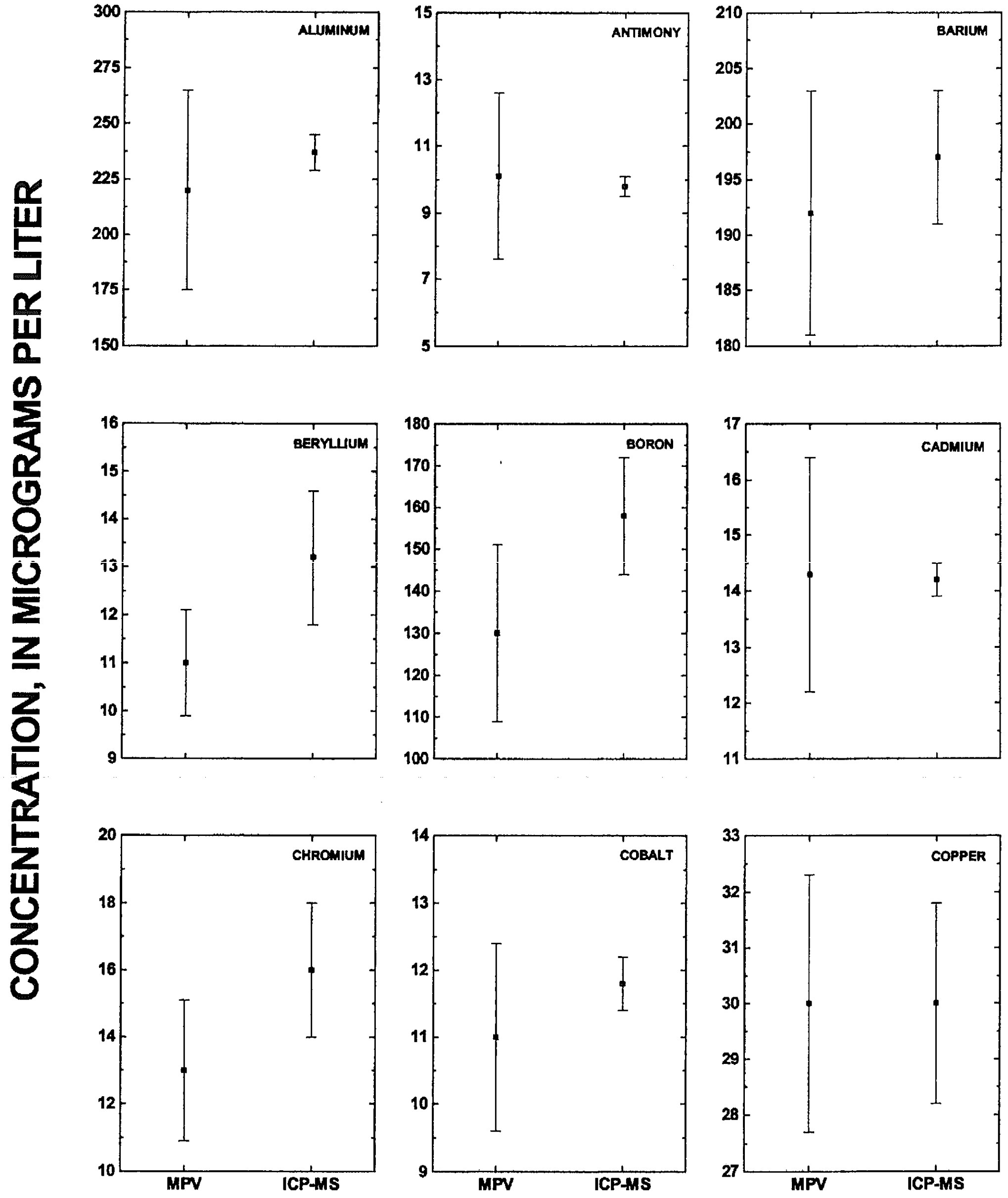


Figure 5b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T107. Error bars represent ± 1 standard deviation from the mean.

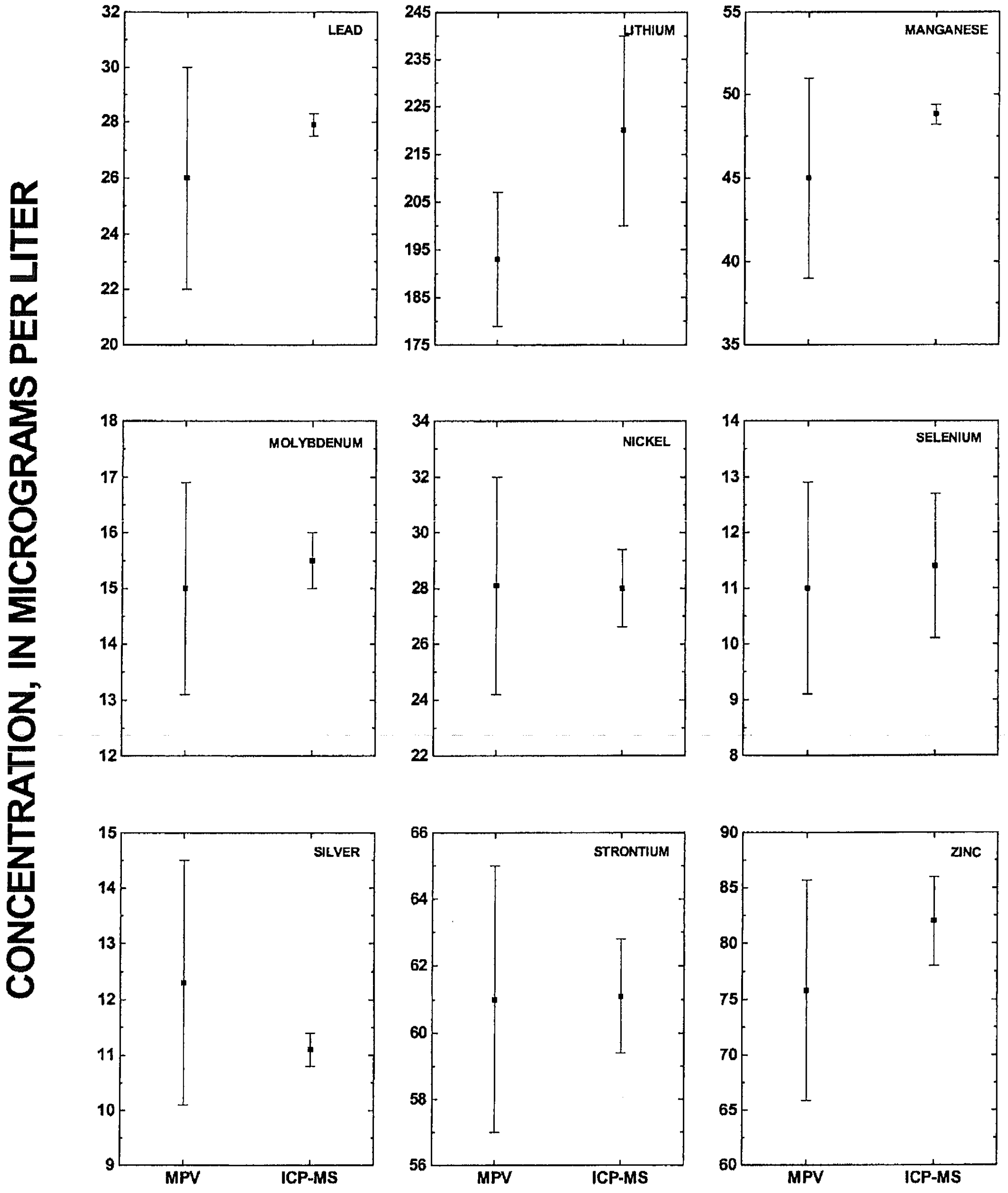


Figure 5b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T107—Continued.

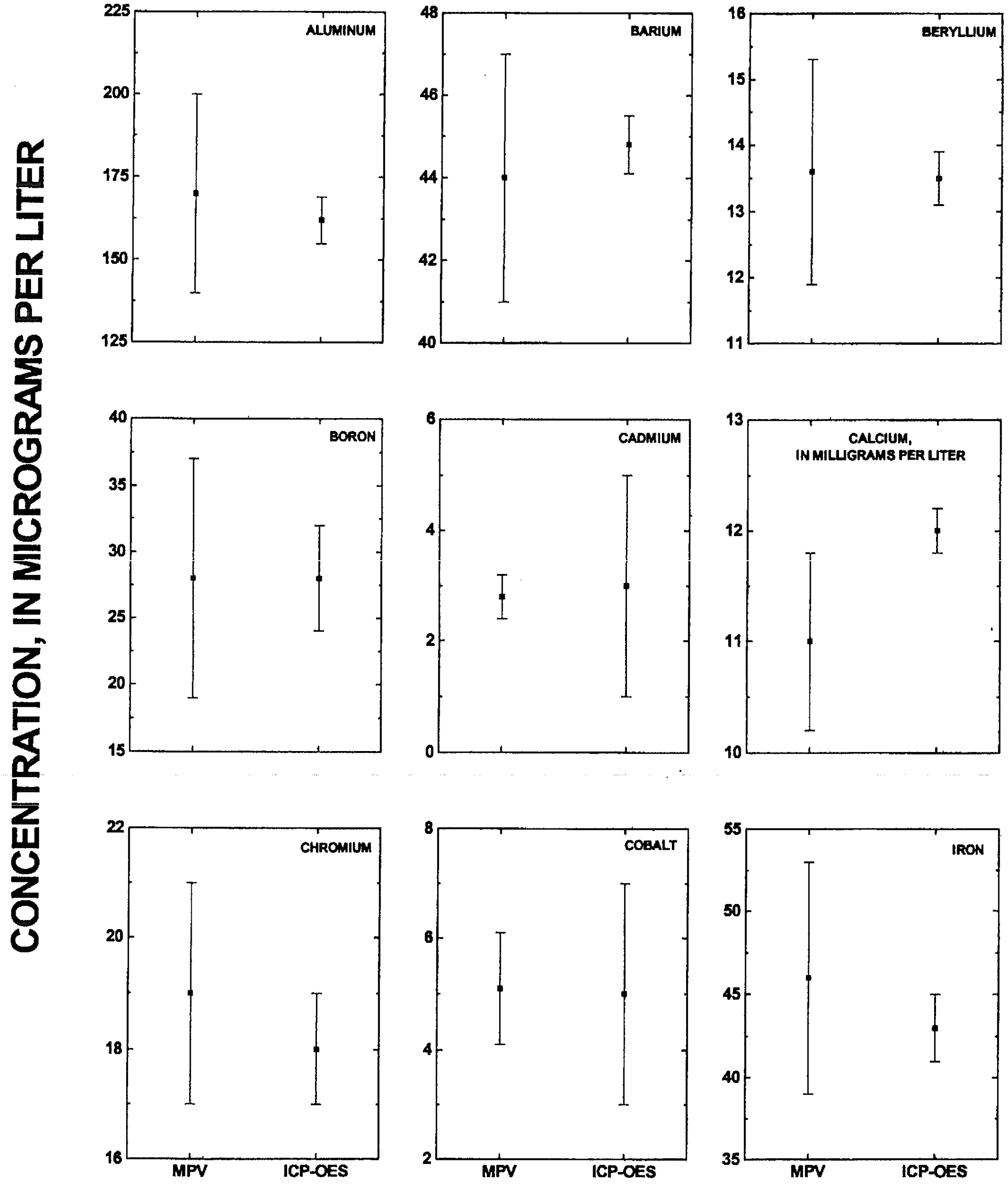


Figure 6a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T119. Error bars represent ± 1 standard deviation from the mean.

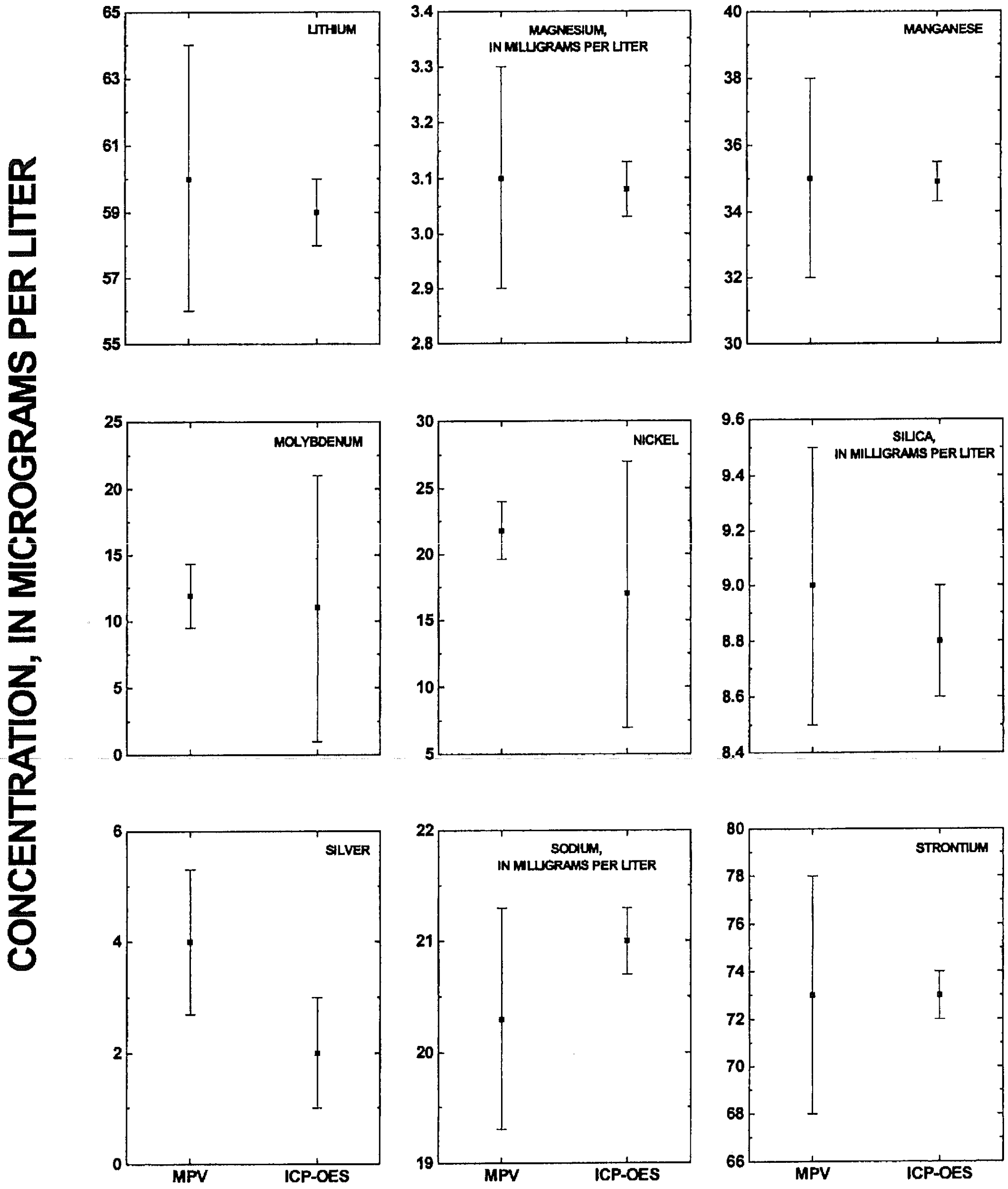


Figure 6a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T119—Continued.

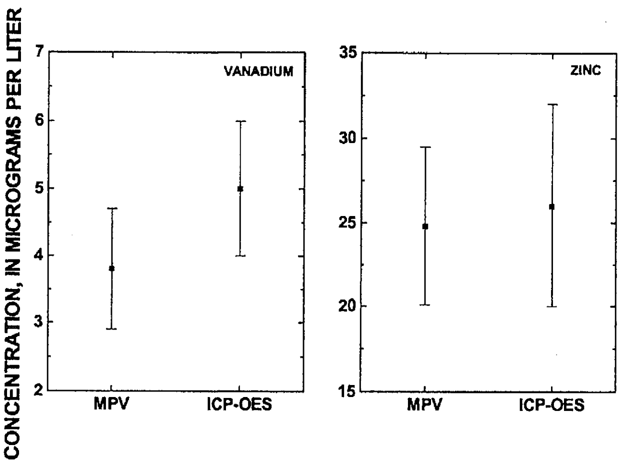


Figure 6a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T119—Continued.

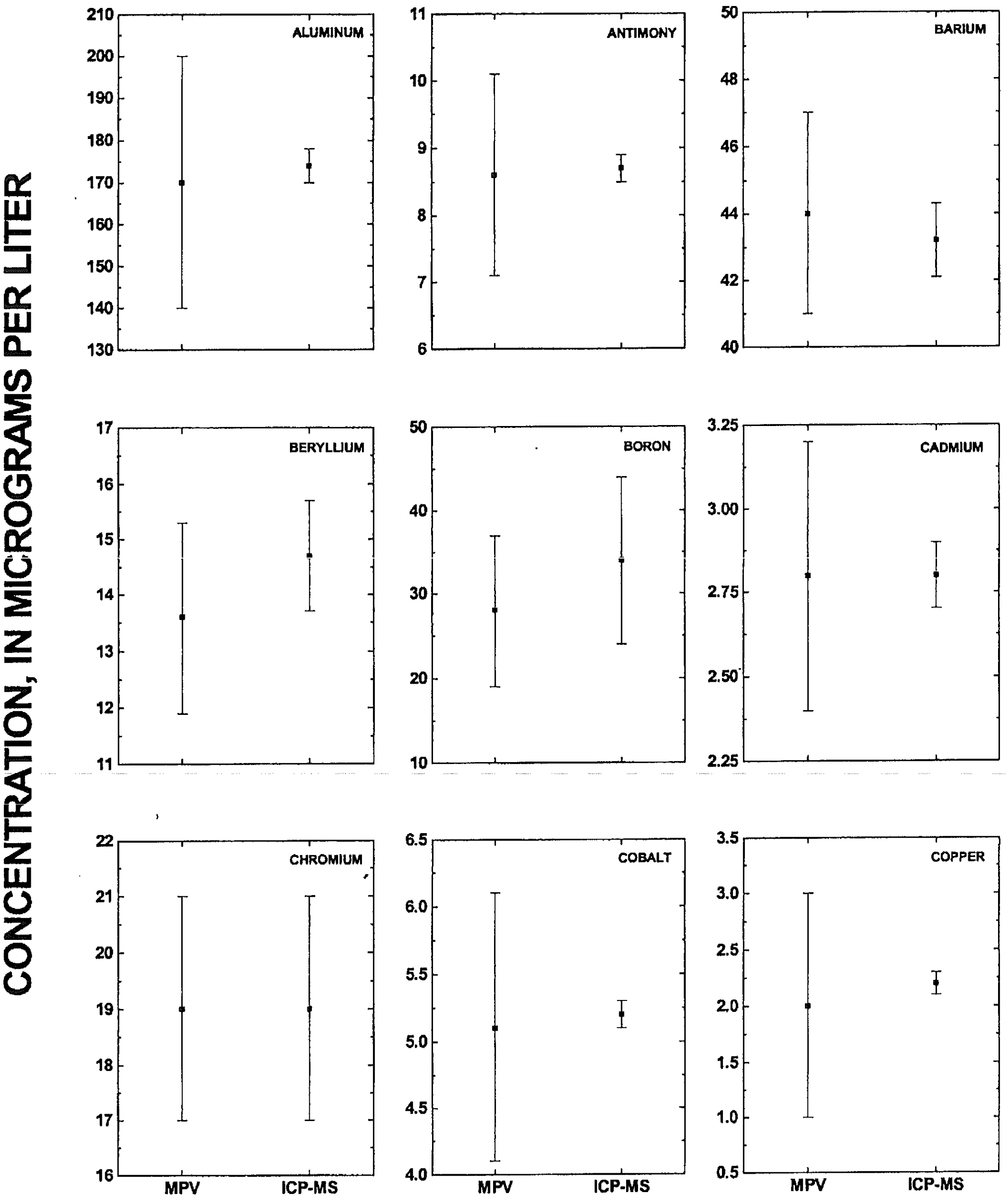


Figure 6b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T119. Error bars represent ± 1 standard deviation from the mean.

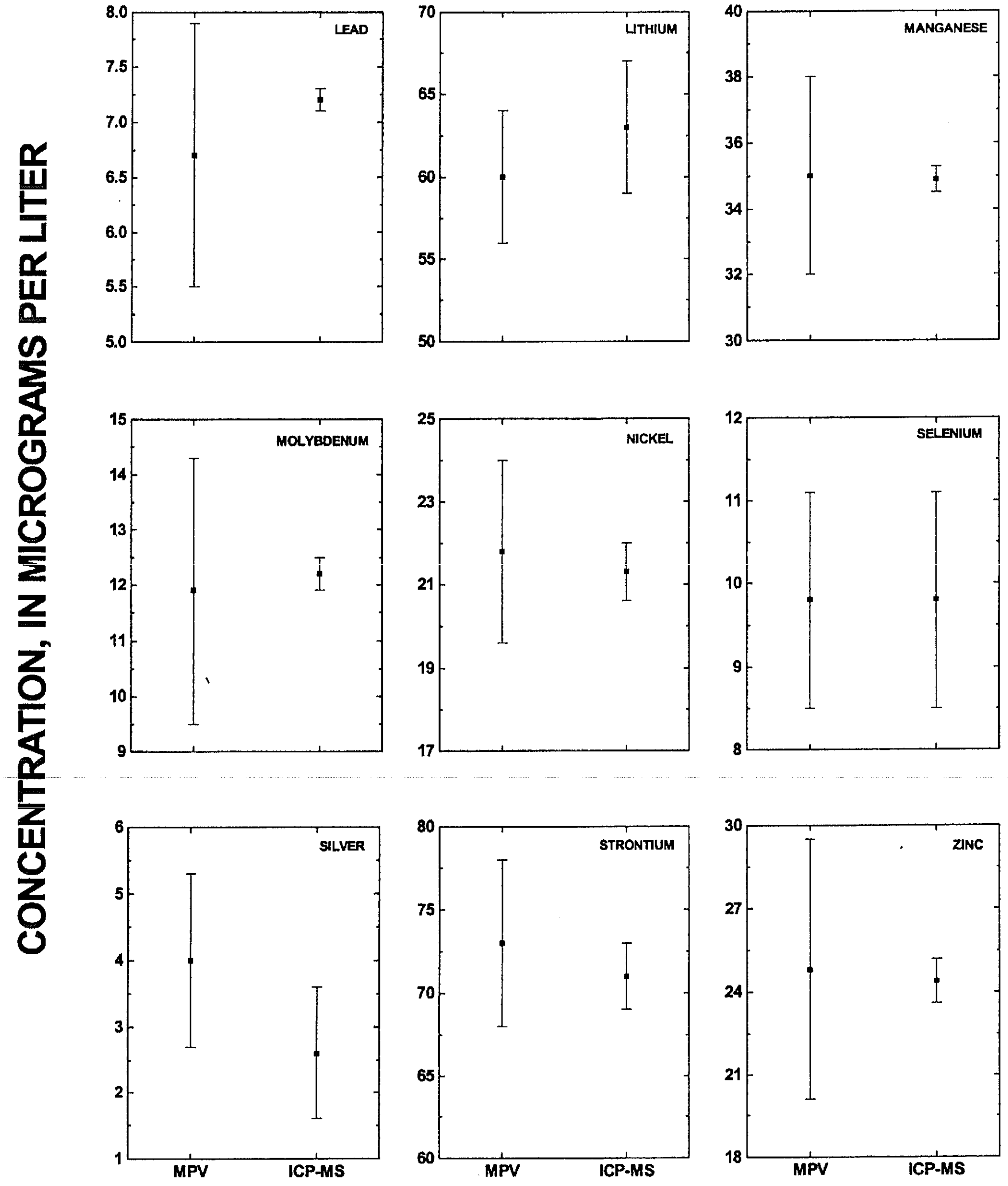


Figure 6b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T119—Continued.

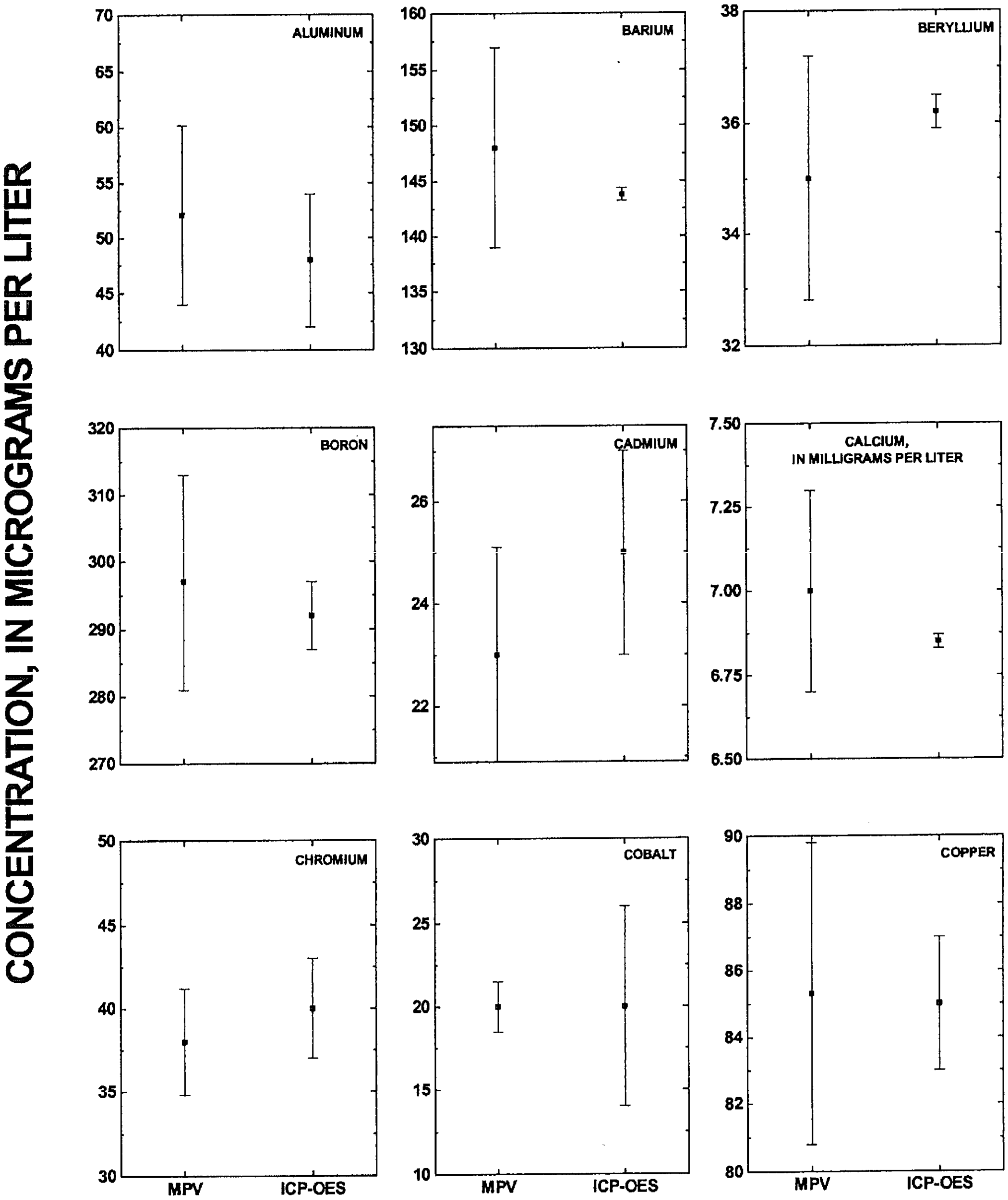


Figure 7a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T133. Error bars represent ± 1 standard deviation from the mean.

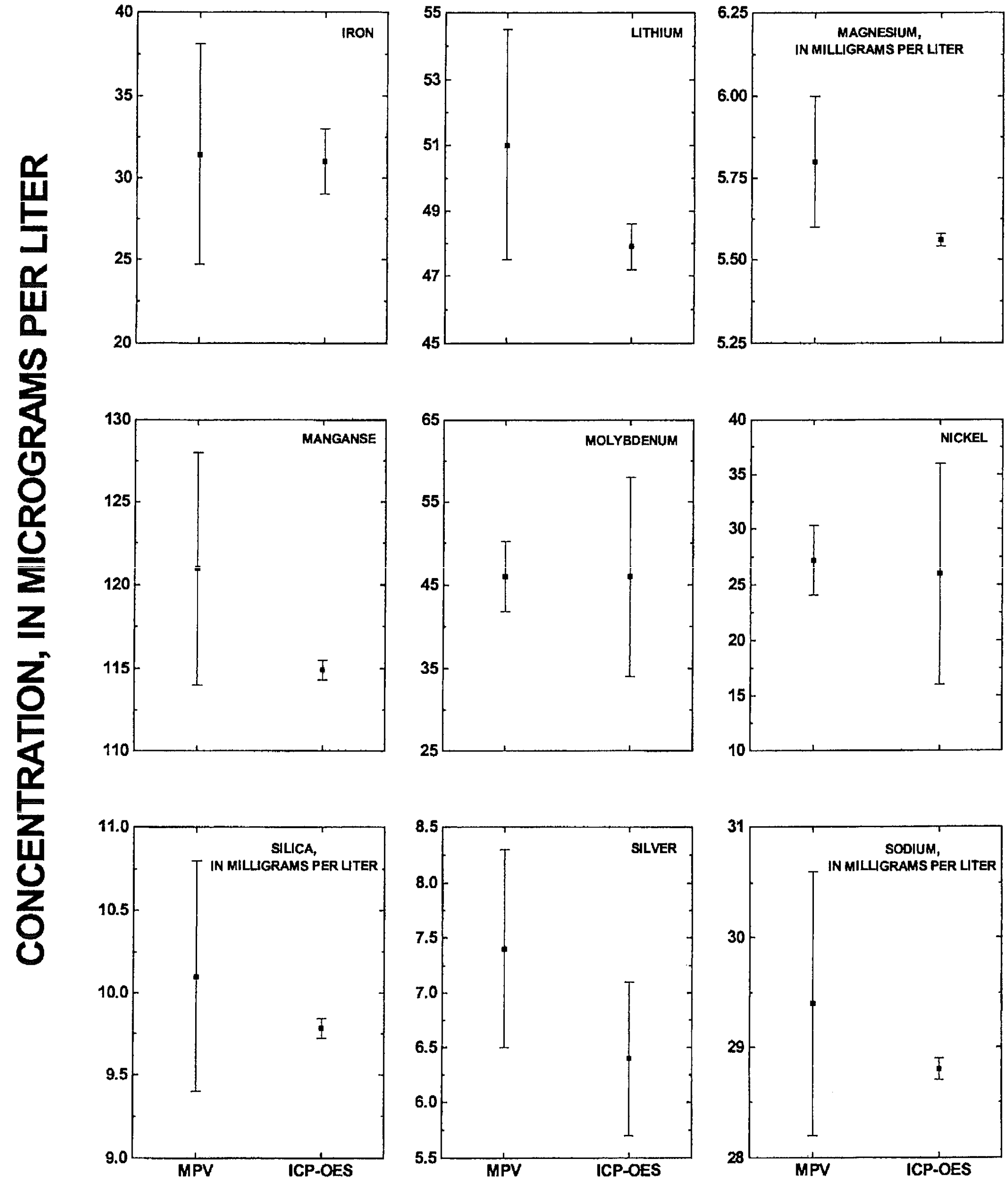


Figure 7a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T133—Continued.

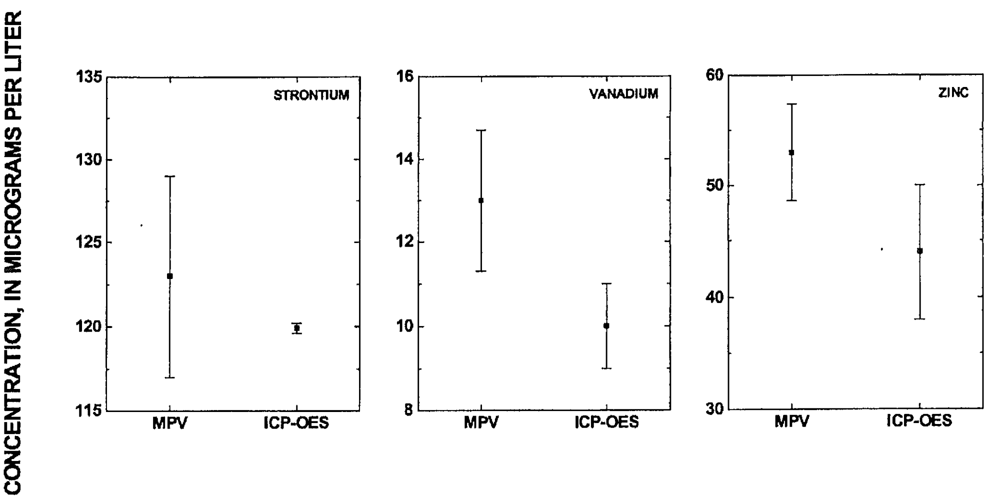


Figure 7a. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T133—Continued.

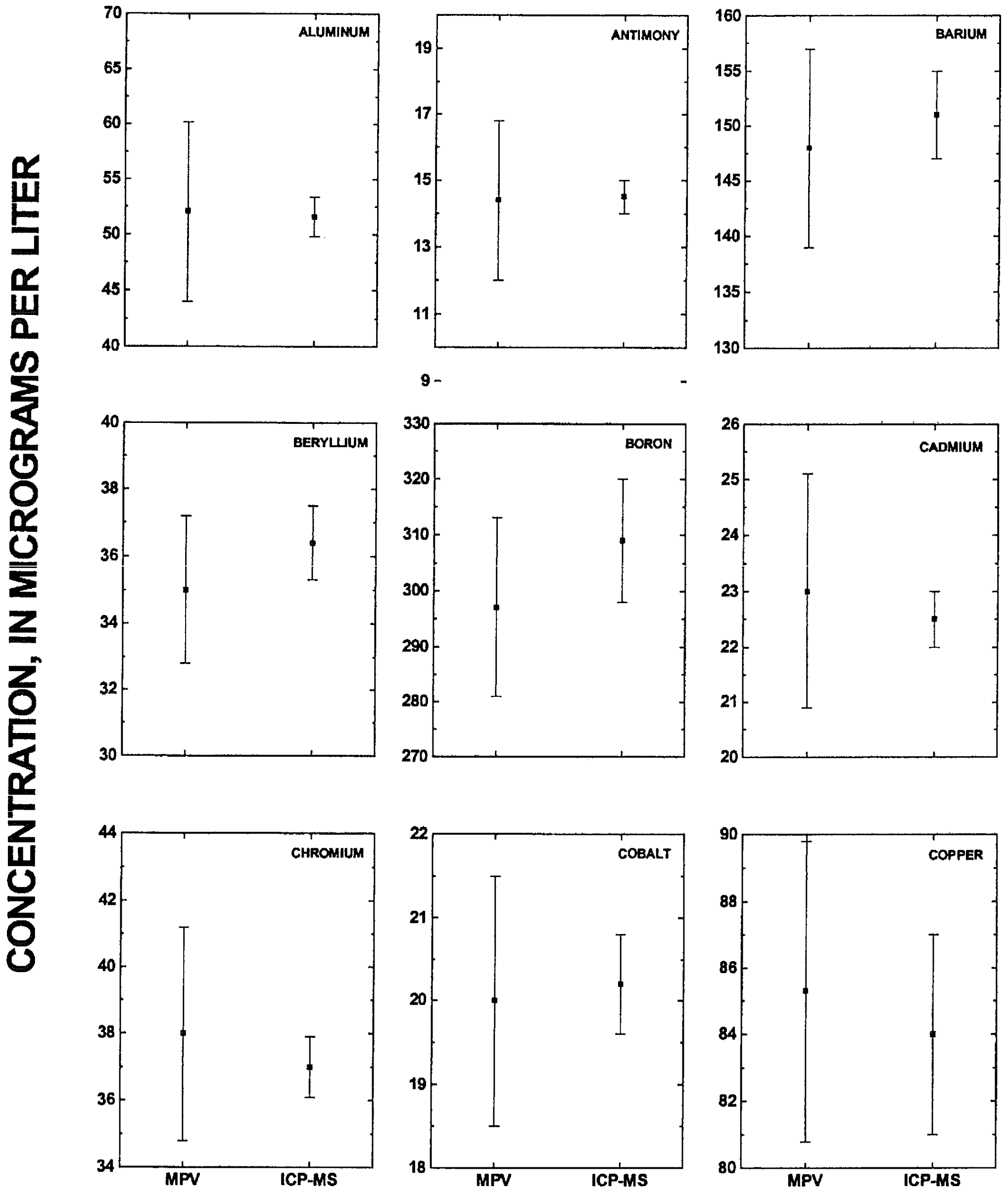


Figure 7b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T133. Error bars represent ± 1 standard deviation from the mean.

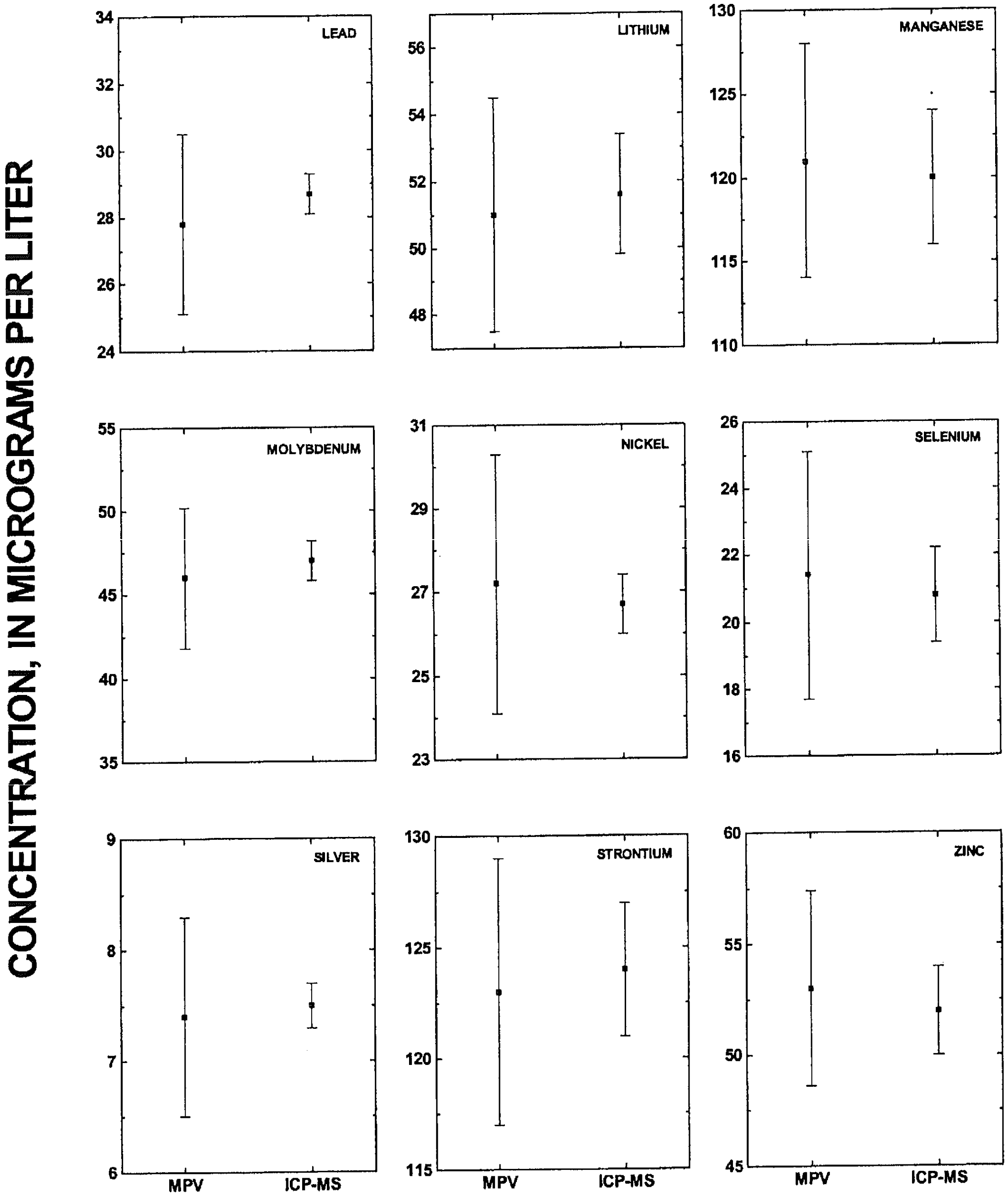


Figure 7b. Long-term inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample T133—Continued.

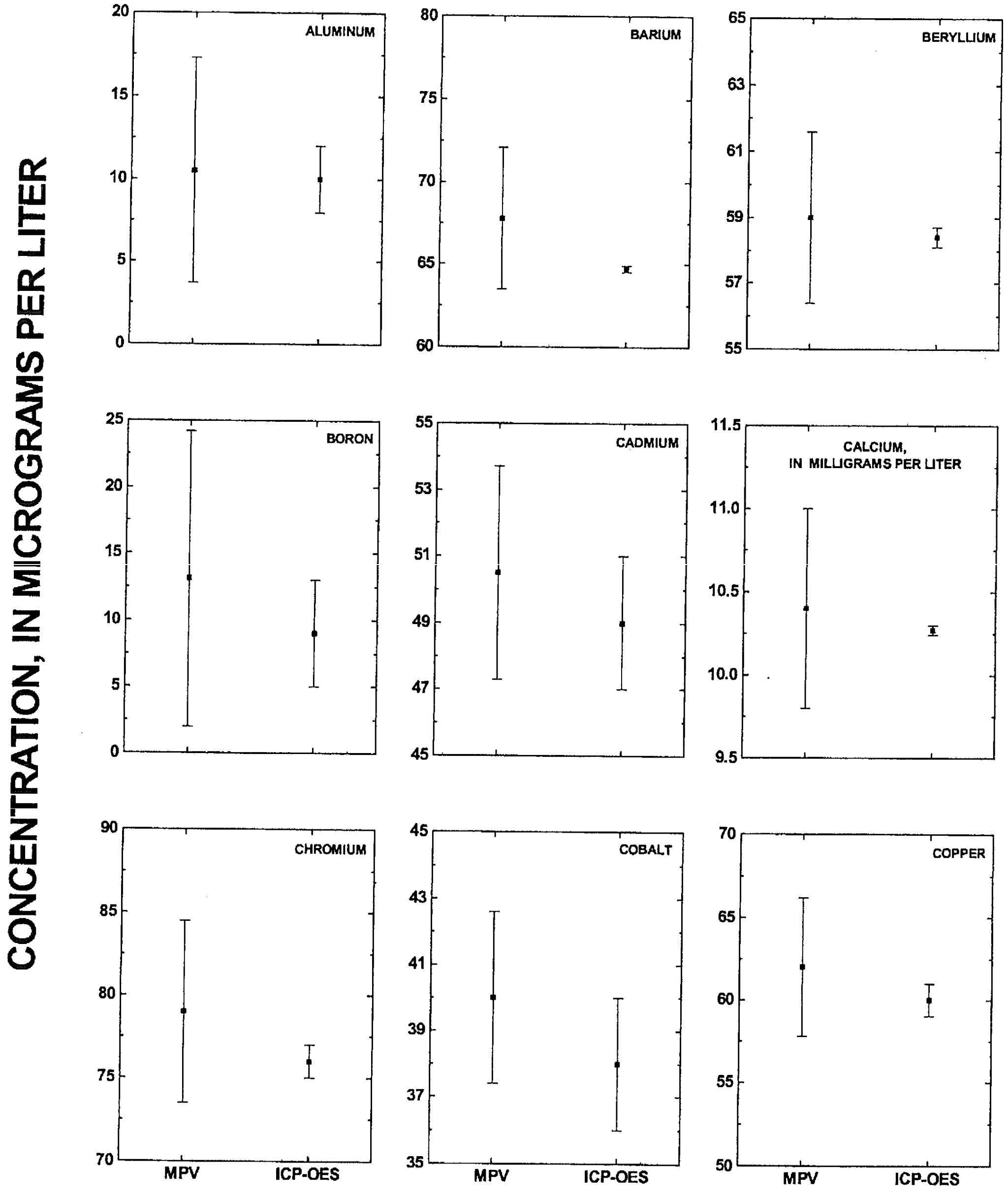


Figure 8. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T135. Error bars represent ± 1 standard deviation from the mean.

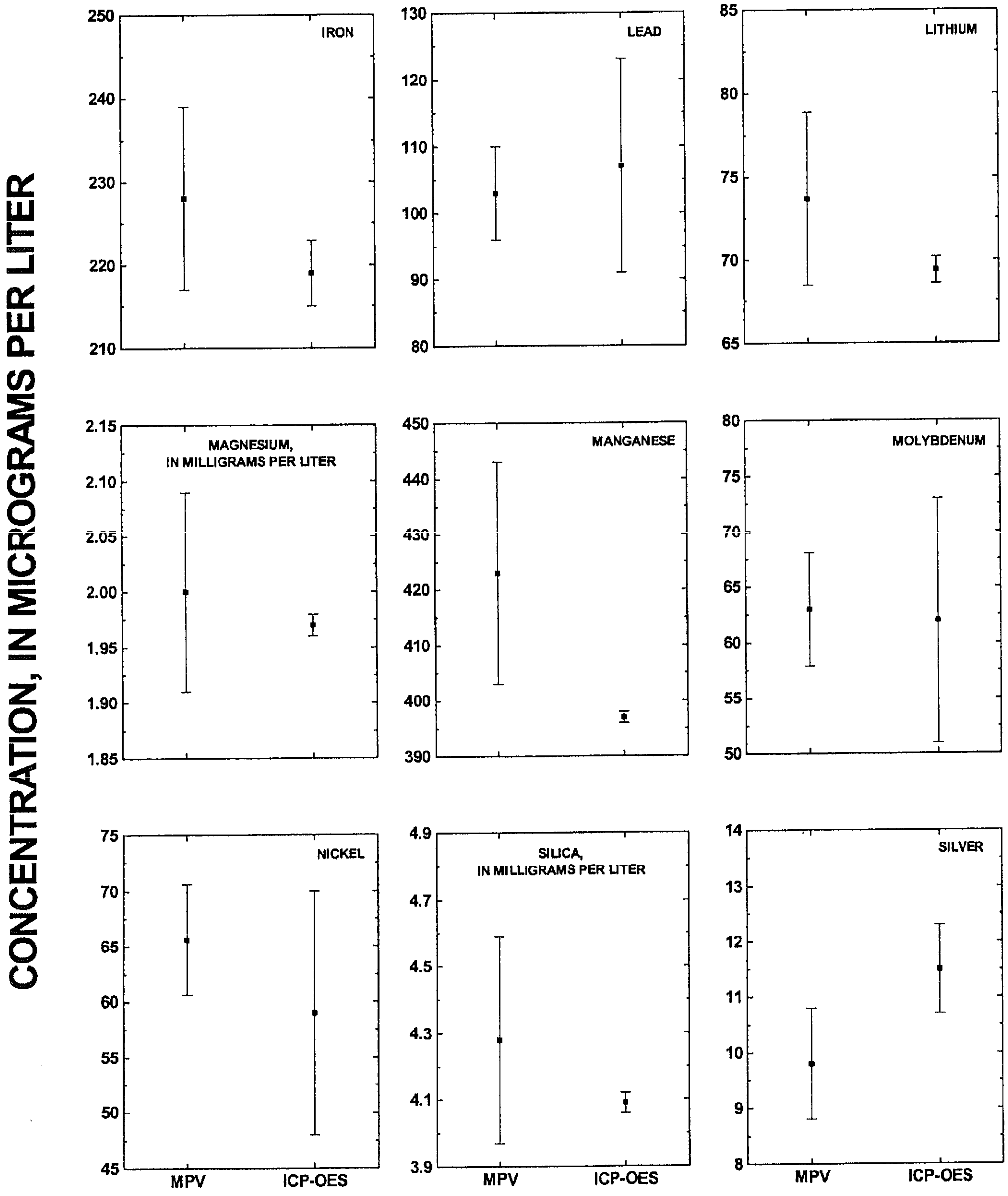


Figure 8. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T135—Continued.

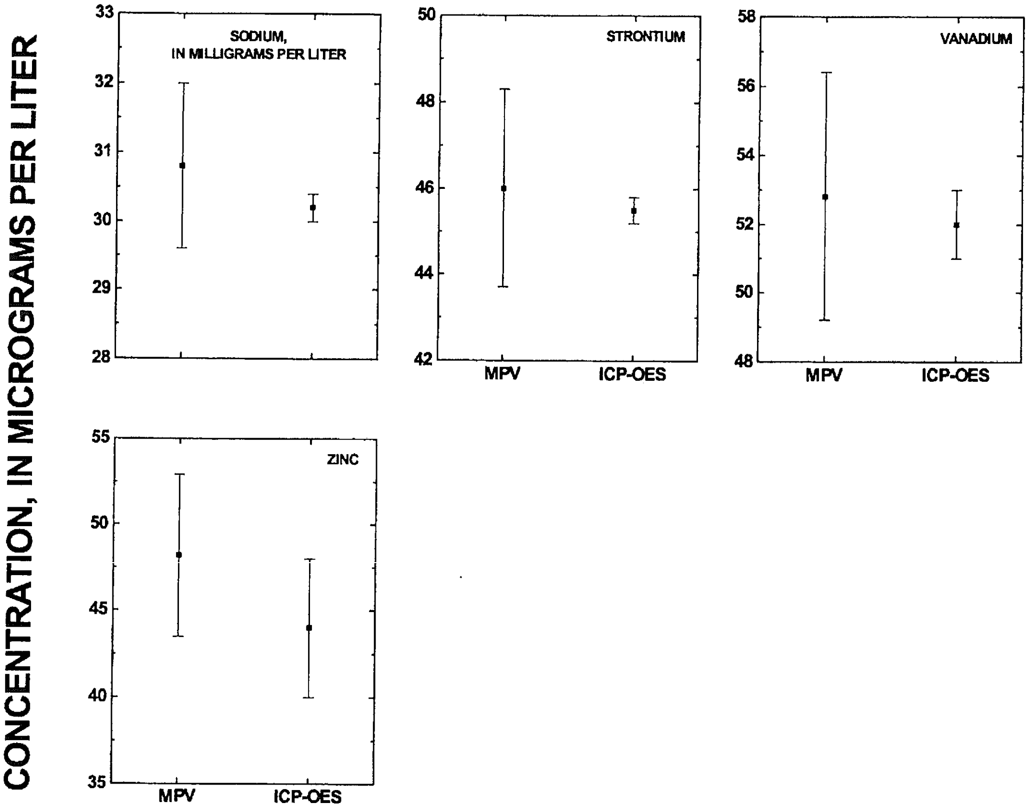


Figure 8. Short-term inductively coupled plasma–optical emission spectrometric (ICP–OES) results in relation to the most probable value (MPV) for Standard Reference Water Sample T135—Continued.

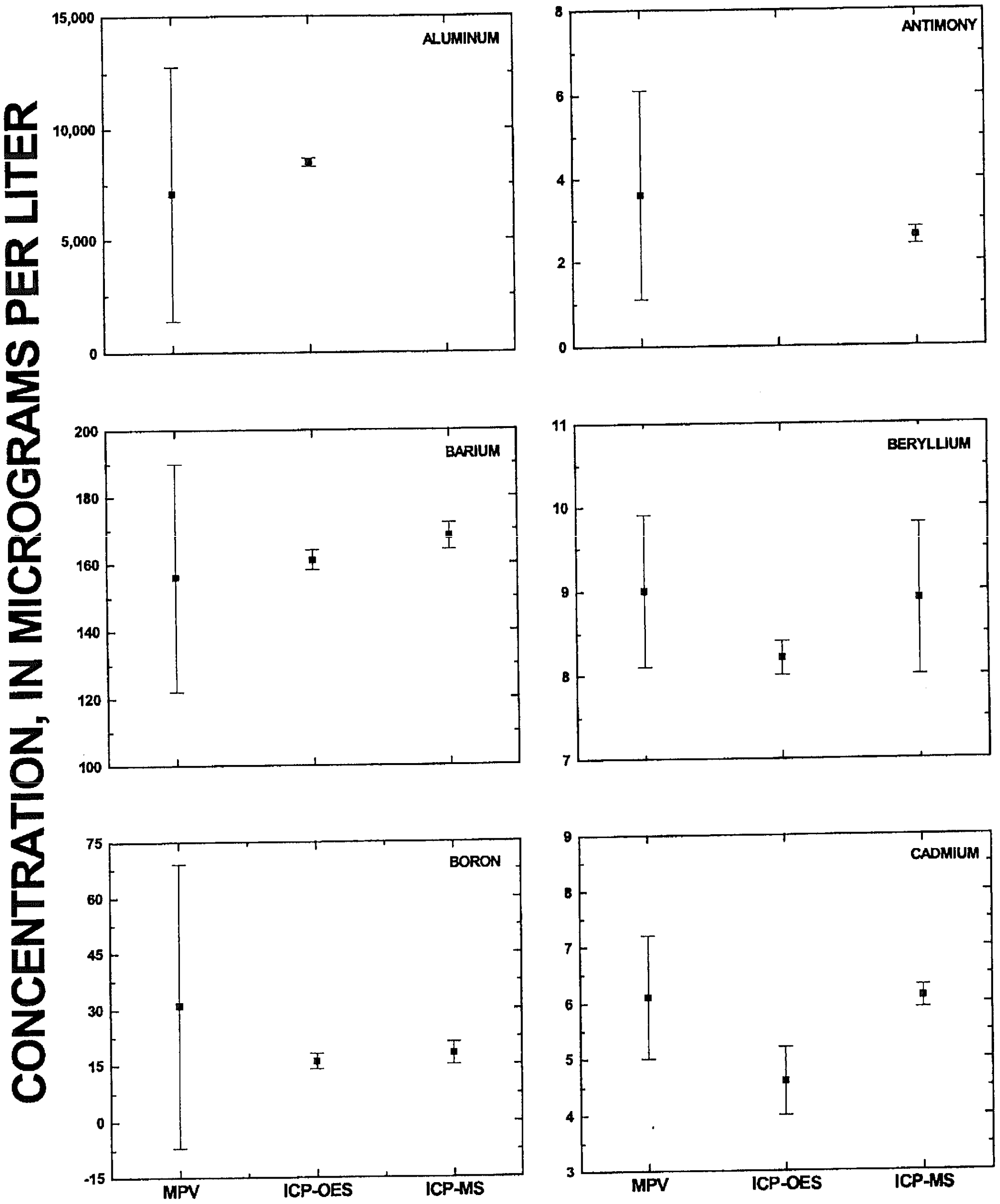


Figure 9. Long-term inductively coupled plasma–optical emission spectrometric (ICP–OES) and inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample WW-1. Error bars represent ± 1 standard deviation from the mean.

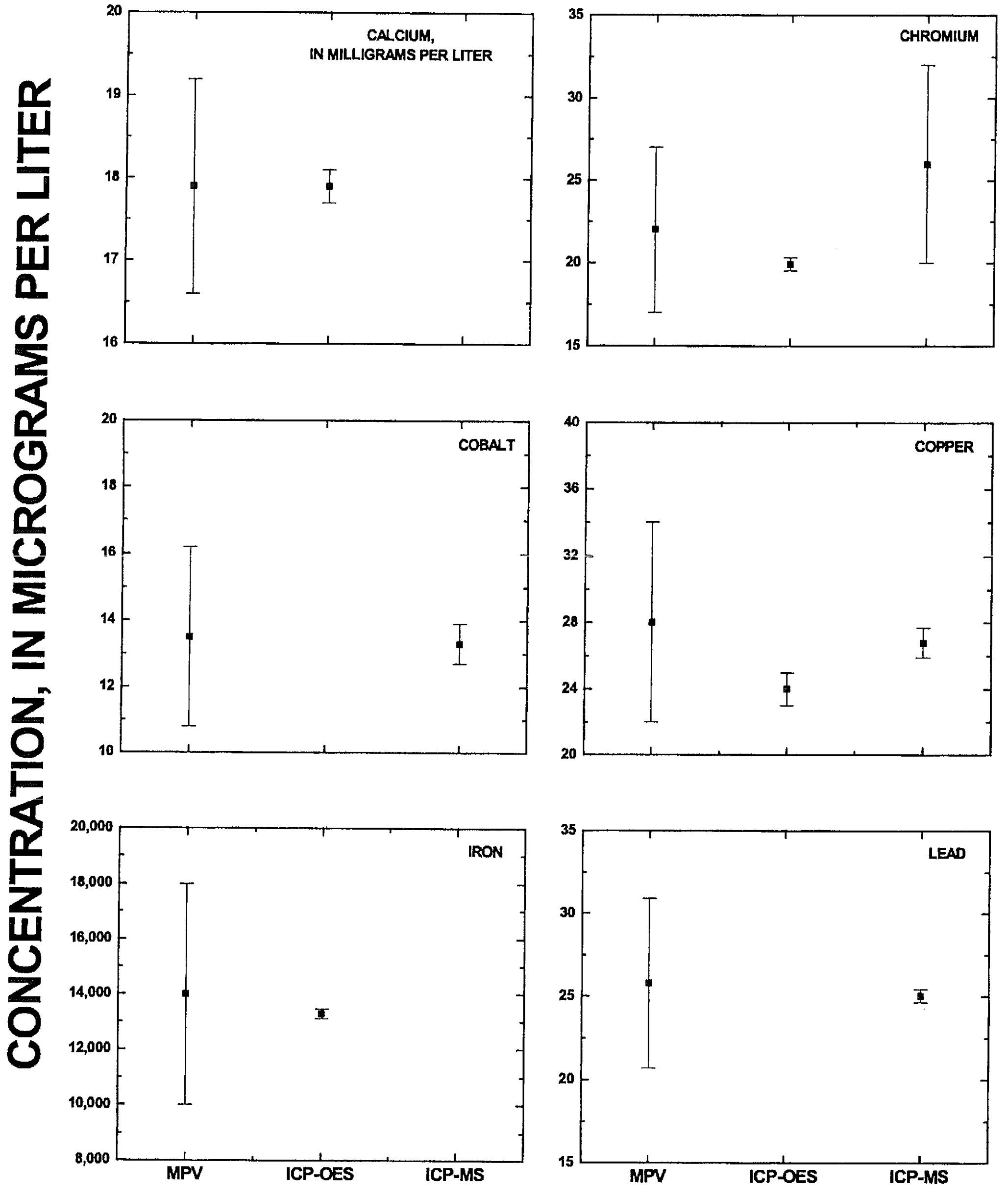


Figure 9. Long-term inductively coupled plasma–optical emission spectrometric (ICP–OES) and inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample WW-1—Continued.

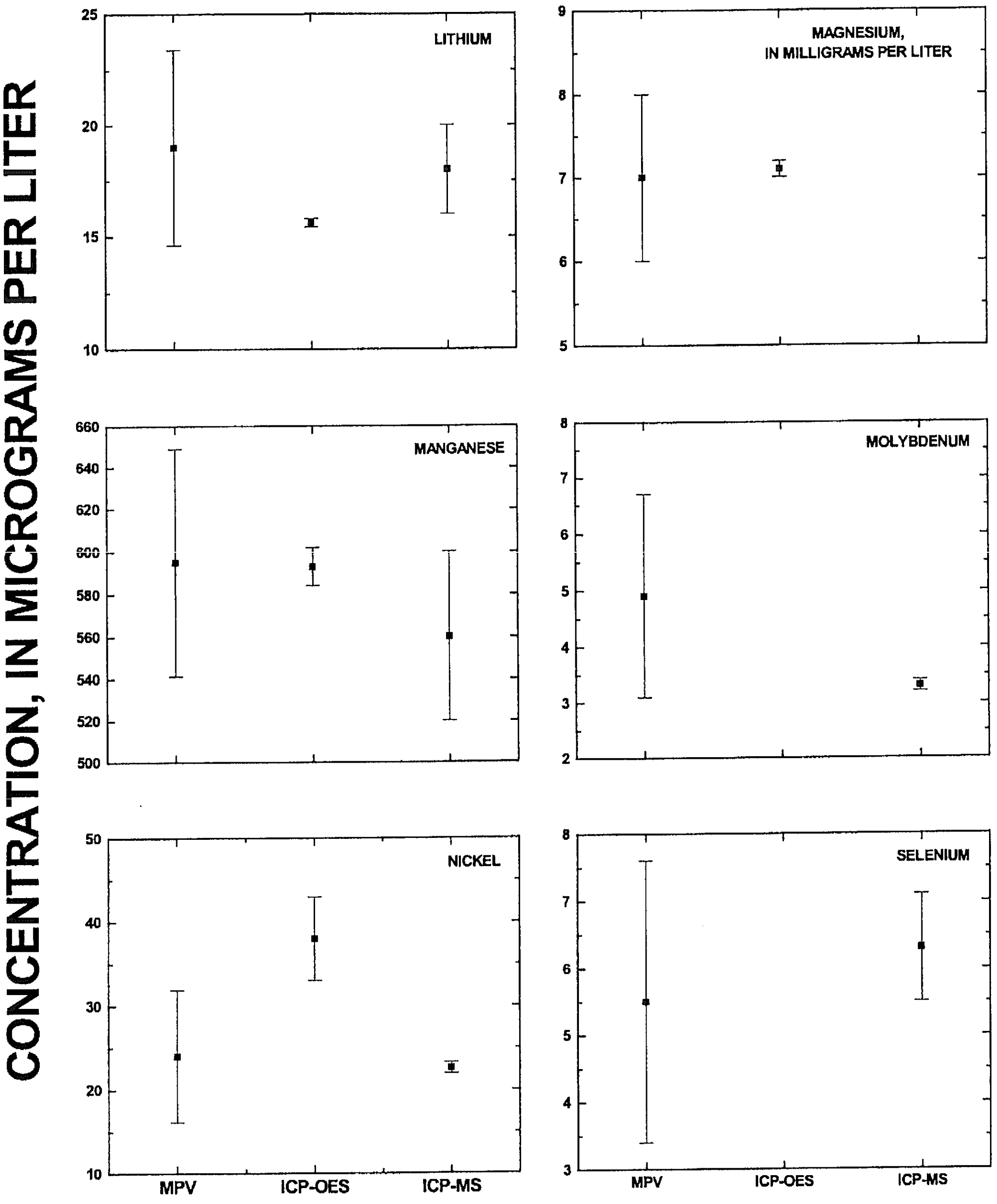


Figure 9. Long-term inductively coupled plasma–optical emission spectrometric (ICP–OES) and inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample WW-1—Continued.

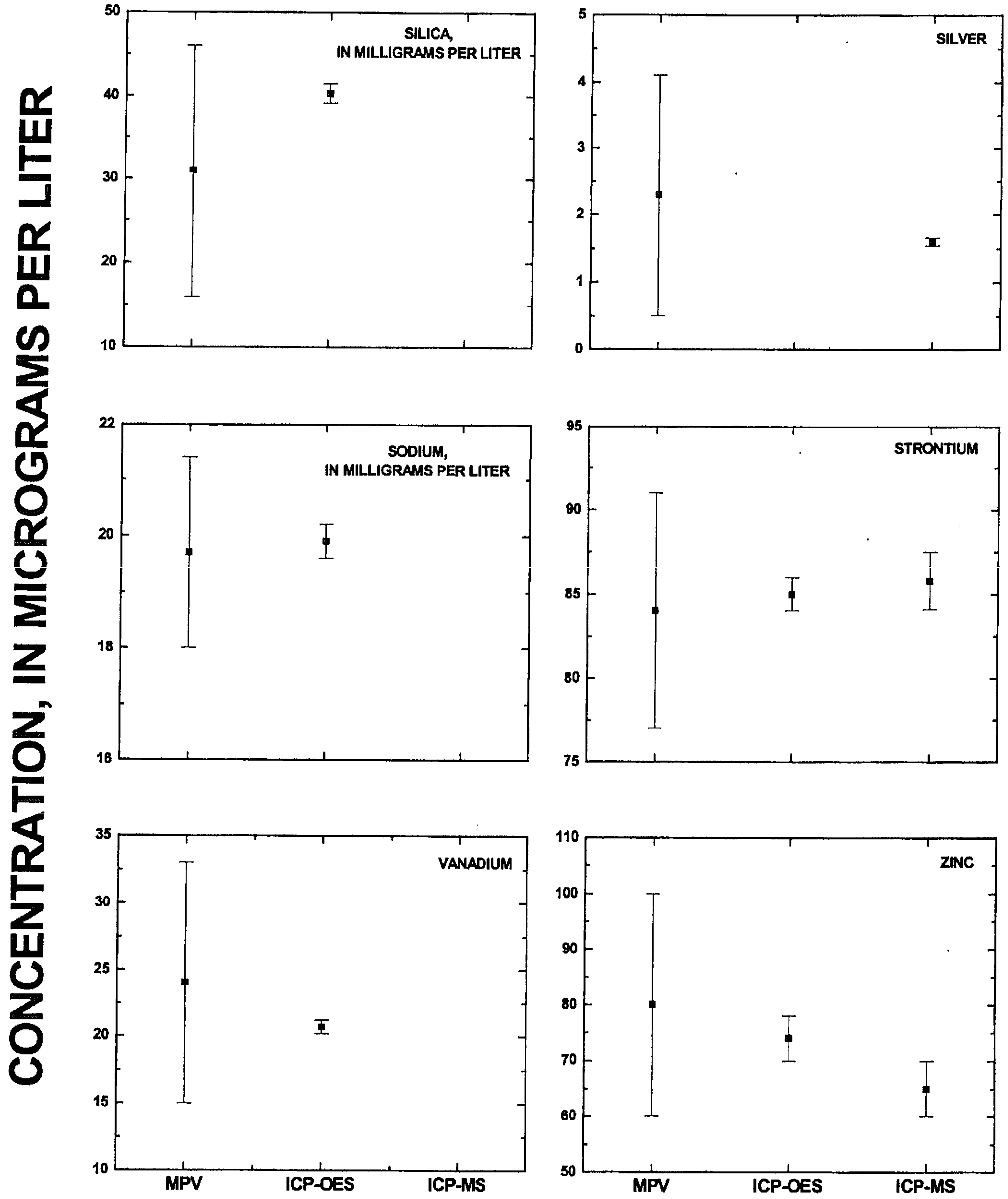
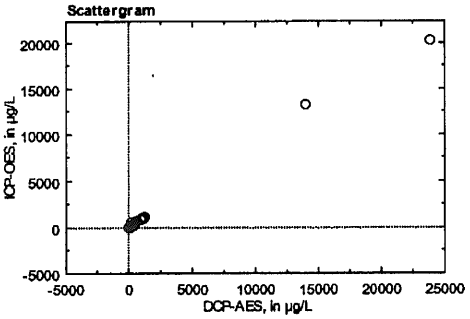
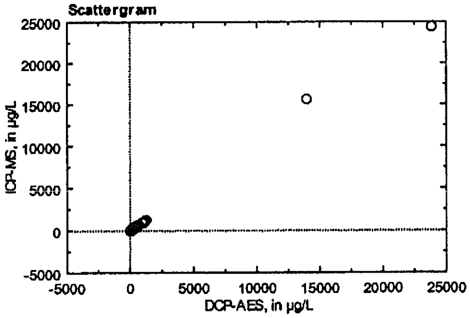


Figure 9. Long-term inductively coupled plasma–optical emission spectrometric (ICP–OES) and inductively coupled plasma–mass spectrometric (ICP–MS) results in relation to the most probable value (MPV) for Standard Reference Water Sample WW-1—Continued.



Confidence Intervals
ICP-OES, in µg/L vs. DCP-AES, in µg/L

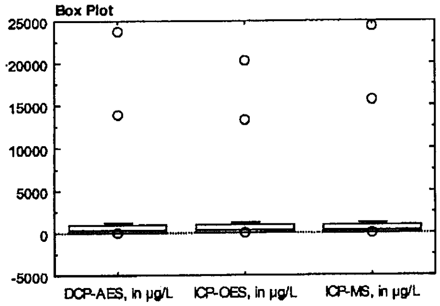
	Coefficient	95% Lower	95% Upper
Intercept	62.58	-45.25	170.40
DCP-AES, in µg/L	0.88	0.86	0.90



Confidence Intervals
ICP-MS, in µg/L vs. DCP-AES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-3.85	-108.17	100.47
DCP-AES, in µg/L	1.04	1.03	1.06

Figure 10a. Scattergrams and regression analyses showing **aluminum** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former direct current plasma–atomic emission spectrometric (DCP–AES) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	0
H	0.05
P-Value	0.9750
H corrected for ties	0.05
Tied P-Value	0.9750

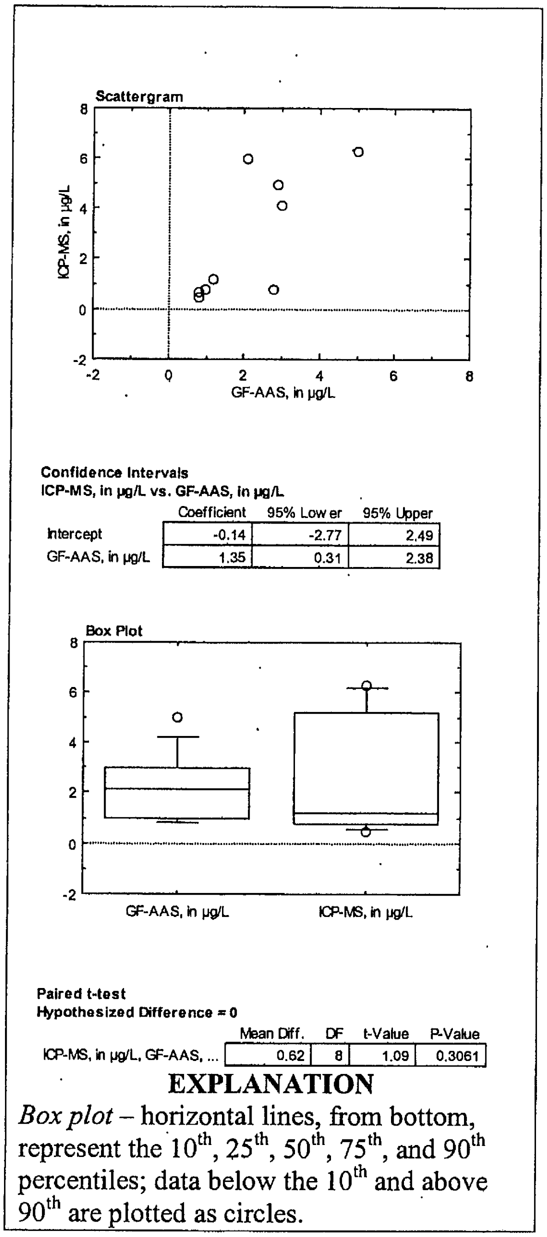
Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	25	931.00	37.24
2	25	954.00	38.16
3	25	965.00	38.60

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.
DF – Degrees of Freedom
H – Null hypothesis test statistic
P-Value – Level of significance

Figure 10b. Box plots and Kruskal-Wallis Test results showing **aluminum** data from the former direct current plasma–atomic emission spectrometric (DCP–AES) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-0.14	-2.77	2.49
GF-AAS, in µg/L	1.35	0.31	2.38

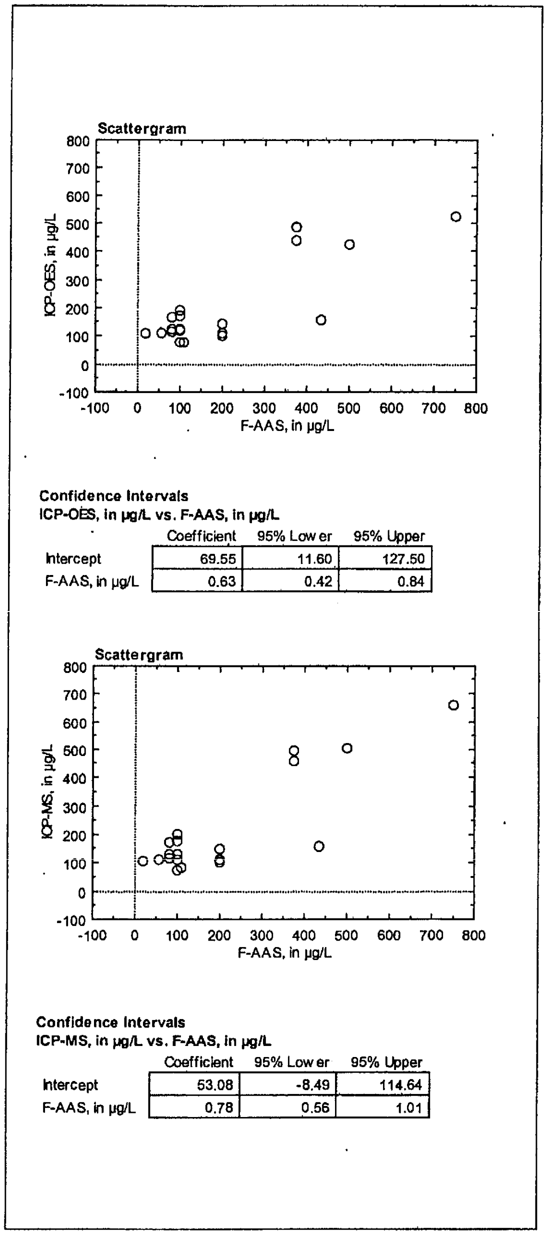
Paired t-test
Hypothesized Difference = 0

	Mean Diff.	DF	t-Value	P-Value
ICP-MS, in µg/L, GF-AAS, ...	0.62	8	1.09	0.3061

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 11. Scattergram, box plots, Paired *t*-Test results, and regression coefficients showing **antimony** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



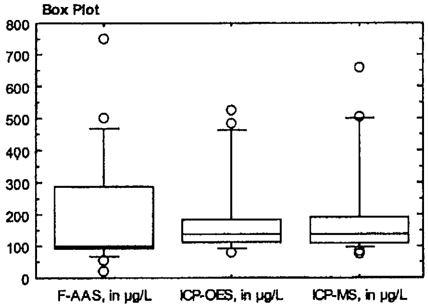
Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	69.55	11.60	127.50
F-AAS, in µg/L	0.63	0.42	0.84

Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	53.08	-8.49	114.64
F-AAS, in µg/L	0.78	0.56	1.01

Figure 12a. Scattergrams and regression analyses showing **barium** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former flame–atomic absorption spectrophotometric (F–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	4
H	1.96
P-Value	0.3754
H corrected for ties	1.96
Tied P-Value	0.3749

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	20	667.00	33.35
2	20	641.00	32.05
3	20	522.00	26.10

EXPLANATION

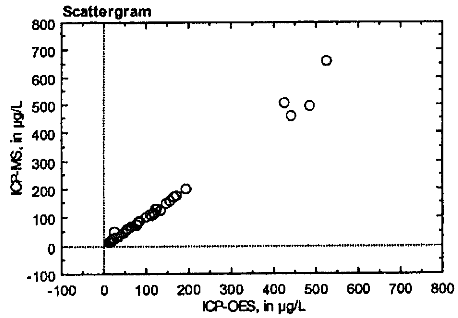
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

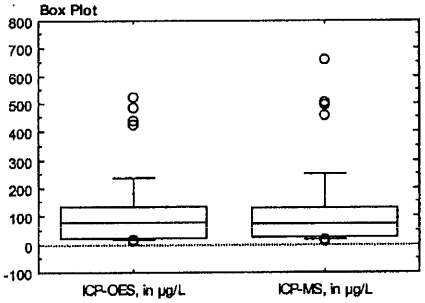
P-Value – Level of significance

Figure 12b. Box plots and Kruskal-Wallis Test results showing **barium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. ICP-OES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-7.55	-14.77	-0.34
ICP-OES, in µg/L	1.13	1.09	1.17



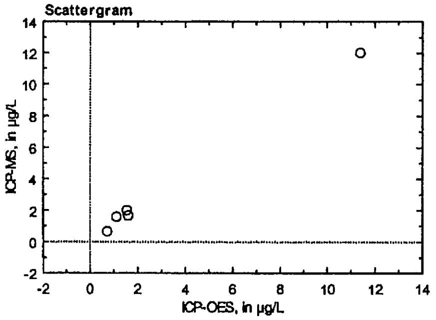
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	13
# Obs. < Hyp. Value	30
# Obs. = Hyp. Value	0
P-Value	0.0137

EXPLANATION

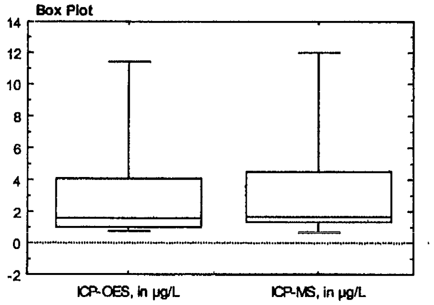
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 12c. Scattergram, box plots, One-sample Sign Test, and regression coefficients showing **barium** data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. ICP-OES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.18	-0.37	0.72
ICP-OES, in µg/L	1.04	0.93	1.14



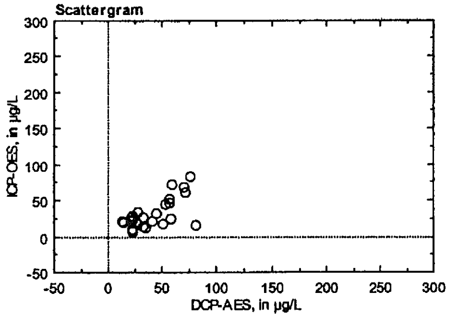
Paired t-test
Hypothesized Difference = 0

	Mean Diff.	DF	t-Value	P-Value
ICP-OES, in µg/L, ICP-MS, ...	-0.30	4	-2.16	0.0974

EXPLANATION

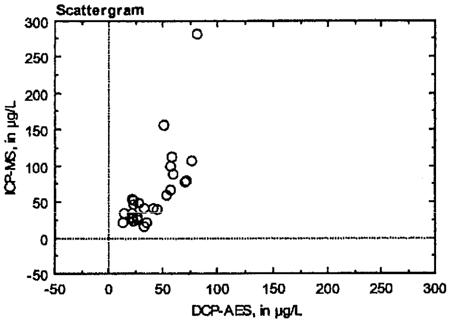
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 13. Scattergram, box plots, Paired *t*-Test results, and regression coefficients showing **beryllium** data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. DCP-AES, in µg/L

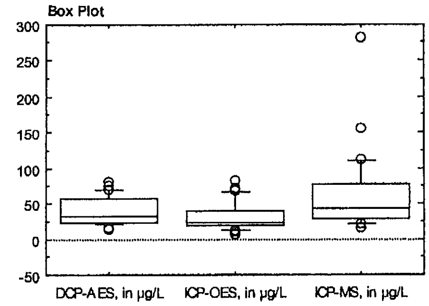
	Coefficient	95% Lower	95% Upper
Intercept	3.92	-9.12	16.96
DCP-AES, in µg/L	0.67	0.38	0.97



Confidence Intervals
ICP-MS, in µg/L vs. DCP-AES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-17.79	-50.30	14.71
DCP-AES, in µg/L	2.01	1.27	2.74

Figure 14a. Scattergrams and regression analyses showing **boron** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former direct current plasma–atomic emission spectrometric (DCP–AES) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	2
H	12.37
P-Value	0.0021
H corrected for ties	12.37
Tied P-Value	0.0021

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	28	855.00	30.54
2	28	1495.00	53.39
3	28	1220.00	43.57

EXPLANATION

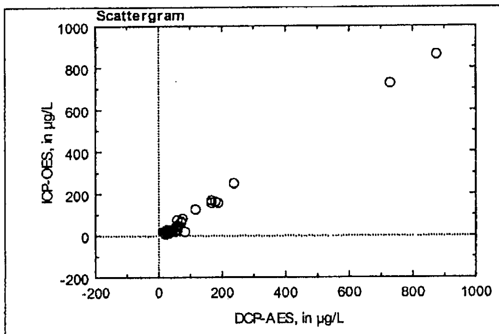
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

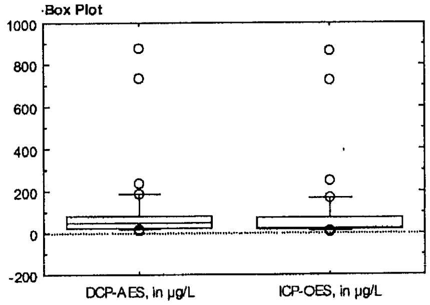
P-Value – Level of significance

Figure 14b. Box plots and Kruskal-Wallis Test results showing **boron** data from the former direct current plasma–atomic emission spectrometric (DCP–AES) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. DCP-AES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-8.41	-14.60	-2.21
DCP-AES, in µg/L	1.00	0.97	1.03



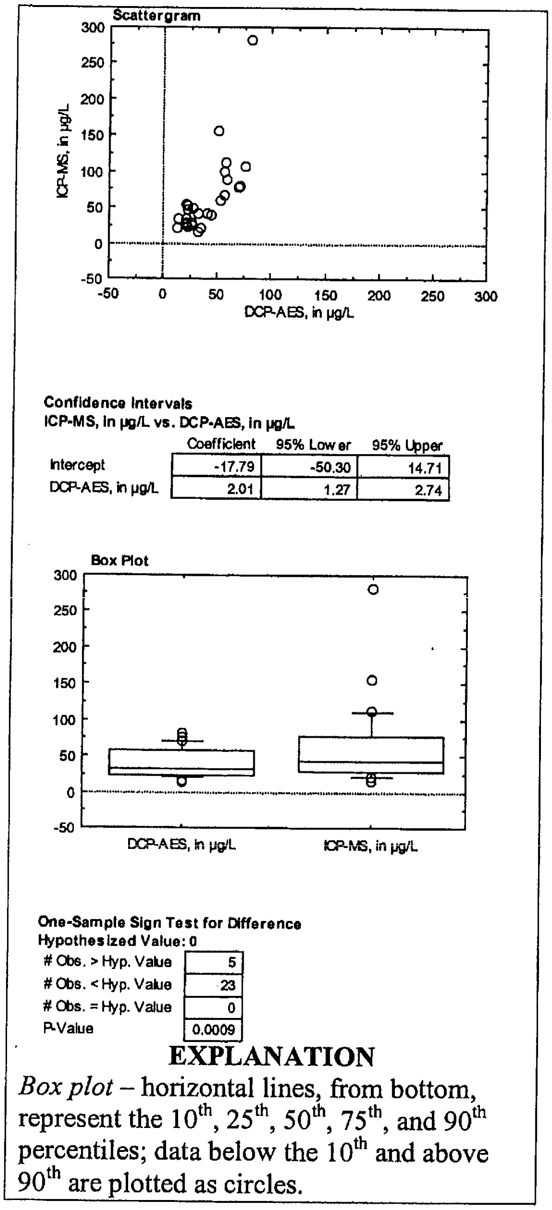
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	25
# Obs. < Hyp. Value	11
# Obs. = Hyp. Value	0
P-Value	0.0288

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 14c. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **boron** data from the former direct current plasma–atomic emission spectrometric (DCP–AES) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. DCP-AES, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-17.79	-50.30	14.71
DCP-AES, in µg/L	2.01	1.27	2.74

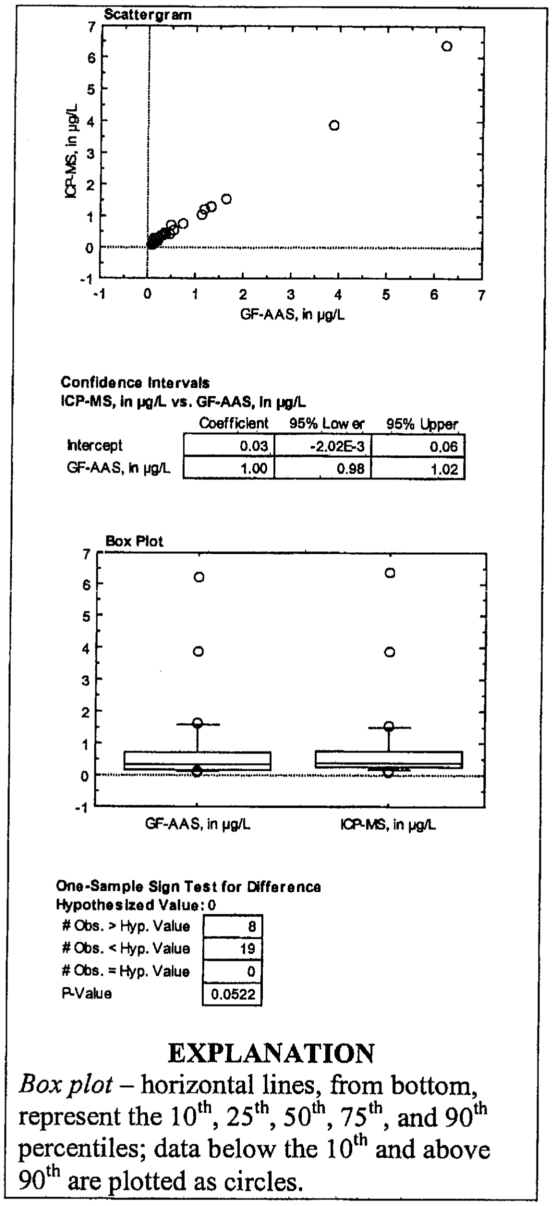
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	5
# Obs. < Hyp. Value	23
# Obs. = Hyp. Value	0
P-Value	0.0009

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 14d. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **boron** data from the former direct current plasma–atomic emission spectrometric (DCP–AES) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.03	-2.02E-3	0.06
GF-AAS, in µg/L	1.00	0.98	1.02

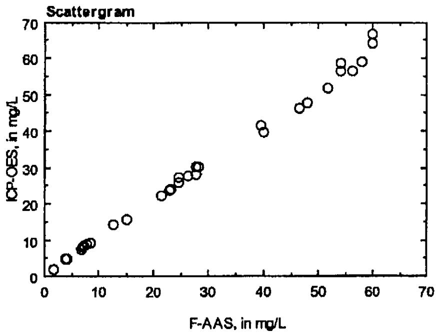
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	8
# Obs. < Hyp. Value	19
# Obs. = Hyp. Value	0
P-Value	0.0522

EXPLANATION

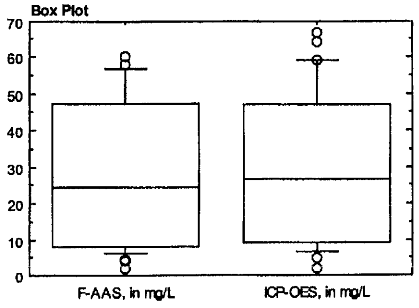
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 15. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **cadmium** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in mg/L vs. F-AAS, in mg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.48	-0.42	1.38
F-AAS, in mg/L	1.03	1.00	1.06



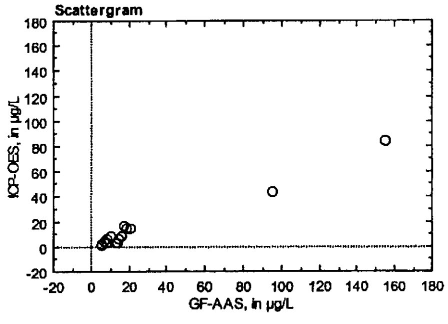
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	3
# Obs. < Hyp. Value	29
# Obs. = Hyp. Value	0
P-Value	<0.0001

EXPLANATION

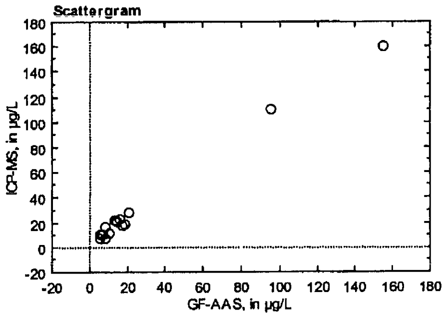
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 16. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **calcium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in milligrams per liter (mg/L).



Confidence Intervals
ICP-OES, in µg/L vs. GF-AAS, in µg/L

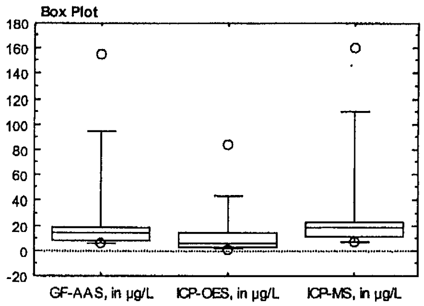
	Coefficient	95% Lower	95% Upper
Intercept	3.86E-3	-2.54	2.55
GF-AAS, in µg/L	0.52	0.47	0.58



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	3.76	1.01	6.51
GF-AAS, in µg/L	1.04	0.98	1.09

Figure 17a. Scattergrams and regression analyses showing **chromium** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	0
H	9.71
P-Value	0.0078
H corrected for ties	9.71
Tied P-Value	0.0078

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	15	225.00	15.00
2	15	447.00	29.80
3	15	363.00	24.20

EXPLANATION

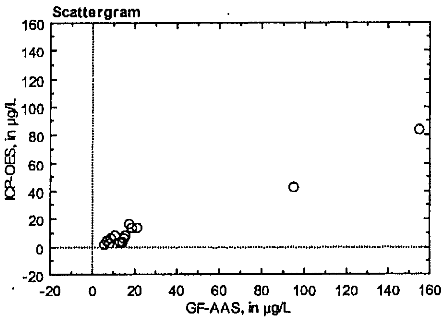
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

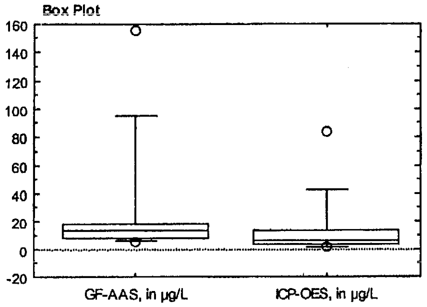
P-Value – Level of significance

Figure 17b. Box plots and Kruskal-Wallis Test results showing **chromium** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	3.86E-3	-2.54	2.55
GF-AAS, in µg/L	0.52	0.47	0.58



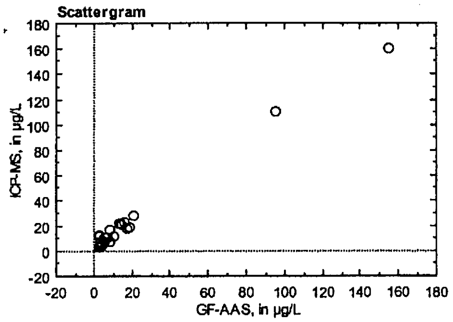
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	15
# Obs. < Hyp. Value	0
# Obs. = Hyp. Value	0
P-Value	<0.0001

EXPLANATION

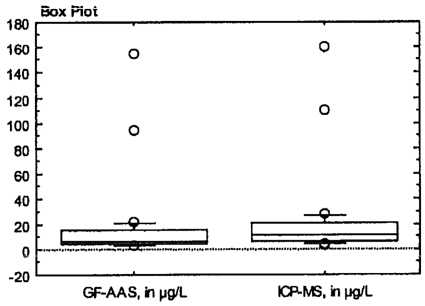
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 17c. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **chromium** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	3.24	1.53	4.94
GF-AAS, in µg/L	1.04	1.00	1.09



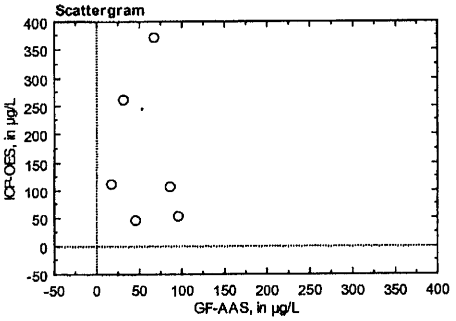
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	3
# Obs. < Hyp. Value	23
# Obs. = Hyp. Value	0
P-Value	<0.0001

EXPLANATION

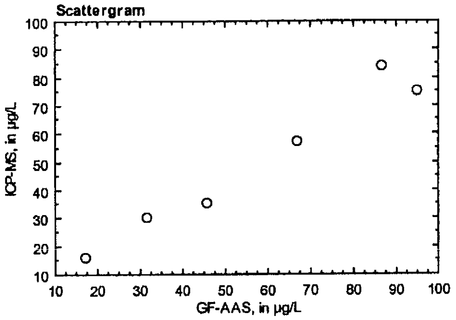
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 17d. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **chromium** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. GF-AAS, in µg/L

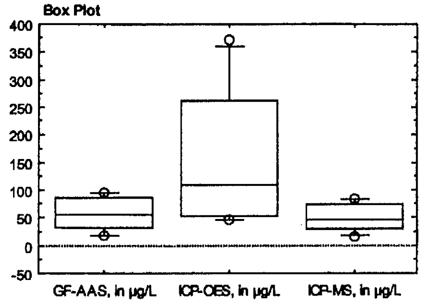
	Coefficient	95% Lower	95% Upper
Intercept	193.26	-175.66	562.18
GF-AAS, in µg/L	-0.61	-6.40	5.18



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	1.10	-15.19	17.40
GF-AAS, in µg/L	0.85	0.60	1.11

Figure 18a. Scattergrams and regression analyses showing **cobalt** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	0
H	5.24
P-Value	0.0728
H corrected for ties	5.24
Tied P-Value	0.0728

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	6	81.00	13.50
2	6	41.00	6.83
3	6	49.00	8.17

EXPLANATION

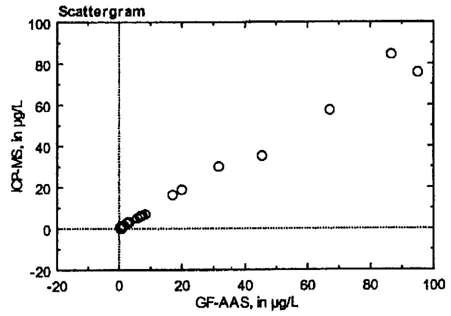
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

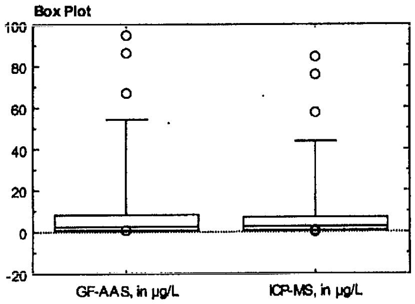
P-Value – Level of significance

Figure 18b. Box plots and Kruskal-Wallis Test results showing **cobalt** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.16	-0.85	1.16
GF-AAS, in µg/L	0.87	0.83	0.90



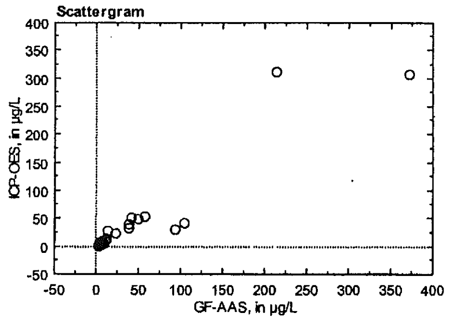
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	24
# Obs. < Hyp. Value	7
# Obs. = Hyp. Value	0
P-Value	0.0033

EXPLANATION

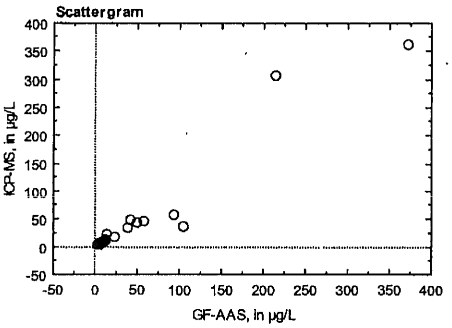
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 18c. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **cobalt** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. GF-AAS, in µg/L

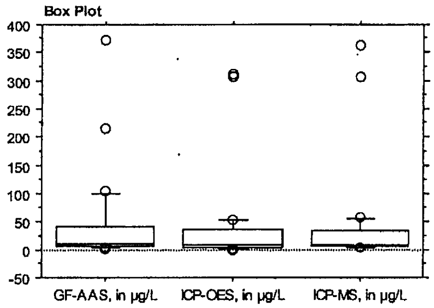
	Coefficient	95% Lower	95% Upper
Intercept	-1.30	-13.71	11.11
GF-AAS, in µg/L	0.93	0.79	1.07



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-2.81	-13.36	7.74
GF-AAS, in µg/L	1.04	0.92	1.16

Figure 19a. Scattergrams and regression analyses showing **copper** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	0
H	1.28
P-Value	0.5285
H corrected for ties	1.28
Tied P-Value	0.5285

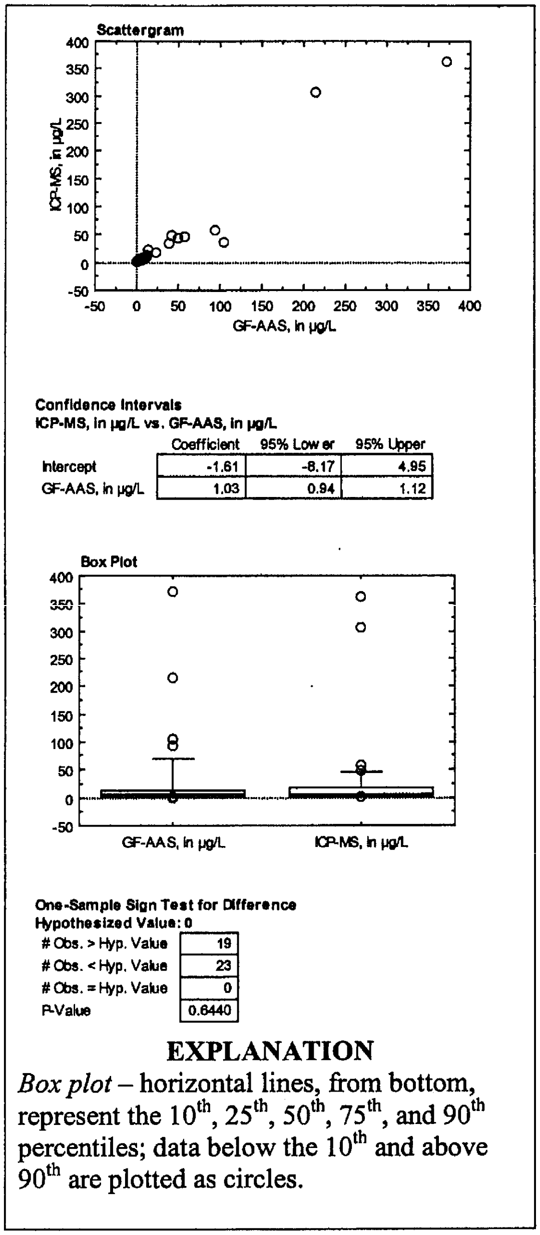
Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	28	1071.00	38.25
2	28	1248.00	44.57
3	28	1251.00	44.68

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.
DF – Degrees of Freedom
H – Null hypothesis test statistic
P-Value – Level of significance

Figure 19b. Box plots and Kruskal-Wallis Test results showing **copper** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-1.61	-8.17	4.95
GF-AAS, in µg/L	1.03	0.94	1.12

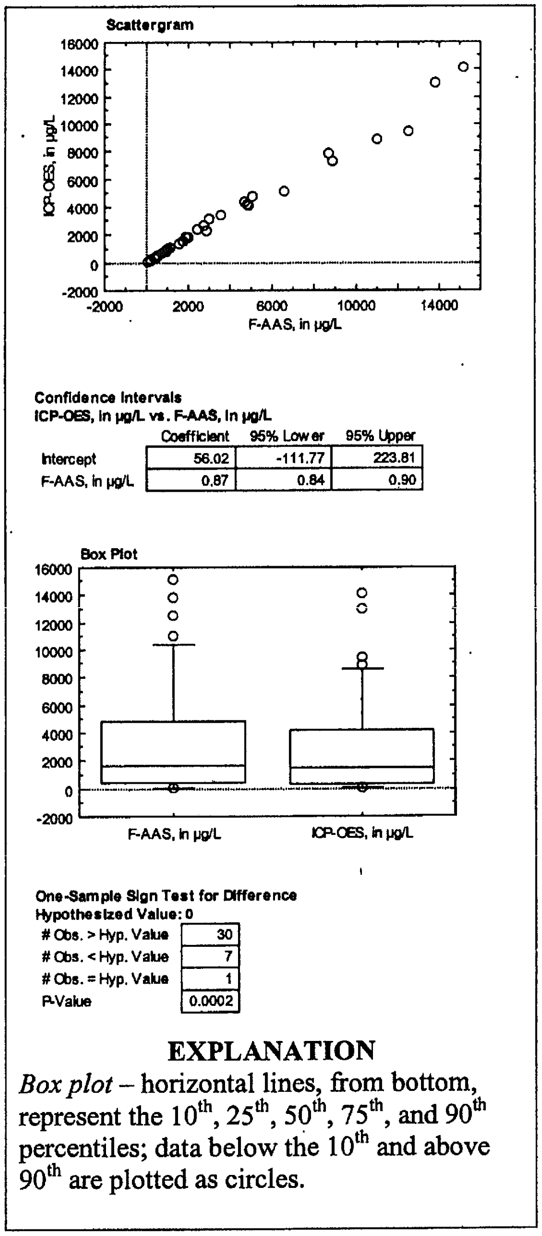
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	19
# Obs. < Hyp. Value	23
# Obs. = Hyp. Value	0
P-Value	0.6440

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 19c. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **copper** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	56.02	-111.77	223.81
F-AAS, in µg/L	0.87	0.84	0.90

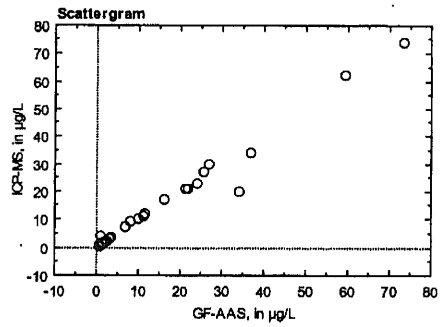
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	30
# Obs. < Hyp. Value	7
# Obs. = Hyp. Value	1
P-Value	0.0002

EXPLANATION

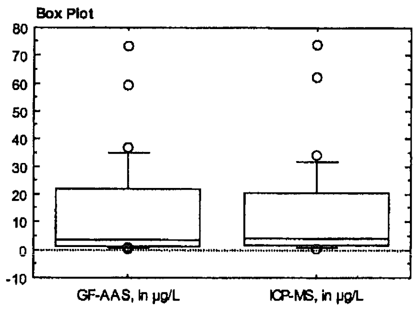
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 20. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **iron** data from the former flame–atomic absorption spectrophotometric (F–AAS) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.12	-1.19	1.43
GF-AAS, in µg/L	0.98	0.92	1.04



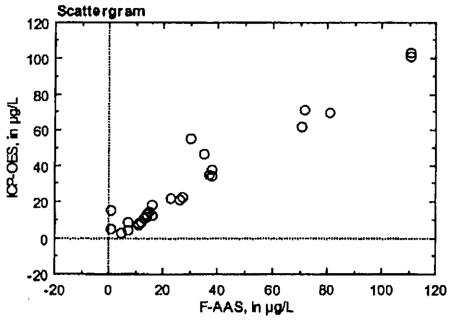
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	12
# Obs. < Hyp. Value	19
# Obs. = Hyp. Value	0
P-Value	0.2810

EXPLANATION

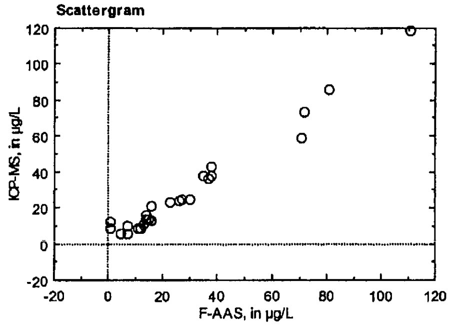
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 21. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **lead** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

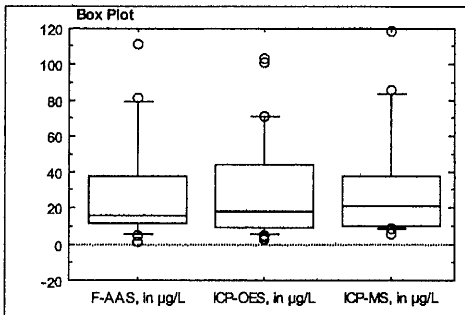
	Coefficient	95% Lower	95% Upper
Intercept	1.93	-2.10	5.96
F-AAS, in µg/L	0.90	0.81	1.00



Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-2.49	-7.48	2.50
F-AAS, in µg/L	1.14	1.03	1.26

Figure 22a. Scattergrams and regression analyses showing **lithium** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former flame–atomic absorption spectrophotometric (F–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	7
H	0.17
P-Value	0.9191
H corrected for ties	0.17
Tied P-Value	0.9191

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	27	1066.00	39.48
2	27	1128.00	41.78
3	27	1127.00	41.74

EXPLANATION

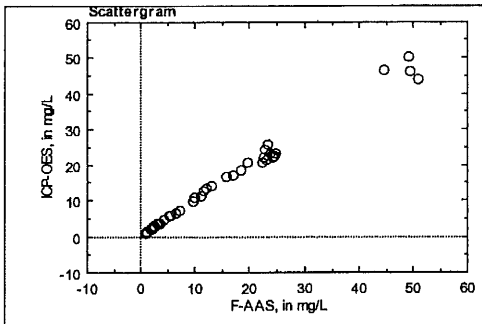
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

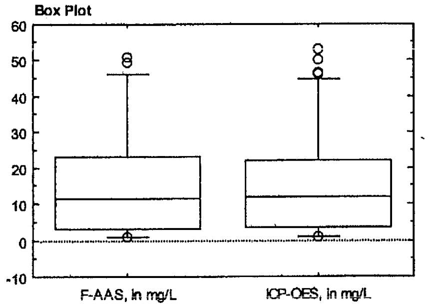
P-Value – Level of significance

Figure 22b. Box plots and Kruskal-Wallis Test results showing **lithium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in mg/L vs. F-AAS, in mg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.78	0.07	1.49
F-AAS, in mg/L	0.93	0.90	0.96



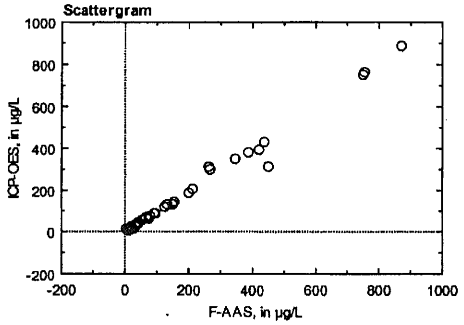
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	19
# Obs. < Hyp. Value	23
# Obs. = Hyp. Value	0
P-Value	0.6440

EXPLANATION

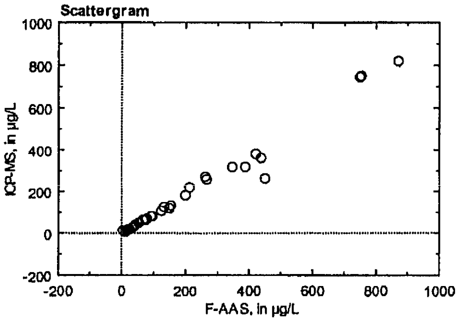
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 23. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **magnesium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in milligrams per liter (mg/L).



Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

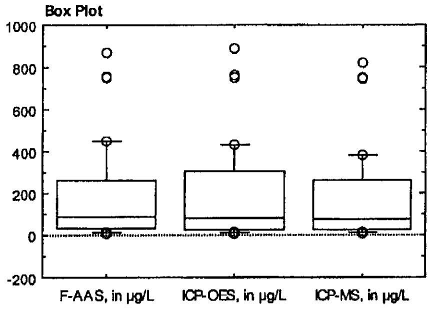
	Coefficient	95% Lower	95% Upper
Intercept	-3.91	-15.84	8.02
F-AAS, in µg/L	0.99	0.95	1.04



Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-6.24	-20.07	7.59
F-AAS, in µg/L	0.94	0.89	0.98

Figure 24a. Scattergrams and regression analyses showing **manganese** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former flame–atomic absorption spectrophotometric (F–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	3
H	0.29
P-Value	0.8669
H corrected for ties	0.29
Tied P-Value	0.8669

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	36	1960.00	54.44
2	36	1892.00	52.56
3	36	2034.00	56.50

EXPLANATION

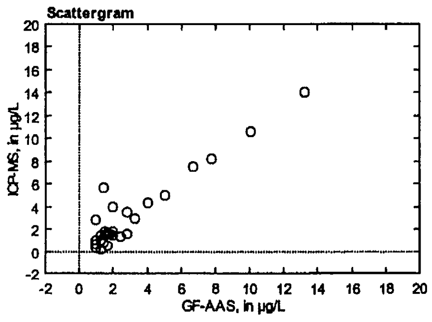
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

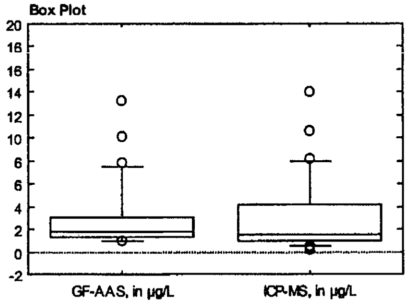
P-Value – Level of significance

Figure 24b. Box plots and Kruskal-Wallis Test results showing **manganese** data from the former flame–atomic absorption spectrophotometric (F–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-0.03	-0.66	0.60
GF-AAS, in µg/L	1.05	0.90	1.20



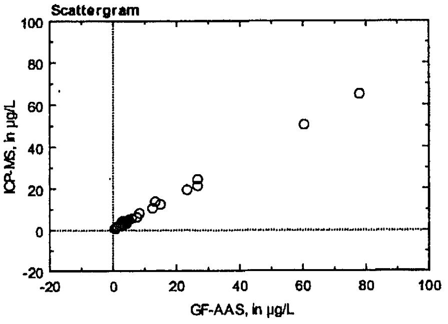
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	16
# Obs. < Hyp. Value	12
# Obs. = Hyp. Value	0
P-Value	0.5716

EXPLANATION

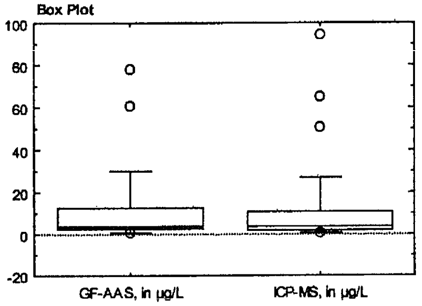
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 25. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **molybdenum** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	0.17	-0.35	0.70
GF-AAS, in µg/L	0.67	0.85	0.89



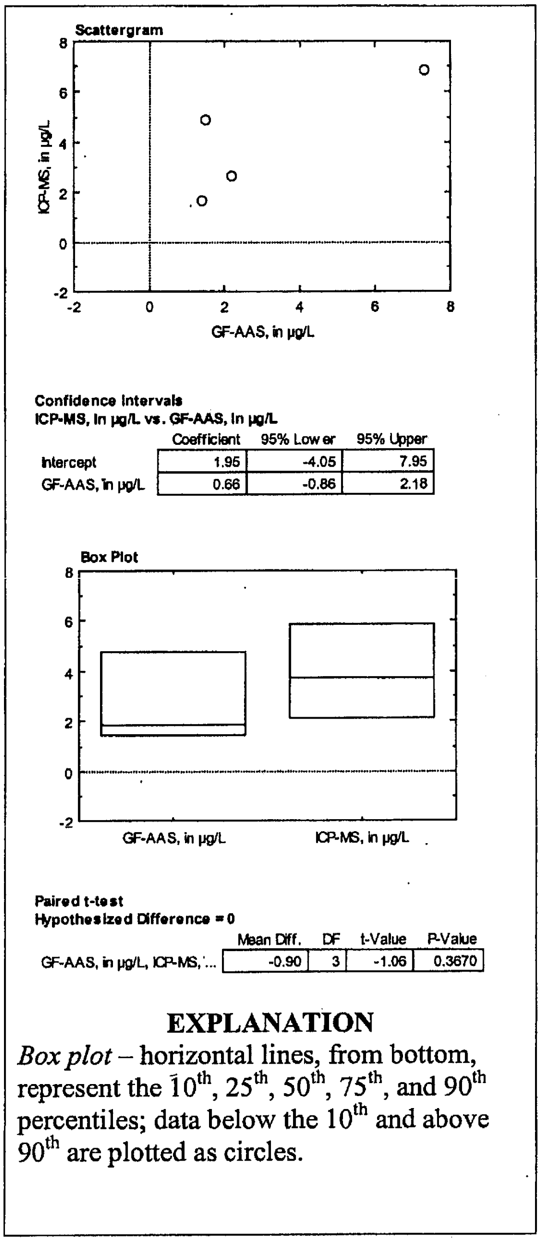
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	24
# Obs. < Hyp. Value	10
# Obs. = Hyp. Value	0
P-Value	0.0243

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 26. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **nickel** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. GF-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	1.95	-4.05	7.95
GF-AAS, in µg/L	0.66	-0.86	2.18

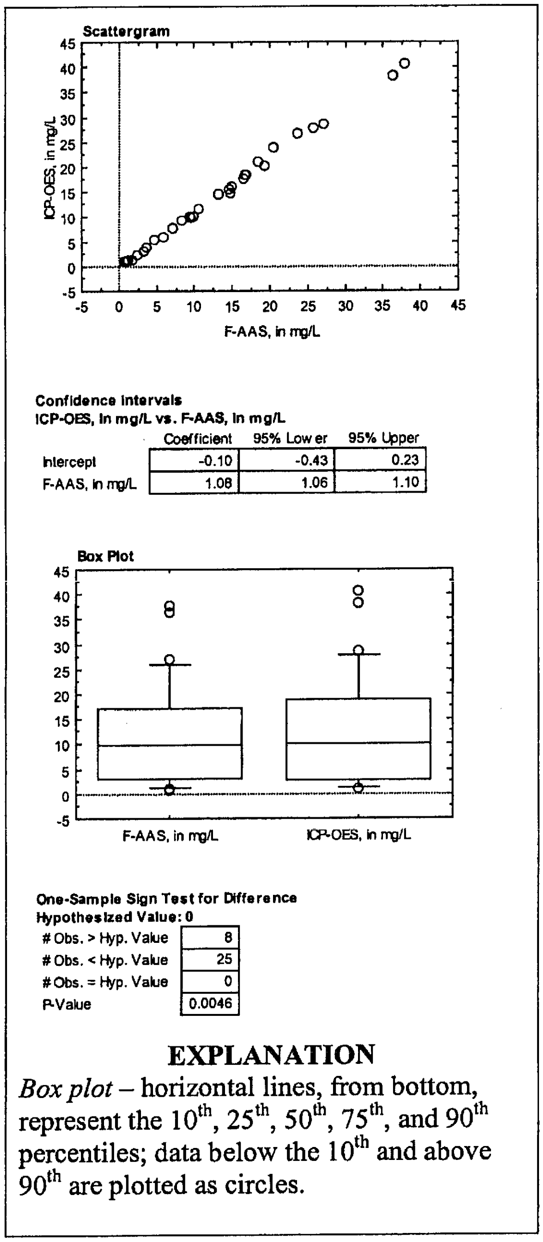
Paired t-test
Hypothesized Difference = 0

	Mean Diff.	DF	t-Value	P-Value
GF-AAS, in µg/L, ICP-MS, ...	-0.90	3	-1.06	0.3670

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 27. Scattergram, box plots, Paired *t*-Test results, and regression coefficients showing **selenium** data from the former graphite furnace–atomic absorption spectrophotometric (GF–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in mg/L vs. F-AAS, in mg/L

	Coefficient	95% Lower	95% Upper
Intercept	-0.10	-0.43	0.23
F-AAS, in mg/L	1.08	1.06	1.10

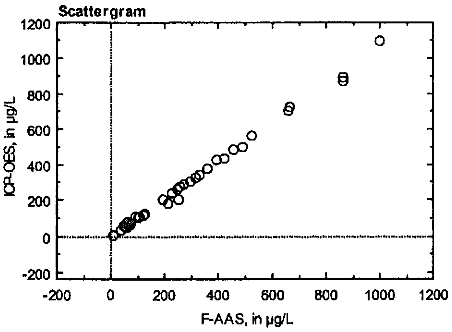
One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	8
# Obs. < Hyp. Value	25
# Obs. = Hyp. Value	0
P-Value	0.0046

EXPLANATION

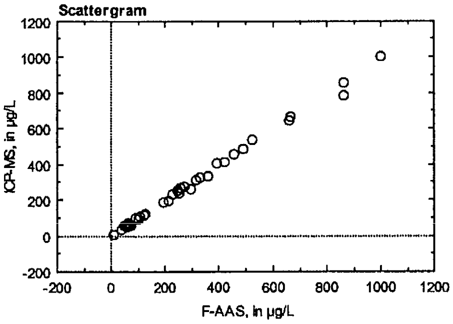
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 28. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **sodium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method and inductively coupled plasma–optical emission spectrometry (ICP–OES) for whole-water digests. Concentrations are in milligrams per liter (mg/L).



Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

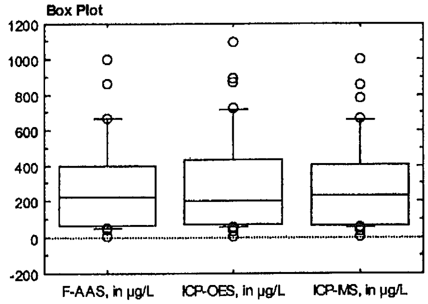
	Coefficient	95% Lower	95% Upper
Intercept	-7.40	-16.59	1.80
F-AAS, in µg/L	1.06	1.04	1.09



Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	-0.71	-8.44	7.03
F-AAS, in µg/L	0.98	0.96	1.00

Figure 29a. Scattergrams and regression analyses showing **strontium** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former flame–atomic absorption spectrophotometric (F–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	2
H	0.13
P-Value	0.9369
H corrected for ties	0.13
Tied P-Value	0.9369

Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	37	2022.00	54.65
2	37	2122.00	57.35
3	37	2072.00	56.00

EXPLANATION

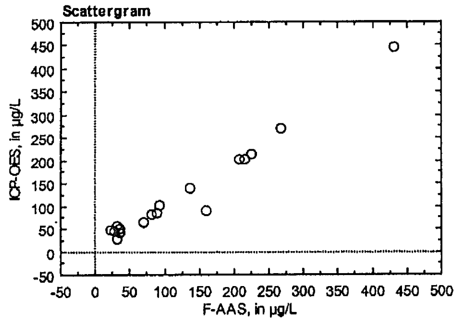
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

DF – Degrees of Freedom

H – Null hypothesis test statistic

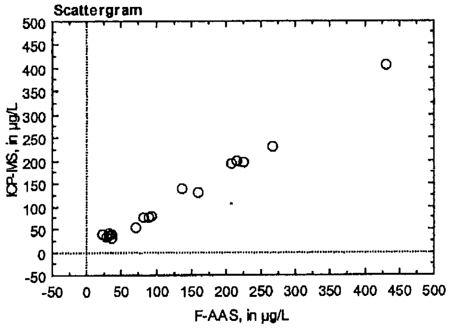
P-Value – Level of significance

Figure 29b. Box plots and Kruskal-Wallis Test results showing **strontium** data from the former flame–atomic absorption spectrophotometric (F–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-OES, in µg/L vs. F-AAS, in µg/L

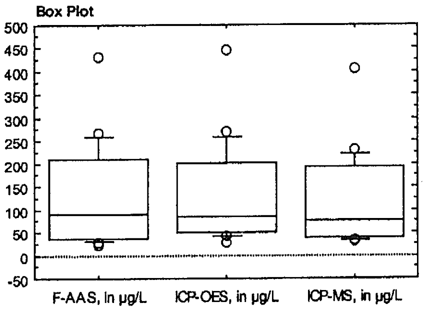
	Coefficient	95% Lower	95% Upper
Intercept	4.55	-12.55	21.65
F-AAS, in µg/L	0.96	0.86	1.06



Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	2.67	-5.46	10.80
F-AAS, in µg/L	0.90	0.85	0.95

Figure 30a. Scattergrams and regression analyses showing **zinc** whole-water digest data from inductively coupled plasma–optical emission spectrometry (ICP–OES) and inductively coupled plasma–mass spectrometry (ICP–MS) in relation to the former flame–atomic absorption spectrophotometric (F–AAS) method. Concentrations are in micrograms per liter (µg/L).



Kruskal-Wallis Test for Data
Grouping Variable: Method

DF	2
# Groups	3
# Ties	2
H	0.42
P-Value	0.8097
H corrected for ties	0.42
Tied P-Value	0.8097

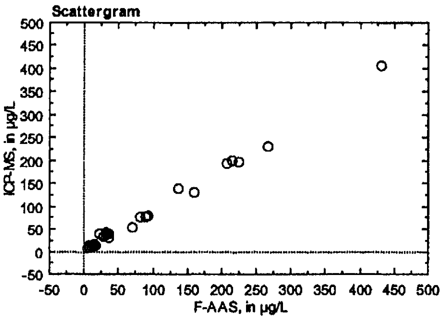
Kruskal-Wallis Rank Info for Data
Grouping Variable: Method

	Count	Sum Ranks	Mean Rank
1	17	473.00	27.82
2	17	418.00	24.59
3	17	435.00	25.59

EXPLANATION

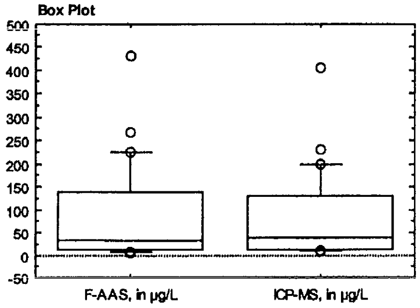
Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.
DF – Degrees of Freedom
H – Null hypothesis test statistic
P-Value – Level of significance

Figure 30b. Box plots and Kruskal-Wallis Test results showing **zinc** data from the former flame–atomic absorption spectrophotometric (F–AAS) method (group 3), inductively coupled plasma–optical emission spectrometry (ICP–OES, group 1), and inductively coupled plasma–mass spectrometry (ICP–MS, group 2) for whole-water digests. Concentrations are in micrograms per liter (µg/L).



Confidence Intervals
ICP-MS, in µg/L vs. F-AAS, in µg/L

	Coefficient	95% Lower	95% Upper
Intercept	2.24	-2.08	6.55
F-AAS, in µg/L	0.90	0.67	0.93



One-Sample Sign Test for Difference
Hypothesized Value: 0

# Obs. > Hyp. Value	13
# Obs. < Hyp. Value	11
# Obs. = Hyp. Value	2
P-Value	0.6388

EXPLANATION

Box plot – horizontal lines, from bottom, represent the 10th, 25th, 50th, 75th, and 90th percentiles; data below the 10th and above 90th are plotted as circles.

Figure 30c. Scattergram, box plots, One-sample Sign Test results, and regression coefficients showing **zinc** data from the former flame–atomic absorption spectrophotometric (F–AAS) method and inductively coupled plasma–mass spectrometry (ICP–MS) for whole-water digests. Concentrations are in micrograms per liter (µg/L).

Table 8. Statistical analysis of short-term ICP–OES results for U.S. Geological Survey's Standard Reference Water Sample T107

[ICP–OES, inductively coupled plasma–optical emission spectrometry; element results are in micrograms per liter except for calcium, magnesium, silicon, and sodium, which are in milligrams per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance; ld, less than the method detection limit (see table 1); <, less than]

Element	MPV	ICP–OES Experimental mean, n=10	Test	Test statistic	p-value
Aluminum [1]	220 ± 45	204 ± 7	T	-7.0	<0.0001
Barium	192 ± 11	192.6 ± 0.5	T	3.6	0.0058
Beryllium	11.0 ± 1.1	11.7 ± 0.2	T	9.6	<0.0001
Boron	130 ± 21	135 ± 3	T	4.5	0.0015
Cadmium	14.3 ± 2.1	13 ± 2	T	-2.0	0.073
Calcium [1]	11.7 ± 0.7	11.32 ± 0.02	T	-47	<0.0001
Chromium	13.0 ± 2.1	13 ± 3	T	0.47	0.65
Cobalt	11.0 ± 1.4	12 ± 2	T	1.6	0.14
Copper	30.0 ± 2.3	29 ± 1	W	5.0	0.025
Iron	52 ± 7	50 ± 2	T	-2.8	0.020
Lead	26 ± 4	ld	ld	ld	ld
Lithium	193 ± 14	191 ± 2	T	-3.8	0.0042
Magnesium [1]	2.10 ± 0.13	2.02 ± 0.01	W	0	0.006
Manganese	45 ± 6	45.4 ± 0.4	T	3.2	0.011
Molybdenum	15.0 ± 1.9	ld	ld	ld	ld
Nickel	28.1 ± 3.9	ld	ld	ld	ld
Silicon as SiO_2	7.7 ± 0.5	7.42 ± 0.02	T	-33	<0.0001
Silver	12.3 ± 2.2	11 ± 6	T	8.8	<0.0001
Sodium [1]	20.7 ± 1.1	20.6 ± 0.2	W	19	0.42
Strontium	61 ± 4	60.5 ± 0.2	T	-6.8	0.0001
Vanadium	14.0 ± 2.8	12 ± 1	T	-4.1	0.0029
Zinc	75.8 ± 9.9	74 ± 4	T	-0.94	0.37

[1] Used emission wavelength that was most suitable.

Table 9. Statistical analysis of short-term ICP–OES results for U.S. Geological Survey's Standard Reference Water Sample T119

[ICP–OES, inductively coupled plasma–optical emission spectrometry; element results are in micrograms per liter except for calcium, magnesium, silicon, and sodium, which are in milligrams per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance; ld, less than the method detection limit (see table 1); <, less than]

Element	MPV	ICP–OES			
		Experimental mean, n=10	Test	Test statistic	p-value
Aluminum [1]	170 ± 30	162 ± 7	T	-4.0	0.0026
Barium	44 ± 3	44.8 ± 0.7	T	3.6	0.0056
Beryllium	13.6 ± 1.7	13.5 ± 0.4	T	-1.1	0.31
Boron	28 ± 9	28 ± 4	T	-0.17	0.87
Cadmium	2.8 ± 0.4	ld	ld	ld	ld
Calcium [1]	11.0 ± 0.8	12.0 ± 0.2	T	15	<0.0001
Chromium	19 ± 2	18 ± 1	T	-0.46	0.65
Cobalt	5.1 ± 1.0	5 ± 2	T	-0.58	0.58
Copper	2.0 ± 1.0	ld	ld	ld	ld
Iron	46 ± 7	43 ± 2	T	-5.1	0.0007
Lead	6.7 ± 1.2	ld	ld	ld	ld
Lithium	60 ± 4	59 ± 1	T	-4.1	0.0028
Magnesium [1]	3.1 ± 0.2	3.08 ± 0.05	T	-1.1	0.31
Manganese	35 ± 3	34.9 ± 0.6	T	-0.67	0.52
Molybdenum	11.9 ± 2.4	ld	ld	ld	ld
Nickel	21.8 ± 2.2	ld	ld	ld	ld
Silicon as SiO_2	9.0 ± 0.5	8.8 ± 0.2	T	-4.0	0.0033
Silver	4.0 ± 1.3	ld	ld	ld	ld
Sodium [1]	20.3 ± 1.0	21.0 ± 0.3	T	7.1	<0.0001
Strontium	73 ± 5	73 ± 1	T	0.56	0.59
Vanadium	3.8 ± 0.9	5 ± 1	T	2.4	0.042
Zinc	24.8 ± 4.7	26 ± 6	W	40	0.22

[1] Used emission wavelength that was most suitable.

Table 10. Statistical analysis of short-term ICP–OES results for U.S. Geological Survey's Standard Reference Water Sample T133

[ICP–OES, inductively coupled plasma–optical emission spectrometry; element results are in micrograms per liter except for calcium, magnesium, silicon, and sodium, which are in milligrams per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; p-value, level of significance; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; ld, less than the method detection limit (see table 1); <, less than]

Element	MPV	ICP–OES			
		Experimental mean, n=10	Test	Test statistic	p-value
Aluminum [1]	52.1 ± 8.1	48 ± 6	T	-2.2	0.052
Barium	148 ± 9	143.8 ± 0.6	T	-24	<0.0001
Beryllium	35.0 ± 2.2	36.2 ± 0.3	T	12	<0.0001
Boron	297 ± 16	292 ± 5	T	-3.3	0.0091
Cadmium	23.0 ± 2.1	25 ± 2	T	2.1	0.077
Calcium [1]	7.0 ± 0.3	6.85 ± 0.02	W	0	0.006
Chromium	38.0 ± 3.2	40 ± 3	T	2.0	0.087
Cobalt	20.0 ± 1.5	20 ± 6	T	0.03	0.97
Copper	85.3 ± 4.5	85 ± 2	T	-1.2	0.24
Iron	31.4 ± 6.7	31 ± 2	T	-0.35	0.73
Lead	27.8 ± 2.7	ld	ld	ld	ld
Lithium	51.0 ± 3.5	47.9 ± 0.7	T	-15	<0.0001
Magnesium [1]	5.8 ± 0.2	5.56 ± 0.02	W	0	0.006
Manganese	121 ± 7	114.9 ± 0.6	T	-32	<0.0001
Molybdenum	46.0 ± 4.2	46 ± 12	T	-0.10	0.92
Nickel	27.2 ± 3.1	ld	ld	ld	ld
Silicon as SiO_2	10.1 ± 0.7	9.78 ± 0.06	W	0	0.006
Silver	7.4 ± 0.9	6.4 ± 0.7	T	-4.7	0.0011
Sodium [1]	29.4 ± 1.2	28.8 ± 0.1	T	-17	<0.0001
Strontium	123 ± 6	119.9 ± 0.3	T	-31	<0.0001
Vanadium	13.0 ± 1.7	10 ± 1	T	-9.4	<0.0001
Zinc	53.0 ± 4.4	44 ± 6	T	-4.4	0.0017

[1] Used emission wavelength that was most suitable.

Table 11. Statistical analysis of short-term ICP–OES results for U.S. Geological Survey's Standard Reference Water Sample T135

[ICP–OES, inductively coupled plasma–optical emission spectrometry; element results are in micrograms per liter except for calcium, magnesium, silicon, and sodium, which are in milligrams per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance; ld, less than the method detection limit (see table 1); <, less than]

Element	MPV	ICP–OES			
		Experimental mean, n=10	Test	Test statistic	p-value
Aluminum [1]	10.5 ± 6.8	ld	ld	ld	ld
Barium	67.8 ± 4.3	64.7 ± 0.2	W	0	0.006
Beryllium	59.0 ± 2.6	58.4 ± 0.3	T	-7.4	<0.0001
Boron	13.1 ± 11.1	ld	ld	ld	ld
Cadmium	50.5 ± 3.2	49 ± 2	T	-1.9	0.092
Calcium [1]	10.4 ± 0.6	10.27 ± 0.03	T	-14	<0.0001
Chromium	79.0 ± 5.5	76 ± 1	T	-5.7	0.0003
Cobalt	40.0 ± 2.6	38 ± 2	T	-1.8	0.097
Copper	62.0 ± 4.2	60 ± 1	T	-7.3	<0.0001
Iron	228 ± 11	219 ± 4	T	-6.3	0.0001
Lead	103 ± 7	107 ± 16	T	0.80	0.45
Lithium	73.7 ± 5.2	69.4 ± 0.8	T	-17	<0.0001
Magnesium [1]	2.00 ± 0.09	1.97 ± 0.01	W	0	0.006
Manganese	423 ± 20	397 ± 1	T	-61	<0.0001
Molybdenum	63.0 ± 5.1	62 ± 11	W	13	0.15
Nickel	65.6 ± 5.0	59 ± 11	T	-2.1	0.068
Silicon as SiO_2	4.28 ± 0.31	4.09 ± 0.03	W	0	0.006
Silver	9.8 ± 1.0	11.5 ± 0.8	T	7.1	<0.0001
Sodium [1]	30.8 ± 1.2	30.2 ± 0.2	T	-11	<0.0001
Strontium	46.0 ± 2.3	45.5 ± 0.3	T	-5.2	0.0005
Vanadium	52.8 ± 3.6	52 ± 1	T	-1.1	0.30
Zinc	48.2 ± 4.7	44 ± 4	T	-3.1	0.012

[1] Used emission wavelength that was most suitable.

Table 12. Statistical analysis of long-term ICP–MS results for U.S. Geological Survey's Standard Reference Water Sample T107

[ICP–MS, inductively coupled plasma–mass spectrometry; element results are in micrograms per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance; <, less than]

		ICP–MS			
Element	**MPV**	**Experimental mean, n=10**	**Test**	**Test statistic**	**p-value**
Aluminum	220 ± 45	237 ± 8	T	6.4	0.0001
Antimony	10.1 ± 2.5	9.8 ± 0.3	T	-3.1	0.013
Barium	192 ± 11	197 ± 6	W	50	0.025
Beryllium	11.0 ± 1.1	13.2 ± 1.4	T	5.0	0.0007
Boron	130 ± 21	158 ± 14	T	6.0	0.0002
Cadmium	14.3 ± 2.1	14.2 ± 0.3	T	-0.67	0.52
Chromium	13.0 ± 2.1	16 ± 2	W	55	0.006
Cobalt	11.0 ± 1.4	11.8 ± 0.4	W	55	0.006
Copper	30.0 ± 2.3	30.0 ± 1.8	T	0.07	0.94
Lead	26 ± 4	27.9 ± 0.4	T	14	<0.0001
Lithium	193 ± 14	220 ± 20	T	4.2	0.0025
Manganese	45 ± 6	48.8 ± 0.6	T	21	<0.0001
Molybdenum	15.0 ± 1.9	15.5 ± 0.5	T	3.4	0.0075
Nickel	28.1 ± 3.9	28.0 ± 1.4	T	-0.23	0.82
Selenium	11.0 ± 1.9	11.4 ± 1.3	T	0.99	0.35
Silver	12.3 ± 2.2	11.1 ± 0.3	T	-11	<0.0001
Strontium	61 ± 4	61.1 ± 1.7	T	0.18	0.86
Zinc	75.8 ± 9.9	82 ± 4	T	4.3	0.0020

Table 13. Statistical analysis of long-term ICP–MS results for U.S. Geological Survey's Standard Reference Water Sample T119

[ICP–MS, inductively coupled plasma–mass spectrometry; element results are in micrograms per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance]

Element	MPV	ICP–MS			
		Experimental mean, n=10	Test	Test statistic	p-value
Aluminum	170 ± 30	174 ± 4	T	2.0	0.076
Antimony	8.6 ± 1.5	8.7 ± 0.2	T	1.0	0.34
Barium	44 ± 3	43.2 ± 1.1	T	-2.4	0.040
Beryllium	13.6 ± 1.7	14.7 ± 1.0	T	3.4	0.0074
Boron	28 ± 9	34 ± 10	T	5.1	0.0006
Cadmium	2.8 ± 0.4	2.8 ± 0.1	W	46	0.067
Chromium	19 ± 2	19 ± 2	W	24	0.76
Cobalt	5.1 ± 1.0	5.2 ± 0.1	T	1.5	0.17
Copper	2.0 ± 1.0	2.2 ± 0.1	T	5.6	0.0003
Lead	6.7 ± 1.2	7.2 ± 0.1	T	13	<0.0001
Lithium	60 ± 4	63 ± 4	T	2.18	0.057
Manganese	35 ± 3	34.9 ± 0.4	T	-0.61	0.55
Molybdenum	11.9 ± 2.4	12.2 ± 0.3	T	2.6	0.029
Nickel	21.8 ± 2.2	21.3 ± 0.7	T	-2.1	0.066
Selenium	9.8 ± 1.3	9.8 ± 1.3	T	-0.07	0.95
Silver	4.0 ± 1.3	2.6 ± 1.0	T	-4.5	0.0015
Strontium	73 ± 5	71 ± 2	T	-2.8	0.021
Zinc	24.8 ± 4.7	24.4 ± 0.8	T	-1.6	0.14

Table 14. Statistical analysis of long-term ICP–MS results for U.S. Geological Survey's Standard Reference Water Sample T133

[ICP–MS, inductively coupled plasma–mass spectrometry; element results are in micrograms per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental column; n, equals the number of replicates used to calculate the mean; T, indicates the Student's *t*-Test; W, indicates the Wilcoxon Signed Rank Test; p-value, level of significance]

Element	MPV	ICP–MS Experimental mean, n=10	Test	Test statistic	p-value
Aluminum	52.1 ± 8.1	51.6 ± 1.8	T	-0.79	0.45
Antimony	14.4 ± 2.4	14.5 ± 0.5	T	0.39	0.71
Barium	148 ± 9	151 ± 4	T	2.2	0.051
Beryllium	35.0 ± 2.2	36.4 ± 1.1	T	4.1	0.0027
Boron	297 ± 16	309 ± 11	T	3.5	0.0067
Cadmium	23.0 ± 2.1	22.5 ± 0.5	T	-3.0	0.016
Chromium	38.0 ± 3.2	37.0 ± 0.9	T	-3.4	0.0076
Cobalt	20.0 ± 1.5	20.2 ± 0.6	T	1.4	0.21
Copper	85.3 ± 4.5	84 ± 3	W	18	0.36
Lead	27.8 ± 2.7	28.7 ± 0.6	T	4.3	0.0021
Lithium	51.0 ± 3.5	51.6 ± 1.8	T	1.01	0.34
Manganese	121 ± 7	120 ± 4	W	28	1.0
Molybdenum	46.0 ± 4.2	47.0 ± 1.2	T	2.7	0.026
Nickel	27.2 ± 3.1	26.7 ± 0.7	T	-2.1	0.064
Selenium	21.4 ± 3.7	20.8 ± 1.4	T	-1.5	0.16
Silver	7.4 ± 0.9	7.5 ± 0.2	T	1.8	0.10
Strontium	123 ± 6	124 ± 3	T	0.99	0.35
Zinc	53.0 ± 4.4	52 ± 2	T	-1.2	0.26

Table 15. Statistical analysis of long-term ICP–OES and ICP–MS results for U.S. Geological Survey's Standard Reference Water Sample WW-1

[ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; element results are in micrograms per liter except for calcium, magnesium, silicon, and sodium, which are in milligrams per liter; MPV, the published most probable value; ±, the plus or minus symbol precedes the F-pseudosigma in the MPV column and the standard deviation at 1σ in the experimental columns; n, equals the number of replicates used to calculate the mean; T, indicates the Student's t-Test; W, indicates the Wilcoxon Signed Rank Test; nd, element was not determined by specific analytical method; ld, less than the method detection limit (see table 1); p-value, level of significance; gl, greater than upper calibration limit of the analytical method; <, less than]

Element	MPV	ICP–OES				ICP–MS			
		Experimental mean, n=20	Test	Test statistic	p-value	Experimental mean, n=20	Test	Test statistic	p-value
Aluminum[1]	7,080 ± 5,700	8,500 ± 200	W	210	<0.0001	gl	gl	gl	gl
Antimony	3.6 ± 2.5	nd	nd	nd	nd	2.6 ± 0.2	T	14	<0.0001
Barium	156 ± 34	161 ± 3	T	8.0	<0.0001	168 ± 4	T	14	<0.0001
Beryllium	9.0 ± 0.9	8.2 ± 0.2	T	-8.8	<0.0001	8.9 ± 0.9	T	-0.51	0.61
Boron	31 ± 38	16 ± 2	T	-11	<0.0001	18 ± 3	T	-18	<0.0001
Cadmium	6.1 ± 1.1	4.6 ± 0.6	T	-3.3	0.0037	6.1 ± 0.2	T	0.74	0.47
Calcium[1]	17.9 ± 1.3	17.9 ± 0.2	T	0.29	0.78	nd	nd	nd	nd
Chromium	22 ± 5	19.9 ± 0.4	T	-4.5	0.0003	26 ± 6	T	3.1	0.0065
Cobalt[2]	13.5 ± 2.7	ld	ld	ld	ld	13.3 ± 0.6	T	-1.7	0.10
Copper	28 ± 6	24 ± 1	T	-7.9	<0.0001	26.8 ± 0.9	T	-6.6	<0.0001
Iron	14,000 ± 4,000	13,280 ± 170	T	-19	<0.0001	nd	nd	nd	nd
Lead	25.8 ± 5.1	ld	ld	ld	ld	25.0 ± 0.4	T	-9.6	<0.0001
Lithium	19.0 ± 4.4	15.6 ± 0.2	W	0	<0.0001	18 ± 2	W	76	0.29
Magnesium[1]	7 ± 1	7.1 ± 0.1	T	2.2	0.040	nd	nd	nd	nd
Manganese	595 ± 54	593 ± 9	T	-1.2	0.26	560 ± 40	W	14	0.001

Table 15. Statistical analysis of long-term ICP–OES and ICP–MS results for U.S. Geological Survey's Standard Reference Water Sample WW-1—Continued

Element	MPV	ICP–OES				ICP–MS			
		Experimental mean, n=20	Test	Test statistic	p-value	Experimental mean, n=20	Test	Test statistic	p-value
Molybdenum	4.9 ± 1.8	ld	ld	ld	ld	3.3 ± 0.1	T	-59	<0.0001
Nickel	24.0 ± 7.9	ld	ld	ld	ld	22.6 ± 0.7	T	-8.9	<0.0001
Selenium	5.5 ± 2.1	nd	nd	nd	nd	6.3 ± 0.8	T	4.4	0.0003
Silicon as SiO_2	31 ± 15	40.3 ± 1.2	W	210	<0.0001	nd	nd	nd	nd
Silver	2.3 ± 1.8	ld	ld	ld	ld	1.60 ± 0.06	T	-49	<0.0001
Sodium [1]	19.7 ± 1.7	19.9 ± 0.3	T	4.5	0.0002	nd	nd	nd	nd
Strontium	84 ± 7	85 ± 1	T	4.8	0.0001	85.8 ± 1.7	T	4.7	0.0002
Vanadium	24 ± 9	20.7 ± 0.5	W	0	<0.0001	nd	nd	nd	nd
Zinc	80 ± 20	74 ± 4	W	120	0.72	65 ± 5	T	-8.5	<0.0001

[1] The most suitable emission wavelength was used for ICP–OES.

[2] Cobalt result is not reported because iron concentration exceeds correction limit for ICP–OES.

Table 16. Analytical variability of ICP–OES and ICP–MS results for Standard Reference Water Sample WW-1

[ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; based on three sequential determinations of an aliquot of Standard Reference Water Sample (SRWS) WW-1 in-bottle digest; μg/L, microgram per liter; %RSD, percent relative standard deviation; nd, not determined; ld, less than method detection limit (see table 1); mg/L, milligram per liter]

Element	Concentration, in μg/L	%RSD ICP–OES	%RSD ICP–MS
Aluminum [1]	220	4	0.4
Antimony	3.6	nd	3
Barium	156	0.1	1
Beryllium	9.0	0.07	2
Boron	31	10	4
Cadmium	6.1	50	2
Calcium, mg/L	18	0.1	nd
Chromium	22	5	2
Cobalt [1]	11	20	2
Copper	28	9	4
Iron	14,000	0.2	nd
Lead [2]	160	20	0.1
Lithium	19	2	2
Magnesium, mg/L	7.0	0.04	nd
Manganese	595	0.05	3
Molybdenum [2]	65	6	2
Nickel	24	ld	0.2
Selenium	5.5	nd	20
Silicon, mg/L as SiO_2	31	0.2	nd
Silver [1]	12	10	3
Sodium, mg/L	20	0.5	nd
Strontium	84	0.05	1
Thallium [3]	0.18	nd	6
Uranium [3]	1.0	nd	3
Vanadium	24	2	nd
Zinc	80	8	4

[1] Results are for SRWS T107 digest.

[2] Estimated concentration for spiked SRWS T117 digest.

[3] Unpublished mean concentration for WW-1 digest based on numerous determinations.

Table 17. Analytical variability of ICP–OES and ICP–MS over an extended concentration range

[ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; based on three sequential determinations of an aliquot of standard prepared in calibration blank solution; µg/L, microgram per liter; mg/L, milligram per liter; RSD, relative standard deviation; <MDL, less than method detection limit; na, not applicable; nd, not determined]

Concentration (µg/L)	Percent RSD		Percent RSD		Percent RSD		Percent RSD	
	ICP–OES	ICP–MS	ICP–OES	ICP–MS	ICP–OES	ICP–MS	ICP–OES	ICP–MS
	Aluminum		**Antimony**		**Barium**		**Beryllium**	
5	<MDL	2	na	2	0.8	5	4	2
12.5	<MDL	0.8	na	0.9	1	1	2	1
25	20	0.5	na	2	0.8	2	1	1
50	8	0.6	na	0.4	0.08	1	1	0.9
100	3	0.2	na	1	0.5	0.8	0.7	1
250	5	0.5	na	0.5	0.4	0.9	0.5	0.7
500	2	0.9	na	0.4	0.2	0.9	0.3	0.6
1,000	2	0.3	na	nd	0.2	2	0.2	nd
2,500	0.5	nd	na	nd	0.6	nd	0.4	nd
	Boron		**Cadmium**		**Chromium**		**Cobalt**	
5	<MDL	16	<MDL	10	<MDL	3	50	1
12.5	<MDL	4	20	4	10	3	20	1
25	20	2	6	1	10	8	10	2
50	6	2	5	0.6	10	3	3	1
100	8	2	6	1	0.7	1	4	0.7
250	3	0.8	0.8	0.6	2	0.3	2	0.2
500	2	1	1	0.9	1	2	0.8	0.6
1,000	2	nd	0.5	nd	0.6	nd	0.7	nd
2,500	0.6	nd	0.4	nd	0.2	nd	0.6	nd
	Copper		**Lead**		**Lithium**		**Manganese**	
5	<MDL	20	<MDL	1	<MDL	5	10	3
12.5	30	4	<MDL	0.4	10	2	1	2
25	1	2	<MDL	0.7	3	1	0.8	1
50	1	2	<MDL	0.7	1	2	0.7	1
100	1	2	60	0.3	2	1	1	1
250	2	2	20	2	0.7	0.6	0.2	0.7
500	0.6	0.8	7	0.4	0.2	2	0.4	2
1,000	0.5	nd	7	nd	0.1	nd	0.1	1
2,500	0.5	nd	2	nd	0.6	nd	0.5	nd
	Molybdenum		**Nickel**		**Selenium**		**Silver**	
5	<MDL	3	<MDL	4	na	70	30	1
12.5	<MDL	2	<MDL	4	na	20	10	2
25	<MDL	3	<MDL	3	na	20	7	1
50	20	2	3	1	na	6	4	nd
100	8	1	30	2	na	2	2	nd
250	3	0.7	8	2	na	4	0.6	nd
500	3	0.7	2	1	na	1	0.4	nd
1,000	2	nd	3	nd	na	nd	0.7	nd
2,500	0.9	nd	2	nd	na	nd	nd	nd

Table 17. Analytical variability of ICP–OES and ICP–MS over an extended concentration range—Continued

Concentration (µg/L)	Percent RSD ICP–OES	Percent RSD ICP–MS	Percent RSD ICP–OES	Percent RSD ICP–MS	Percent RSD ICP–OES	Percent RSD ICP–MS	Percent RSD ICP–OES	Percent RSD ICP–MS
	Strontium		**Thallium**		**Uranium**		**Vanadium**	
5	0.7	1	na	1	na	0.3	<MDL	na
12.5	3	0.4	na	2	na	0.4	6	na
25	0.7	2	na	0.5	na	1	10	na
50	0.4	0.8	na	0.6	na	1	2	na
100	0.8	1	na	0.6	na	1	2	na
250	0.4	0.8	na	2	na	1	0.4	na
500	0.2	0.8	na	0.08	na	0.4	0.9	na
1,000	0.2	nd	na	nd	na	nd	0.4	na
2,500	0.6	nd	na	nd	na	nd	0.3	na
	Zinc							
5	<MDL	3						
12.5	<MDL	0.4						
25	4	2						
50	10	4						
100	20	0.8						
250	10	1						
500	2	0.9						
1,000	3	0.4						
2,500	0.3	nd						
Concentration (µg/L)	**Calcium**		**Iron**		**Magnesium**		**Silicon as SiO_2**	
0.01	5	na	0.7	na	5	na	<MDL	na
0.05	0.8	na	4	na	0.8	na	<MDL	na
0.1	0.3	na	4	na	0.7	na	20	na
0.5	0.3	na	0.2	na	0.3	na	5	na
1	0.3	na	0.1	na	0.5	na	3	na
5	0.2	na	0.5	na	0.2	na	2	na
10	0.7	na	0.7	na	0.8	na	1	na
50	0.6	na	0.8	na	0.4	na	2	na
100	0.4	na	0.4	na	0.2	na	1	na
	Sodium							
0.01	<MDL	na						
0.05	<MDL	na						
0.1	6	na						
0.5	4	na						
1	0.3	na						
5	0.7	na						
10	0.8	na						
50	0.09	na						
100	0.5	na						

Table 18. Spike recovery results for whole-water digests

[µS/cm, microsiemens per centimeter at 25 °C; µg/L, microgram per liter; % rec, percent spike recovery; ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; nd, not determined]

Specific conductance, µS/cm[1]	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS
	Aluminum				Antimony				Barium			
103	340	98	340	99	nd	nd	10	98	50	99	52	92
230	710	95	720	96	nd	nd	10	100	61	100	64	96
519	1,520	94	1,520	99	nd	nd	10	100	40	101	40	95
683	610	97	660	105	nd	nd	10	100	61	100	76	93
1,600	130	110	17	82	nd	nd	10	102	180	100	220	106
1,900	130	84	30	92	nd	nd	10	98	81	99	82	96
Average % rec		96		96		nd		100		100		96
	Beryllium				Boron				Cadmium			
103	15	92	0.4	120	81	92	102	96	50	105	0.8	81
230	15	92	0.4	120	120	98	140	103	50	120	0.8	84
519	15	92	4.0	120	101	98	50	109	50	98	0.8	94
683	15	92	0.4	120	101	104	92	120	50	97	1.3	96
1,600	15	91	0.4	93	101	95	102	87	50	99	0.8	82
1,900	15	88	0.4	104	250	103	280	96	50	109	0.8	89
Average % rec		91		113		98		102		105		88
	Chromium				Cobalt				Copper			
103	50	110	5.0	80	71	95	1.3	98	50	96	7.6	107
230	50	97	9.6	74	71	99	1.3	93	50	97	8.8	94
519	50	99	7.8	99	160	99	150	98	50	108	30	106
683	50	104	15	97	71	102	1.0	105	50	110	11	103
1,600	50	105	82	80	71	94	1.1	79	50	105	8.0	87
1,900	50	101	12	91	71	98	0.6	92	50	97	6.2	92
Average % rec		103		87		98		94		102		98

Table 18. Spike recovery results for whole-water digests—Continued

Specific conductance, µS/cm [1]	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS
	Iron				Lead				Lithium			
103	1,010	101	nd	nd	505	106	1.3	101	71	103	6.4	103
230	182	97	nd	nd	505	105	3.2	99	71	102	24	108
519	4,848	101	nd	nd	505	98	5.4	97	71	100	42	120
683	859	102	nd	nd	505	107	1.3	97	71	99	22	120
1,600	1,616	104	nd	nd	505	98	0.9	102	71	98	10	82
1,900	303	105	nd	nd	505	97	1.0	99	71	96	88	102
Average % rec		102		nd		102		99		100		106
	Manganese				Molybdenum				Nickel			
103	320	101	300	93	303	96	5.0	99	303	100	2.6	110
230	202	100	200	89	303	101	5.0	89	303	102	2.4	96
519	4,850	99	nd	nd	303	101	5.0	99	303	108	240	98
683	71	101	70	92	303	99	6.0	102	30	72	7.8	95
1,600	20	98	13	74	303	105	6.0	87	303	109	24	74
1,900	404	103	340	87	303	100	5.0	89	303	99	2.4	90
Average % rec		100		87		100		94		98		94
	Selenium				Silver				Strontium			
103	nd	nd	20	94	26	108	10	87	120	103	120	97
230	nd	nd	20	90	26	102	10	91	120	104	120	92
519	nd	nd	20	95	26	106	10	89	130	104	140	94
683	nd	nd	17	100	26	107	10	89	1,620	103	1,800	91
1,600	nd	nd	20	93	26	102	10	86	1,210	104	1,300	90
1,900	nd	nd	20	78	26	106	10	82	660	105	700	88
Average % rec		nd		92		105		87		104		92

Table 18. Spike recovery results for whole-water digests—Continued

Specific conductance, µS/cm[1]	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS	Spike, µg/L	% rec ICP–OES	Spike, µg/L	% rec ICP–MS
	Thallium				Uranium				Vanadium			
103	nd	nd	2.0	94	nd	nd	4.0	90	40	96	nd	nd
230	nd	nd	2.0	91	nd	nd	4.0	102	40	92	nd	nd
519	nd	nd	2.0	89	nd	nd	4.0	96	40	100	nd	nd
683	nd	nd	2.0	93	nd	nd	3.0	102	40	100	nd	nd
1,600	nd	nd	2.0	98	nd	nd	6.8	96	40	99	nd	nd
1,900	nd	nd	2.0	95	nd	nd	4.4	98	40	103	nd	nd
Average % rec		nd		93		nd		97		98		nd
	Zinc											
103	202	105	10	97								
230	202	96	17	92								
519	760	102	720	102								
683	505	105	10	100								
1,600	202	100	7.2	64								
1,900	202	112	6.2	92								
Average % rec		103		91								

[1] Specific conductance of sample before acidification and in-bottle digestion.

Table 19. Chemical characteristics of natural whole-water samples

[< MDL, less than the method detection limit; ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; µg/L, microgram per liter; mg/L, milligram per liter; µS/cm, microsiemens per centimeter at 25°C; nd, not determined by method; no, no former method is available; —, not applicable]

Element or constituent	25th percentile	Median	75th percentile	Maximum	Fraction of samples < MDL for the former method	Fraction of samples < MDL for the ICP–OES method	Fraction of samples < MDL for the ICP–MS method
Aluminum, in µg/L	60	320	850	20,400	1/43	1/43	0/43
Antimony, in µg/L	0.8	1	5	6	31/43	nd	31/43
Barium, in µg/L	110	140	180	660	23/43	0/43	0/43
Beryllium, in µg/L	0.9	2	2	12	43/43	28/43	21/43
Boron, in µg/L	19	22	36	83	7/43	6/43	2/43
Cadmium, in µg/L	0.2	0.4	0.7	6	14/43	42/43	4/43
Calcium, in mg/L	9	27	47	67	10/43	0/43	nd
Chromium, in µg/L	6	11	20	160	3/43	28/43	17/43
Cobalt, in µg/L	0.8	3	7	84	12/43	37/43	0/43
Copper, in µg/L	2	6	17	360	1/43	15/43	0/43
Iron, in µg/L	380	1,400	4,200	14,000	1/43	1/43	nd
Lead, in µg/L	2	4	20	74	9/43	39/43	0/43
Lithium, in µg/L	10	20	40	160	15/43	11/43	0/43
Magnesium, in mg/L	3	11	22	50	0/43	0/43	nd
Manganese, in µg/L	24	76	260	820	1/43	1/43	0/43
Molybdenum, in µg/L	1	2	4	14	15/43	43/43	11/43
Nickel, in µg/L	2	4	10	95	7/43	36/43	2/43
Selenium, in µg/L		Limited data set			40/43	nd	39/43
Silicon, in mg SiO_2/L	9	17	30	90	no	0/43	nd
Silver, in µg/L		Limited data set			42/43	43/43	42/43
Sodium, in mg/L	3	10	18	40	0/43	0/43	nd
Strontium, in µg/L	60	230	400	1,000	0/43	0/43	0/43
Thallium, in µg/L		Limited data set			no	nd	41/43
Uranium, in µg/L	0.5	1	2	16	no	nd	5/43
Vanadium, in µg/L	8	9	20	60	no	23/43	nd
Zinc, in µg/L	14	38	120	400	19/43	24/43	1/43
Alkalinity, in mg/L	43	68	130	410	—	—	—
Chloride, in mg/L	6	12	36	9,500	—	—	—
Cond., in µS/cm [1]	170	300	620	25,400	—	—	—
Sulfate, in mg/L	5	28	60	1,600	—	—	—

[1] Specific conductance (Cond.) in microsiemens per centimeter (µS/cm) of the whole-water sample prior to digestion.

Table 20. Statistical analysis summary of ICP–OES and ICP–MS results for natural whole-water digests

[ICP–OES, inductively coupled plasma–optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; DCP–AES, direct current plasma–atomic emission spectrometry; GF–AAS, stabilized temperature graphite furnace–atomic absorption spectrophotometry; F–AAS, flame–atomic absorption spectrophotometry; n, number of sample results used in the statistical analysis; id, insufficient data; nd, not determined by an analytical method; —, no data; <, less than]

Element	Former method	Former method to ICP–OES to ICP–MS		Former method to ICP–OES		Former method to ICP–MS	
		n	Kruskal-Wallis p-value	n	One-sample Sign Test p-value	n	One-sample Sign Test p-value
Aluminum	DCP–AES	25	0.9750	—	Redundant	—	Redundant
Antimony [1]	GF–AAS	—	Inappropriate	—	nd	9	0.3061
Barium	F–AAS	20	0.3749	—	Redundant	—	Redundant
Beryllium	F–AAS	—	id	—	id	—	id
Boron	DCP–AES	28	0.0021	36	0.0288	28	0.0009
Cadmium	GF–AAS	—	id	—	id	27	0.0522
Calcium	F–AAS	—	Inappropriate	42	<0.0001	—	nd
Chromium	GF–AAS	15	0.0078	15	<0.0001	26	<0.0001
Cobalt	GF–AAS	6	0.0728	—	Redundant	31	0.0033
Copper	GF–AAS	28	0.5285	—	Redundant	42	0.6440
Iron	F–AAS	—	Inappropriate	38	0.0002	—	nd
Lead	GF–AAS	—	id	—	id	31	0.2810
Lithium	F–AAS	27	0.9191	—	Redundant	—	Redundant
Magnesium	F–AAS	—	Inappropriate	42	0.6440	—	nd
Manganese	F–AAS	36	0.8669	—	Redundant	—	Redundant
Molybdenum	GF–AAS	—	id	—	id	28	0.5716
Nickel	GF–AAS	—	id	—	id	34	0.0243
Selenium [1]	GF–AAS	—	Inappropriate	—	nd	4	0.3670
Silicon as SiO_2	None	—	Inappropriate	—	id	—	nd
Silver	GF–AAS	—	id	—	id	—	id
Sodium	GF–AAS	—	Inappropriate	33	0.0046	—	nd
Strontium	GF–AAS	37	0.9369	—	Redundant	—	Redundant
Thallium	None	—	Inappropriate	—	nd	—	id
Uranium	None	—	Inappropriate	—	nd	—	id
Vanadium	None	—	Inappropriate	—	id	—	nd
Zinc	F–AAS	17	0.8097	—	Redundant	26	0.8388

[1] The paired Student *t*-test was used on a limited data set.

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