A COMPARISON OF SIMULTANEOUS PLASMA, ATOMIC ABSORPTION, AND IRON COLORIMETRIC DETERMINATIONS OF MAJOR AND TRACE CONSTITUENTS IN ACID MINE WATERS

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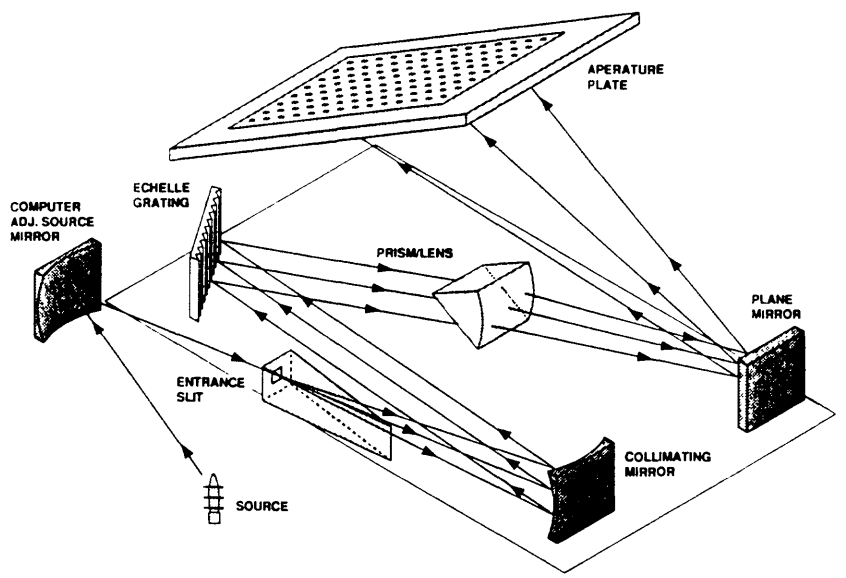

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By James W. Ball and D. Kirk Nordstrom

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
liter (L)	0.2642	gallon (gal)
milliliter (mL)	3.381×10^{-2}	fluid ounce (fl oz)
microliter (µL)	3.381×10^{-5}	fluid ounce (fl oz)
gram (g)	3.520×10^{-2}	ounce (oz)
milligram (mg)	3.520×10^{-5}	ounce (oz)
microgram (µg)	3.520×10^{-8}	ounce (oz)
picogram (pg)	3.520×10^{-11}	ounce (oz)
kilogram per square centimeter (kg cm^{-2})	14.223	pound per square inch (psi)
millimeter (mm)	3.937×10^{-2}	inch (in)
micrometer (µm)	3.937×10^{-5}	inch (in)

Temperature in degrees Fahrenheit (°C) as follows:

°F = 1.8 x °C + 32

Explanation of abbreviations:

M (Molar, moles per liter)
N (Normal, equivalents per liter)
mg L^{-1} (milligrams per liter)
nm (nanometers)
µg L^{-1} (micrograms per liter)

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ABSTRACT

Sixty-three water samples collected during June to October 1982 from the Leviathan/Bryant Creek drainage basin were originally analyzed by simultaneous multielement direct-current plasma (DCP) atomic-emission spectrometry, flame atomic-absorption spectrometry, graphite-furnace atomic-absorption spectrometry (GFAAS) (thallium only), ultraviolet-visible spectrometry, and hydride-generation atomic-absorption spectrometry. Determinations were made for the following metallic and semi-metallic constituents: Al, As, B, Ba, Be, Bi, Cd, Ca, Cr, Co, Cu, Fe(II), Fe(total), Li, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Si, Na, Sr, Tl, V, and Zn. These samples were re-analyzed later by simultaneous multielement inductively coupled plasma (ICP) atomic-emission spectrometry and Zeeman-corrected GFAAS to determine the concentrations of many of the same constituents with improved accuracy, precision, and sensitivity. The result of this analysis has been the generation of comparative concentration values for a significant subset of the solute constituents. Many of the more recently determined values replace less-than-detection values for the trace metals; others constitute duplicate analyses for the major constituents. The multiple determinations have yielded a more complete, accurate, and precise set of analytical data. They also have resulted in an opportunity to compare the performance of the plasma-emission instruments operated in their respective simultaneous multielement modes.

Flame atomic-absorption spectrometry was judged best for Na and K and hydride-generation atomic-absorption spectrometry was judged best for As because of their lower detection limit and relative freedom from interelement spectral effects. Colorimetric determination using ferrozine as the color agent was judged most accurate, precise, and sensitive for Fe. Cadmium, lead, and vanadium concentrations were too low in this set of samples to enable a determination of whether ICP or DCP is a more suitable technique. Of the remaining elements, Ba, Be, Ca, Cr, Mg, Mn, Sr, and Zn have roughly equivalent accuracy, precision, and detection limit by ICP and DCP. Cobalt and Ni were determined to be better analyzed by ICP, because of lower detection limits; B, Cu, Mo, and Si were determined to be better analyzed by DCP, because of relative freedom from interferences. The determination of Al by DCP was far more sensitive, owing to the use of a more sensitive wavelength, compared with the ICP. However, there is a very serious potential interference from a strong Ca emission line near the 396.15 nanometer DCP wavelength. Thus, there is no clear choice between the plasma techniques tested, for the determination of Al. The ICP and DCP detection limits are typically between 0.001 and 0.5 milligrams per liter in acid mine waters. For those metals best analyzed by ICP and/or DCP, but below these limits, GFAAS is the method of choice because of its relatively greater sensitivity and specificity. Six of the elements were not determined by DCP, ICP or Zeeman-corrected GFAAS, and are not discussed in this report. These elements are: Bi, Fe(II), Li, Sb, Se, and Tl.

INTRODUCTION

The U.S. Geological Survey is active in monitoring the chemical composition of many natural water systems, and in developing and testing geochemical models describing the sources, reaction paths and ultimate fate of the chemical constituents of natural waters. Complete and accurate concentration data are essential to the geochemical modeling of natural waters. Several modern instrumental techniques, described below, are commonly used by Survey laboratories to analyze natural waters.

Inductively-coupled plasma atomic-emission spectrometry (ICP-AES or ICP) can be used to determine major and trace concentrations of many metals simultaneously over a wide concentration range in aqueous solution. The technique is sensitive, precise, accurate, and rapid, with little or no sample pretreatment required other than occasional dilution of concentrated samples. In addition, automated analysis and data reduction systems are readily available from virtually all manufacturers of ICP-AES instruments.

Direct-current plasma atomic-emission spectrometry (DCP-AES or DCP) is an alternative technique for rapidly determining major and trace concentrations of metals in aqueous solution. The ICP and DCP techniques are similar in analytical speed, sensitivity, and range of elements and concentrations analyzed. The primary difference between the ICP and DCP instruments is in the plasma generation and the nature of the sample/plasma interaction. Virtually all the other differences, from atom/ion ratios to torch geometry and design to nebulizer characteristics, are a result of the basic source characteristics.

Taylor (1981) has summarized the application of plasma AES to natural waters. He considered three common techniques: ICP, DCP, and microwave-induced plasma. In the present paper, ICP and DCP are discussed with respect to a set of acid mine water samples having a large range of concentrations.

The results and conclusions presented in this report provide the justification for the revised concentration estimates tabulated by Ball and Nordstrom (1989). The motivation for re-analyzing the samples was to improve and expand the base of trace-element data for modeling the attenuation of major and trace elements during downstream transport using the best available techniques of surface-water flow measurement and elemental analysis. In addition to the modeling objective, the data from both the original and more recent analyses provided a unique opportunity to compare the performance of the various analytical instruments used during the course of this work.

Zeeman-corrected graphite-furnace atomic-absorption spectrometry (Zeeman GFAAS), hydride atomic-absorption spectrometry (hydride AAS), flame atomic-absorption spectrometry (flame AAS), and ultraviolet/visible (UV/VIS) spectrophotometry are techniques for trace analysis that are characterized by high sensitivity, accuracy, and precision, and, like the plasma methods, usually are suitable for the analysis of complex matrices. These four techniques have slower analytical speed than simultaneous plasma techniques because of their inherently single-element nature and, except for analyses in uncomplicated matrices using the flame AAS technique, added requirements for sample pretreatment during analysis prior to the measurement step. For as many as about six elements, flame AAS and plasma spectrometers operated in a sequential multielement mode are capable of equivalent analytical speed.

Direct-current plasma, GFAAS, flame AAS, and UV/VIS spectrometry originally were used to analyze a set of 63 surface water samples from the Leviathan/Bryant Creek drainage basin, California and Nevada (Ball and Nordstrom, 1985). Subsequently, ICP and Zeeman-corrected GFAAS systems were acquired. The entire set of samples was re-analyzed by ICP, and selected samples were analyzed by Zeeman-corrected GFAAS to determine concentrations at levels below the detection limits of the plasma

techniques. These comparisons led to the selection of a "best" method, on an element-by-element basis, for the analysis of waters from this particular drainage basin.

Many of these samples contained the metals Al, As, Cr, Co, Cu, Fe, Mn, Ni, Tl, V, and Zn at levels ranging from about 1 mg L^{-1} to several percent, well above those usually considered "trace." The range of dissolved solids was from about 100 mg L^{-1} to several weight percent. Although the range of concentrations is large, the proportions of the solute constituents varied much less than might be expected, owing to confinement of the sampling to a single drainage basin where dilution and precipitation of Fe and Al were the only major processes affecting concentrations. Thus, these findings may not apply to a wide variety of water types.

Several of the elements mentioned in the abstract are not discussed in this report. Bismuth, Li, Sb, Se, and Tl were not detected in any samples by either of the plasma techniques, and were not determined by Zeeman-corrected GFAAS. Iron (II) is not discussed because the plasma techniques do not distinguish elemental valence states.

The authors assume that the reader understands the basic concepts of atomic-emission and atomic-absorption spectrometry, and the underlying principles of instrumental analysis. Specifically, the concepts of signal-to-noise ratio, sensitivity, and detection limit, and how they are related to these analytical techniques are not discussed at length, beyond giving an operational definition of detection limit for the purpose of discussing the results presented. The reader may consult any modern instrumental analysis text for complete discussions of these subjects.

METHODS DESIGN

Sample Collection and Preservation

A portable peristaltic pump fitted with silicone rubber tubing, which was capable of delivering fluid to the filtration apparatus with a head of at least 1.4 kg cm^{-2} was used to collect water samples. Sample water was pumped directly from the source through a 0.1-µm effective pore size, 142-mm diameter Millipore VCWP membrane placed between two acrylic plastic discs and sealed with a viton or silicone rubber o-ring (Kennedy and others, 1976). Effluent filtrate was directed into an acid-cleaned 250-mL Teflon bottle pre-acidified with 2 mL of ultrapure concentrated (about 15.7*N*) HNO_3. In the absence of acid consumption by protonation reactions, this would result in a pH of about 0.75. Actual pH values were randomly checked with a pH electrode, and all were found to be less than 1.5.

Apparatus

The ICP spectrometer used was a Plasma-Spec III (Leeman Labs, Inc., Lowell, MA) simultaneous direct-reading unit. An autosampler and serial communication interface available from the instrument manufacturer aided rapid sample throughput. The Plasma-Spec III was operated with the factory-installed dynamic off-peak background correction feature active on all channels. This feature operates by directing the instrument to measure the emission either at one or at two wavelengths near each primary emission line immediately after measurement of the emission at the primary wavelength. The analytical program then subtracts the result, consisting of either the single emission value or the mean of two values, from the primary emission. For the data of this report, a single-point correction was used for all elements. The point at which the off-peak measurement was taken was determined by scanning a wavelength range nearby the wavelength of interest while nebulizing a series of solutions containing a high concentration

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

of a single major constituent, and the HNO_3 blank solution. All the scans were then overlaid, and a single point that varied the least between solutions was selected from among the four available.

Standard solutions were interspersed with the unknowns, such that every fourth solution was a standard of known concentration. Instrument output was collected using an American Telephone and Telegraph 6300 International Business Machines Personal Computer (IBM PC) compatible personal computer equipped with an Okidata 192 graphics printer. Results were computed using an IBM PC compatible and a data reduction software package developed by the senior author (Ball, J. W., written commun., 1989), and explained in more detail by Ball and Nordstrom (1985, 1989). Emission intensities for standards analyzed as unknowns are fitted to a straight line using a first-order least squares method. The resulting fit parameters are then combined with emission intensities for unknowns to yield concentration values.

When data for all elements were available, sample concentrations were corrected for inter-element spectral effects that result from the presence of concomitant major elements and are observed when measuring concentrations of minor elements (Ball and Nordstrom, 1989). This correction required the prior collection of background-corrected concentration data for a representative concentration range of the potential interferent in the absence of analyte. The resulting apparent analyte concentration values were fitted to various types of linear and non-linear simple regression equations, and the selected fit parameters were determined. After assembling apparent concentration data for the unknowns, the concentrations of the concomitant elements were sequentially combined with the selected fit parameters to yield concentration values for their interference effects, which were subtracted from the apparent analyte concentration. This inter-element interference correction technique was used to correct for the effects of Ca, Mg, Si, Fe, and Al on the apparent concentrations of Al, As, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Ni, Na, Sr, V, and Zn. No effects of Ca, Mg, Si, Fe or Al at their upper concentration limits (490, 110, 110, 2510, and 620 mg L^{-1}, respectively) were observed on the apparent concentrations of Ba, Be, Co, K or Si. The effect of Ca is the most serious, followed by the effect of Fe, for the analysis of acid mine effluent by ICP spectrometry.

The DCP spectrometer used was a SpectraSpan IIIB (SpectraMetrics, Inc., Andover, MA) simultaneous direct-reading unit, equipped with two cassettes containing apertures designed to direct the wavelengths of 20 elements into a bank of 20 photomultiplier tubes. To increase thermal contact between the plasma and the measuring zone, located directly below the plasma (Johnson and others, 1979c, p. 204), a Li solution was mixed at approximately a 1:11 ratio with the sample just prior to nebulization, such that a total concentration of 2270 mg L^{-1} of Li was generated in the sample (Ball and others, 1978). Instrument output was collected, then reduced using a Tektronix 4052 desktop microcomputer and a serial printer, and data reduction software similar to that described for the ICP spectrometer. All DCP determinations were done without off-peak dynamic background correction. Corrections for interelement spectral effects were done for the DCP results during the data reduction stage using a software package similar to that used for the ICP results (Ball and Nordstrom, 1985). The inter-element interference correction technique was used to correct for the effects of Ca, Mg, Si, K, Na, and Fe on the apparent concentrations of Al, As, B, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, and Zn. No effects of Ca, Mg, Si, K, Na, or Fe at their upper concentration limits (490, 110, 110, 33, 39, and 2510 mg L^{-1}, respectively) were observed on the apparent concentrations of Si, Be, Mg, Ca, Fe, Sr, Ba, K or Na. The effect of Ca is the most serious, followed by the effect of Fe, for the analysis of acid mine effluent by DCP spectrometry.

The Zeeman-corrected GFAAS unit used was a Perkin-Elmer Zeeman/5000 with HGA-500 furnace controller, AS-40 autosampler, and Model 7300 computer running HGA Graphics II software. Follow

cathode source lamps for Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn were used. Analytical procedures supplied by the instrument manufacturer were used with only minor modifications for all elements.

The flame AAS unit used was a Perkin-Elmer Model 306 fitted, for the Na and K determinations, with a 4-inch single-slot burner head. Hollow cathode lamps for Na and K, and an electrodeless discharge lamp for As were used. For hydride As determinations, an aliquot of sample made 1.5*M* in HCl was injected into a reaction vessel containing $NaBH_4$ solution. The resulting gas mixture was purged, using He, into a quartz cuvette positioned in the light beam of the spectrophotometer and externally heated with an air-acetylene flame. Selected samples were analyzed for total As by both hydride AAS with prior oxidation of the sample and Zeeman-corrected GFAAS. These two techniques are described in more detail by Ball and Nordstrom (1985) and Maest and Wing (1987), respectively.

Reagents

All reagents were American Chemical Society Reagent Grade or better.

1. Double distilled water, better than 1 megohm purity.
2. Baker Ultrex HNO_3 and HCl.
3. Multielement working standard solutions for the plasma emission determinations, composed of alkali and alkaline earth salts of purity 99.99 percent or better and other metal and alkaline earth salts, acids and commercially prepared solutions of purity 99.999 percent or better. This set of solutions consisted of a top standard, three additional standards containing 0.5, 0.25, and 0.1 fractions of the concentration of the top standard for each element diluted to volume with 1.0*N* HNO_3, and a 0.1*N* HNO_3 blank solution. Three different sets of standards were prepared, one for the ICP determinations and one for each of the two multielement cassettes for the DCP determinations.
4. $Mg(NO_3)_2$ matrix modifier solution for the GFAAS determinations, 10 g L^{-1} $Mg(NO_3)_2$ (5 µL = 50 µg $Mg(NO_3)_2$). Dissolve 8.6438g Baker Reagent Grade $Mg(NO_3)_2 \cdot 6H_2O$ in 500 mL redistilled water. Purify by solvent extraction with ammonium pyrrolidine dithiocarbamate-diethylammonium diethyl dithiocarbamate and methyl isobutyl ketone. Prepare working solution in concentration appropriate to the element to be analyzed.
5. $NH_4H_2PO_4$ for the GFAAS determination of Cd and Pb, 40 g L^{-1} PO_4 (5 µL = 200 µg PO_4). Dissolve 24.224g of Baker Reagent Grade $NH_4H_2PO_4$ in 500 mL redistilled water. Purify by solvent extraction as in step (4) above. Prepare in concentration appropriate to the element of interest.
6. GFAAS working standard solutions, prepared the day of use in ultrapure 0.1*N* HNO_3.

Procedures

The specific wavelengths for the simultaneous multielement modes were selected by the respective instrument manufacturers at the time of instrument construction. These wavelengths, concentrations of calibrating solutions, operational detection limits, and literature detection limits for the ICP and DCP determinations are shown in Table 1. The operational detection limits were determined in this study. Detection limits, which are discussed in more detail later, are strongly influenced by many factors, one of which is the choice of wavelength. If the wavelength at which a literature detection limit was measured is different from that used for making the measurements of this report, its value is given as a footnote to Table 1. Instrument settings for the ICP spectrometer are shown in Table 2. The reader is referred to Ball and others (1978) for instrument settings for the SpectraSpan IIIB DCP spectrometer.

Table 1.--Wavelengths and analytical ranges for the inductively coupled plasma (ICP) and direct-current plasma (DCP) spectrometers
[nm, nanometers; mg/L, milligrams per liter]

	ICP				DCP			
Element	Wavelength (nm)	Maximum standard concentration (mg/L)	Operational detection limit (mg/L)	Literature detection limit (mg/L)	Wavelength (nm)	Maximum standard concentration (mg/L)	Operational detection limit (mg/L)	Literature detection limit (mg/L)
Al	308.22	2.0	0.5	[1,11]0.005	396.15	0.5	0.01	[1]0.01
As	197.20	20.0	.3	[2].076	193.80	20.0	.4	[20]
Ba	455.40	.5	.005	[4].002	455.40	1.0	.005	[1,3].02
Be	313.04	.1	.001	[4].0005	313.04	.2	.002	[1,6].01
B	249.68	5.0	.02	.003[1,11]	249.77	1.0	.02	[1,7].005
Cd	214.44	.1	.005	[4].001	214.44	1.0	.01	[1].01
Ca	315.89	5.0	.05	[4,12].02	393.37	5.0	.2	[1,3,8].2
Cr	205.55	.5	.01	[1,11].002	425.44	.5	.003	[1].005
Co	228.62	.5	.002	[4,13].003	345.35	.5	.005	[20]
Cu	327.40	1.0	.05	[4,14].01	324.75	.5, [5].2	.01, [5].003	[1].005
Fe	238.20	2.0	.1	[4,15].003	371.99	2.0, [5]1.0	.015, [5].02	[20]

Pb	22.35	1.0	.2	[4].01	405.78	4.0	.02	[1].01
Mg	279.08	2.0	.5	[4].004	279.55	2.0	.02	[1,3].13
Mn	257.61	2.0	.02	[4].001	257.61	.5	.01	[1].01
Mo	202.03	1.0	none[3]	[4,16].01	379.83	1.0	.003	[1].01
Ni	231.60	.5	.003	[1,11].006	341.48	.5	.004	[1].01
K	766.49	20.0	.3	[20]	766.49	20.0	.3	[1,3,9].04
Si	288.16	10.0	.5	[4].004	251.61	10.0	.2	[1].01
Na	589.59	20.0	.2	[4,17].2	589.59	20.0	.2	[1,3].4
Sr	407.77	.5	.002	[4,18].0005	421.55	1.0	.005	[1,3,10].1
V	310.23	1.0	.075	[4,19].006	437.92	1.0	.005	[20]
Zn	206.20	1.0	.01	[4].003	213.86	.5, .5	.02, [5].006	[20]

[1]Johnson and others(1979c).
[2]Taylor, H. E., written commun., 1992.
[3]Attempts to achieve maximum sensitivity were not made since these elements normally are present at higher concentrations in natural and effluent waters.
[4]Garbarino and Taylor (1979), Garbarino and others (1985).
[5]Two values are values for DCP cassettes 1 and 2, respectively. Wavelengths are the same.
[6]Wavelength = 234.86 nm.
[7]Wavelength = 249.68 nm.
[8]Wavelength = 396.85 nm.
[9]Wavelength = 769.90 nm.
[10]Wavelength = 460.73 nm.
[11]Wavelength not given by these authors. They cite Winge and others (1977).
[12]Wavelength = 396.8 nm.
[13]Wavelength = 238.8 nm.
[14]Wavelength = 324.7 nm.
[15]Wavelength = 259.9 nm.
[16]Wavelength = 203.8 nm.
[17]Wavelength = 588.9 nm.
[18]Wavelength = 421.5 nm.
[19]Wavelength = 292.4 nm.
[20]no literature detection limit found for this element.

Table 2.--Torch, nebulizer, and analytical program settings
for the inductively coupled plasma spectrometer

radio frequency current	0.55 amperes (forward power=1.1 kilowatts)
Nebulizer pressure	38 pounds per square inch
Coolant flow	12.5 (arbitrary units)
Auxiliary flow	0
Nebulizer type	Hildebrand grid
Sample uptake rate	1 milliliter per minute
Integration time	3 seconds
Number of replicates	3

Inductively-Coupled Plasma Spectrometer

Before a routine analysis can be made, the instrument must be calibrated, and background corrections must be entered into the analytical program. These procedures are lengthy and complex, and therefore are not deemed appropriate for inclusion in a report of this type. The following generalized procedure is typical of what is needed to execute a single analytical run using the ICP spectrometer.

1. Start the torch; pump redistilled water into the spray chamber for at least 20 minutes.
2. Initiate the program for peaking the alignment of the optical path.
3. Pump a 10 to 20 mg L^{-1} Mn solution into the spray chamber; initiate the programs for peaking the ICP source horizontally, then vertically.
4. Nebulize redistilled water for at least two minutes; initiate a calibration UPDATE sequence for Update Standard 1, redistilled H_2O.
5. Nebulize the most concentrated standard for at least one minute; initiate a calibration UPDATE sequence for Update Standard 2, the most concentrated standard.
6. Load autosampler rack with sample and standard solutions to be analyzed.
7. Program the Update 1 frequency, to re-zero the baseline, to be done every five samples.
8. Start the data collection and storage function on the PC-compatible computer interfaced to the spectrometer. Initiate the analytical cycle. When run is complete, stop the PC-compatible data collection and copy the run data to an appropriate storage device for subsequent data reduction.

Direct-current Plasma Spectrometer

1. Start the torch; pump redistilled water into the spray chamber for at least 20 minutes.
2. Pump a 10 to 20 mg L^{-1} Cu solution into the spray chamber; peak the spectrometer grating using the thumbwheels; peak the DCP source both horizontally and vertically.
3. Nebulize redistilled water for at least two minutes; initiate a standardize sequence for Standard 1.
4. Nebulize top standard for at least one minute; initiate a standardize sequence for Standard 2.
5. Prepare sample and standard solutions for analysis.
6. Start the data collection and storage function on the computer; begin analyzing the samples. When run is complete, stop the data logging and copy the run data to an appropriate storage device for subsequent data reduction.

Zeeman Graphite-Furnace Spectrometer

All analytical parameters for the Zeeman-corrected graphite-furnace spectrometer were those recommended by the manufacturer. Every fourth solution in the autosampler rack was a standard or blank. Pyrolytically coated graphite tubes were used for all elements. Platform atomization was used for all elements except V, for which wall atomization was used. Zeeman background correction was used for all elements. Wavelength settings and analytical limits are in Table 3. Matrix modifier specifications and furnace settings for the individual elements are in Table 4. Sensitivity check concentrations, characteristic masses, and detection limits all were determined several times during the initial stages of analysis for each element. The ranges listed are the entire range of values obtained over the course of the analyses. Large variations from literature values or manufacturer's specifications may be the result of contamination or loss during a single analytical cycle.

Table 3.--Analytical limits and wavelength settings for the graphite-furnace atomic absorption determinations
[µg L^{-1}, micrograms per liter; pg, picogram; abs-sec, absorbance-second]

Element	wavelength (nanometers)	Standard range (µg L^{-1})	Sensitivity check for 0.2 absorbance (µg L^{-1})	Characteristic mass (pg/0.0044 abs-sec)	Detection limit[1] (µg L^{-1})
Al	309.3	5-100	100-200	20	1.0
As	193.7	5-100	50-100	30	1.0
Cd	228.8	1-10	1-10	.018	.015
Co	240.7	10-100	15-75	.5	.1
Cr	357.9	10-100	10-50	.175	.05
Cu	324.7	5-50	20-30	.4	.05
Mn	279.5	1-10	50-100	2	.1
Ni	232.0	5-50	20-50	.45	.5
Pb	283.3	10-100	25-100	.55	.25
V	318.4	20-200	75-200	1.5	1.0
Zn	213.9	1-10	0.1-5	.002	.005

[1]Based on a sample volume of 20 µL.

1. Load the autosampler sample changer with sample, standard, and matrix modifier solutions to be used for the run.
2. Program the furnace controller using the starting parameters in Table 4. Dry for 60 sec; ash for 45 sec, and start "READ" on last second of ashing step. Set ramp for dry, ash, clean, and cool to 1 sec, for atomize to 0 sec. Set gas flow to 300 mL min^{-1} for all steps except atomize (0 mL min^{-1}). Set clean for 6 sec at 2700°C, and cool for 6-10 sec at 30°C.
3. When everything is ready, initiate the analytical cycle. When run is complete, collect table of values from computer.

Table 4.--Analytical settings for the graphite-furnace atomic absorption determinations [µg/5µL, micrograms per 5 microliters]

	Modifier (µg/5µL)		Furnace settings (degrees Celsius)			
Element	PO_4	$Mg(NO_3)_2$	Dry	Ash	Atomize	Clean
Al		10	160	1700	2500	2700
As		[1]10	120	1200	2100	2650
Cd	200	10	120	900	1600	2600
Co		50	120	1400	2400	2650
Cr		50	120	1650	2500	2700
Cu			120	1000	2500	2700
Mn		50	160	1400	2200	2600
Ni		50	120	1400	2400	2650
Pb	200	10	120	600	1900	2600
V			140	1500	2700	2700
Zn		6	120	600	1800	2600

[1]Solution for As determination also contains 15 micrograms Pd from a commercially prepared solution; total matrix modifier solution volume for As determination is 10 microliters.

COMPARISON OF DETERMINATIONS

Selected best values of all concentrations are presented by Ball and Nordstrom (1989). The Appendix contains, in tabular form, the data used to make the selections found in that report and upon which the interpretations in the following sections are made. The data in the Appendix, which do not appear in Ball and Nordstrom (1989), constitute the values referred to in subsequent sections of this report as alternative values. These data were not published in the report of Ball and Nordstrom (1989) because of space considerations. For the tables of the Appendix, unless otherwise noted, ICP values were calculated using in-house microcomputer data-reduction software, with a first-order curve fit. Selected best values determined by DCP are from Ball and Nordstrom (1985). Zeeman GFAAS values were calculated using a first-order regression of standards prepared in dilute acid and analyzed along with the samples.

The ICP analyses were done by grouping the samples into four sets according to their pH and approximate dissolved-solids concentrations and executing a separate instrument calibration, optimization, and data reduction for each set. These sets constitute the analytical runs referred to in the following sections. The intent was to analyze similar samples in sets, but the groupings are somewhat arbitrary. For example, sample 82WA145 ought to have been placed in analytical set 3 rather than set 1, and samples 82WA125, 82WA127, and 82WA156 ought to have been placed in analytical set 1 rather than sets 2, 2, and 3, respectively. All of the analytical runs were abbreviated by the torch becoming unstable and extinguishing itself prematurely. Therefore, as the end of each run was approached, the torch may have been operating in an unstable manner. The concentration and percent difference values used in the

interpretations in the following sections are in tables A-1 to A-88 of the Appendix. A blank field in the tables denotes that either no determination was made or no meaningful calculation was possible.

In the following sections, the determinations of the individual elements and findings regarding comparisons of the various analytical techniques are presented. Percent difference (Δ%) is plotted as a function of element concentration. The general form of the calculation of this Δ% function is:

$$\Delta\% = \frac{(\text{Method A Concentration} - \text{Method B Concentration}) \times 100}{(\text{Method A Concentration} + \text{Method B Concentration})/2}$$

where method A is that method designated for testing purposes as the "primary" method and method B is designated as the "test" method.

The maximum value of the result of this calculation is ±200. This means that a value for Δ% of zero denotes perfect matching of analytical values, whereas a value approaching ±200 means there is no similarity between values.

Another phrase used in the discussion of results for individual elements is the reference to a "false positive" or "false negative" result. This terminology refers to samples in which values less than the detection limit were obtained by one instrument, whereas measurable values were obtained by the other instrument.

Detection Limits

The term detection limit is defined in several ways in the analytical chemistry literature. In this report, only solution concentrations, not absolute quantities, are considered because the instruments used to perform the analyses of this report all required samples to be introduced as solutions. In words, ***detection limit*** should mean the lowest concentration in solution whose presence can be detected with certainty by the analyst. The detection limit is frequently defined in mathematical terms as that concentration which produces a response in the measuring instrument equal to three times the standard deviation of a background signal of the instrument, or of the analysis of a blank solution (Irving and others, 1978). Other multiples used are two and 10 times, the latter referred to in the plasma spectrometric literature as the lowest determinable quantity (LDQ). The statistical significance of the LDQ is that in a signal of magnitude ten times the standard deviation of background, the error in the measured concentration will be less than or equal to 10 percent, relative to the true concentration, 68 percent of the time in the absence of systematic error. Instrument manufacturers tend to prefer the lower multiples, which present the instrument as more sensitive than would use of the LDQ as the detection limit. In practice, acceptable errors tend to be highly subjective and probably need to be set on an analysis-by-analysis basis.

To provide a consistent basis for discussion in this report, the operational definition of the detection limit is arbitrarily selected as that concentration in the sample matrix at which the uncertainty in the reported value is 100 percent. For example, for a determination with a detection limit of 0.1 mg L^{-1}, a reported concentration of 0.1 mg L^{-1} would mean that the range of actual concentration of that constituent is almost certainly between 0 and 0.2 mg L^{-1}. Above the detection limit the percentage of uncertainty in the measured concentration is inversely proportional to the measured concentration. This relation is valid for concentrations as large as 30 times the detection limit. Above this concentration, in the absence of systematic errors, the percentage error in the measured concentration can be fairly accurately estimated as a constant percentage of the measured concentration.

Standard Reference Water Samples

In all cases where Zeeman GFAAS is one of the techniques used, its results are deemed the most accurate, because of its inherently superior specificity, sensitivity, ability to correct for interferences using the Zeeman feature, and in many cases the option of diluting out interferences prior to analysis because of its lower detection limit. Zeeman GFAAS, however, could not be used for a guide to the accuracy of B, Ba, Be, Ca, Fe, Mg, Mo, K, Si, Na, and Sr concentrations for this sample set because no GFAAS determinations were done for these elements. Elements for which only ICP and DCP determinations available are B, Ba, Be, Ca, Mg, Mo, Si, and Sr. For these, other means of estimating accuracy of the determinations, such as results of standard reference water samples, are required. Most of the available standard reference water samples are only of marginal usefulness here because matrix and inter-element effects found in the samples that are the subject of this report cannot be duplicated in these reference materials with any degree of certainty. Also, the "true" concentrations of constituents present in solution are known with variable accuracy. Thus, with the exception of the acid mine water reference samples, the standard reference water samples are the most likely to work well in instances where they are least needed, that is, when sample matrices are already simple enough that accuracy problems are decreased.

Results for the standard reference water samples analyzed by DCP and ICP are presented in Tables 5-10. Standard reference water samples 71 and 72 were prepared by the U.S. Geological Survey's Central Laboratory to conduct interlaboratory comparisons of analytical accuracy and precision. Samples M102, T97, AMW1, and AMW2 were prepared by the U.S. Geological Survey's Standard Reference Water Sample Project in Denver, Colorado.

Table 5.--Analytical results for Standard Reference Water Sample 71
[s.d., standard deviation; DCP, direct-current plasma;
δ%={(DCP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	DCP mean±s.d.	δ%
Al	0.505±0.126	0.431±0.018	-15
Ba	0.085±0.035	0.085±0.006	0.0
Be	0.0077±0.0027	0.0064	-16
Cd	0.0041±0.0019	<0.01	---
Co	0.0076±0.0029	0.007	-7.9
Cr	0.0110±0.0051	0.011	0.0
Cu(cassette 1)	0.0196±0.0050	0.018±0.002	-8.2
Cu(cassette 2)	0.0196±0.0050	0.016	-18
Fe(cassette 1)	0.112±0.018	0.175±0.067	+56
Fe(cassette 2)	0.112±0.018	0.091	-19
K	[1]	1.14±0.07	---
Mg	[1]	2.06±0.10	---
Mn	0.0353±0.0062	0.033±0.005	-6.5
Mo	0.0062±0.0029	0.010	+61
Na	[1]	5.08±0.24	---
Ni	0.0093±0.0060	0.004	-57
Pb	0.0110±0.0075	0.012	+9.1
SiO_2	[1]	8.78±0.56	---
Sr	0.077±0.011	0.084±0.006	+9.1
Zn(cassette 1)	0.0255±0.011	0.026±0.009	+2.0
Zn(cassette 2)	0.0255±0.011	[2]0.0021	-92

[1]No interlaboratory value reported for this constituent.
[2]No DCP readings included dynamic background corrections. Therefore, abnormally low values for this sample may have been the result of Zn contamination of the standards, particularly the blank.

Table 6.--Analytical results for Standard Reference Water Sample 72
[s.d., standard deviation; DCP, direct-current plasma;
δ%={(DCP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	DCP mean±s.d.	δ%
B	0.601±0.058	---	---
Ca	61.8±3.5	---	---
K	3.76±0.46	3.70±0.40	-1.6
Mg	13.6±0.9	13.8±0.5	+1.5
Mo	[1]	0.045	---
Na	56.3±3.4	56.2±4.1	-0.18
SiO_2	8.00±0.72	8.34±0.85	+4.3
Sr	0.448±0.031	0.514±0.032	+15

[1]No interlaboratory value reported for this constituent.

Table 7.--Analytical results for Standard Reference Water Sample M102
[s.d., standard deviation; ICP, inductively coupled plasma;
δ%={(ICP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	ICP	δ%
B	0.31±0.038	0.292	-5.8
Ba	[1]	0.048	---
Ca	82.±4	81.1	-1.1
K	6.9±0.7	6.54	-5.2
Mg	58.±2	63.0	+8.6
Na	108.±5	106.	-1.9
SiO_2	6.9±0.5	7.54	+9.3
Sr	1.34±0.093	1.62	+20.9

[1]No interlaboratory value reported for this constituent.

Table 8.--Analytical results for Standard Reference Water Sample T97
[s.d., standard deviation; ICP, inductively coupled plasma;
δ%={(ICP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	ICP	δ%
Al	0.126±0.042	<0.5	---
B	0.367±0.101	0.389	+6.0
Ba	0.098±0.012	0.101	+3.1
Ca	53.9±2.1	58.3	+8.2
Cd	0.0163±0.0023	0.0171	+4.9
Co	0.0063±0.0024	0.0057	-9.5
Cr	0.0260±0.0043	0.0166	-36
Cu	0.0168±0.0025	<0.05	---
Fe	0.100±0.009	<0.10	---
K	3.65±0.33	3.93	+7.7
Mg	18.9±1.0	20.0	+5.8
Mn	0.0305±0.0032	<0.02	---
Mo	0.0357±0.0036	---	---
Na	59.4±3.1	60.2	+1.3
Ni	0.0152±0.0059	0.0095	-38
Pb	0.0150±0.0037	<0.2	---
SiO_2	7.12±0.52	7.79	+9.4
Sr	0.514±0.019	0.691	+34
V	0.0072±0.0013	<0.075	---
Zn	0.153±0.010	0.091	-41

Table 9.--Analytical results for Standard Reference Water Sample AMW1[1]
[s.d., standard deviation; ICP, inductively coupled plasma;
δ%={(ICP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	ICP	δ%
Al	32.6±1.2	<50	---
Ba	0.0095±0.0065	<0.5	---
Be	0.0169±0.0035	<0.1	---
Ca	[2]	292	---
Cd	0.210±0.024	<0.5	---
Co	0.199±0.026	<0.2	---
Cr	0.0239±0.0123	<1.0	---
Cu	9.118±0.412	<5.0	---
Fe	207.±21.1	220	+6.3
K	[2]	<30	---
Mg	[2]	98.0	---
Mn	104.±6.6	101	-2.9
Na	[2]	<20	---
Ni	0.304±0.115	<0.3	---
Pb	0.0695±0.0440	<20	---
SiO_2	47.7±2.7	<100	---
Sr	1.36±0.04	1.22	-10
Zn	59.3±5.0	60.8	+2.5

[1]This sample was diluted 1/100 for analysis; therefore, the detection limits shown in this table are 100 times those listed in Table 2.
[2]No interlaboratory value reported for this constituent.

Table 10.--Analytical results for Standard Reference Water Sample AMW2
[s.d., standard deviation; ICP, inductively coupled plasma;
δ%={(ICP Mean/Interlaboratory Mean)-1} × 100]

Constituent	Concentration, in milligrams per liter		
	Interlaboratory mean±s.d.	ICP	δ%
Al	21.0±2.0	19.9	-5.2
Ba	0.0054±0.0008	<0.005	---
Be	0.0141±0.0025	0.0134	-5.0
Ca	[1]	316	---
Cd	0.127±0.013	0.158	+24
Co	0.137±0.019	0.151	+10
Cr	0.020±0.013	0.0124	-38.0
Cu	5.15±0.14	5.09	-1.2
Fe	145.±10	151	+4.1
K	[1]	3.44	---
Mg	[1]	91.1	---
Mn	89.0±4	86.6	-2.7
Na	[1]	167	---
Ni	0.249±0.034	0.246	-1.2
Pb	0.045±0.033	<0.2	---
SiO_2	47.0±4.5	50.2	+6.8
Sr	1.57±0.07	1.50	-4.5
Zn	44.0±1.0	44.1	0.23

[1]No interlaboratory value reported for this constituent.

Determinations of Individual Elements

Aluminum

Tables A-1 to A-4 of the Appendix list the sample code number, the primary (Ball and Nordstrom, 1985) and alternative (determined on a different dilution of the sample but not published by Ball and Nordstrom, 1985; 1989) DCP Al concentrations, the ICP Al concentration, the Zeeman GFAAS Al concentration, the Δ% value, compared with the ICP Al concentration, calculated using the primary DCP Al concentration, the Δ% value calculated using the alternative DCP Al concentration, and the Δ% value calculated using the Zeeman GFAAS Al concentration, in columns 1-8, respectively. Note that ICP concentrations below the detection limit of 0.5 mg L^{-1} given in table 2 appear in tables A-1 to A-4 of the Appendix. When the original data base was generated the ICP detection limit had not as yet been determined. The low concentrations shown in tables A-1 to A-4 were an essential ingredient in determining that detection limit, and thus are presented in the appendix.

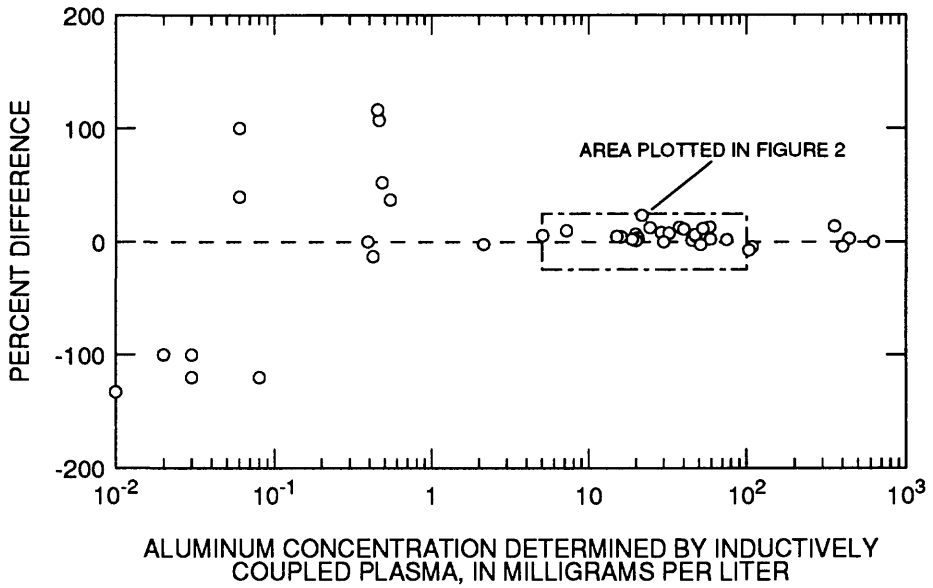

Figure 1. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for aluminum for all data.

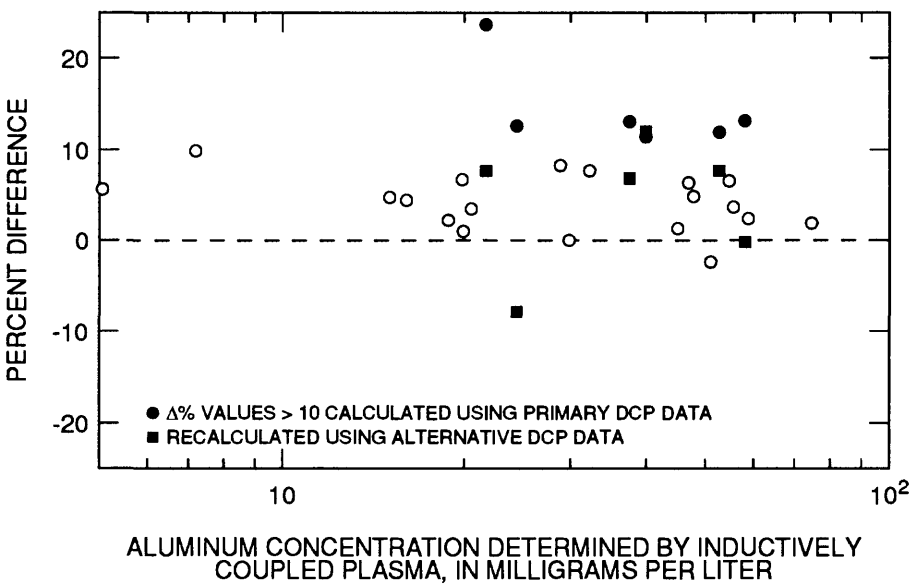

Figure 2. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for aluminum for 5 to 100 milligrams per liter.

than 15% for ICP Al greater than 0.54 mg L^{-1}. Eleven of the Δ% values are greater than 35, but all occur at DCP Al less than 0.5 mg L^{-1}. For DCP Al greater than 0.5 mg L^{-1}, there are 7 values which have Δ% greater than 10. Of these, five have alternative DCP concentrations which would decrease the Δ% values to less than 15%. This is illustrated more clearly using the expanded scale of figure 2, where the solid

and 100 mg L^{-1}. Figure 1 illustrates that the similarity between the ICP and DCP determinations is better than 15% for ICP Al greater than 0.54 mg L^{-1}. Eleven of the Δ% values are greater than 35, but all occur at DCP Al less than 0.5 mg L^{-1}. For DCP Al greater than 0.5 mg L^{-1}, there are 7 values which have Δ% greater than 10. Of these, five have alternative DCP concentrations which would decrease the Δ% values to less than 15%. This is illustrated more clearly using the expanded scale of figure 2, where the solid circles indicate use of primary, and the solid squares indicate use of alternative, DCP data. Five of the 6 values shown are improved, suggesting that either: (1) the method of selecting the primary DCP concentrations may have been faulty, or (2) a physico-chemical interference, which was eliminated by dilution, may have biased the DCP results for the more concentrated solutions. Thus, for the entire set of samples with ICP Al greater than 0.54 mg L^{-1}, there exists a DCP concentration that is within 13.5% of the ICP value.

A graph of Δ% between Zeeman GFAAS and DCP Al concentration for GFAAS Al concentrations between 0 and 0.5 mg L^{-1} is shown in figure 3. If the assumption that the Zeeman-corrected GFAAS Al concentrations are the most accurate is correct, both figures 1 and 3 suggest that both the ICP and DCP

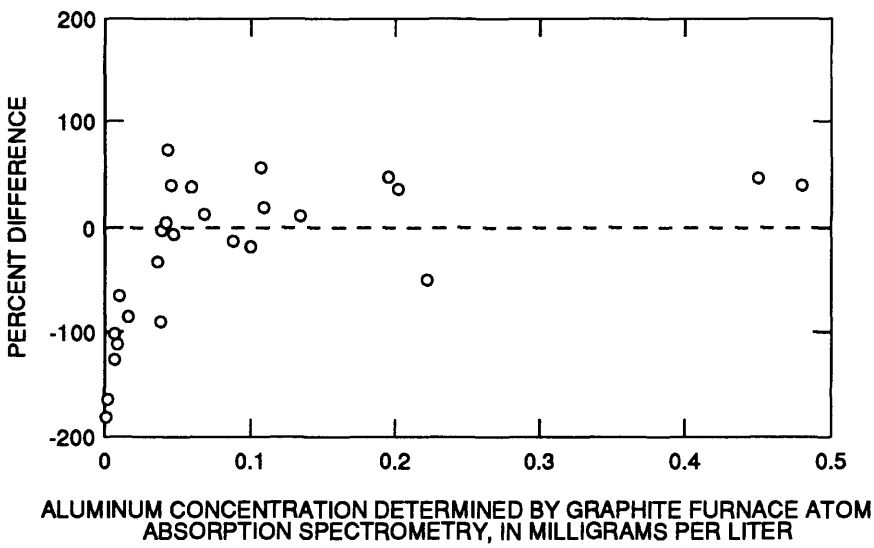

Figure 3. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for aluminum for 0 to 0.5 milligrams per liter.

detection limits for Al in these waters are near 0.5 mg L^{-1}, rather than the concentration of 0.01 mg L^{-1} estimated for the DCP determinations using standards in dilute acid. For Al greater than 0.5 mg L^{-1}, the ICP and DCP techniques appear to have similar accuracy. These assumptions are supported by the results for standard reference water samples 71 (table 5) and AMW2 (table 10). Because of the extreme Ca interference at the wavelength used for DCP analysis, all but one of the concentrations of Ball and Nordstrom (1985) were superseded in Ball and Nordstrom (1989). With the exception of two samples, 82WA155 and 82WA166, GFAAS determinations were done only for samples with DCP Al concentrations less than 2 mg L^{-1}. For this reason, GFAAS concentrations for these samples superseded the earlier (Ball and Nordstrom, 1985) DCP values, with the exception of one sample, for which the GFAAS Al

Arsenic

The As results examined in this report were obtained using two specific instruments that were operated in very specific configurations. It is entirely possible that dramatically lower detection limits could be obtained by equipping a similar plasma spectrometer with a vacuum or purged optical path and using a more sensitive As line in the vacuum-UV range of the spectrum. In the following discussion, data for As obtained by the various techniques are compared with concentrations of inorganic As obtained by the hydride generation technique as the reference method. The hydride data are the most complete and self-consistent, and the technique has a detection limit of about 0.0005 mg L^{-1}. Therefore, the hydride inorganic As data are the most conveniently used as a reference.

None of the standard reference water samples contained As. Tables A-5 to A-8 of the Appendix list the sample code number, the hydride inorganic As concentration, the DCP As concentration, the ICP As concentration, the Zeeman GFAAS As concentration, the Δ% value, compared with the primary hydride inorganic As concentration, calculated using the DCP As concentration, the Δ% value calculated using the ICP As concentration, and the Δ% value calculated using the Zeeman GFAAS As concentration, in columns 1-8, respectively. The hydride data are rounded to two significant figures.

Of the 63 samples in the set, 7 measurable As concentrations were obtained by ICP and 18 by DCP. In the case of the seven measurable concentrations using the ICP spectrometer, the four samples with As less than 25 mg L^{-1} yielded Δ% values of -64, 190, 199, and -9.3 with respect to hydride values. The three samples with As greater than 25 mg L^{-1} gave Δ% values of -2.7, 1.0, and 36.7. The 14 samples with DCP As less than 25 mg L^{-1} yielded Δ% values between 7.6 and 199. The four samples with DCP As greater than 25 mg L^{-1} gave Δ% values of -4.2, -2.6, -1.0, and 22.5. These results suggest that the ICP and DCP have equivalent capability to measure As. The ICP yielded fewer false positive concentrations and the DCP yielded fewer false negative values, as compared with the reference hydride technique. The measuring capabilities of the two plasma spectrometers as configured for this report, that is, with the nebulizers and wavelengths used here, do not appear to extend into the sub-mg L^{-1} range.

There is a spectral interference by Al on the ICP determination of As at 197.2 nm, with the severity of the interference for a given sample depending on the relative concentrations of As and Al. In the more dilute samples of this set in which As was detected by ICP, the Al/As ratios range from 50 to over 100. In these solutions, the correction was up to 32% of the As concentration, whereas in the more concentrated samples, where As is much higher relative to Al, the correction was only 3-5% of the total As.

A graph of Δ% between GFAAS and hydride inorganic As as a function of hydride inorganic As concentration for all data (fig. 4) illustrates that at concentrations greater than about 1 mg L^{-1}, there is acceptable similarity between measured GFAAS and hydride inorganic As concentrations. This is expected, as the bulk solutions comprising these samples were typically diluted by a factor of 100 or more with 3*M* HCl before analysis by either technique. There are only four negative Δ% values, two of which are for As equal to or less than 0.025 mg L^{-1}. The mean Δ% for all 63 samples is about +80. Maest and Wing (1987) presented evidence that for accurate total As determination by hydride generation the sample must be pre-reduced with KI before the sodium borohydride addition. The hydride determination procedure of Ball and Nordstrom (1985) did not include a pre-reduction step. This initially suggested that the hydride concentrations of Ball and Nordstrom (1985) may have been erroneously low. Figure 4 illustrates the distinct positive bias in the GFAAS data at low As concentrations. This suggests that a GFAAS method also presented by Maest and Wing (1987) may contain a systematic positive bias in the concentrations determined. Re-analysis of several samples in this set by both the hydride and the GFAAS

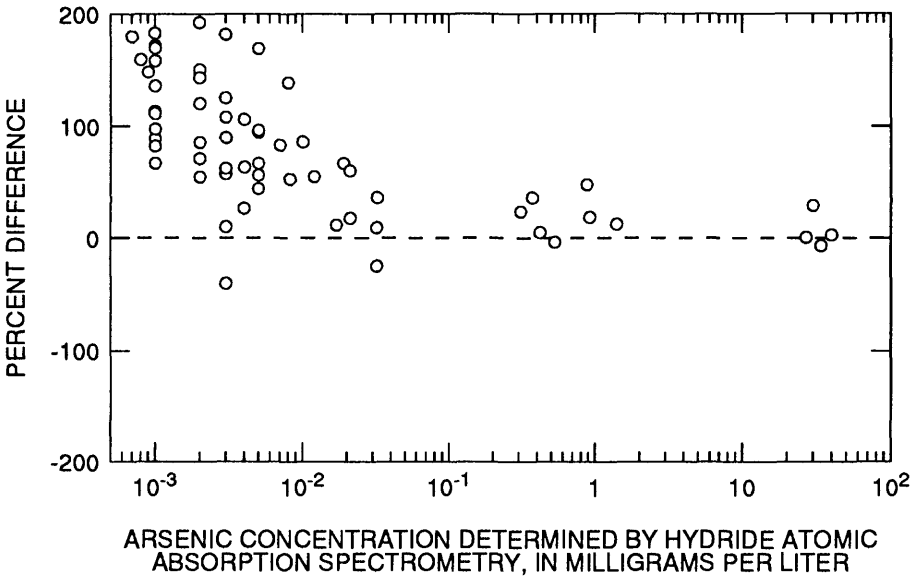

Figure 4. Relation between concentrations determined by graphite furnace atomic absorption spectrometry and hydride atomic absorption spectrometry (AAS), in percent difference, as a function of concentration determined by hydride AAS for all data.

techniques (table 11) strongly reinforces this hypothesis. For example, the second sample, which gave an initial GFAAS As concentration of 0.022 mg L^{-1}, yielded a hydride-with-pre-reduction As concentration of 0.0016 mg L^{-1}, over an order of magnitude lower. Similarly, the third sample, which gave an initial GFAAS As concentration of 0.062 mg L^{-1}, yielded a GFAAS concentration of 0.006 mg L^{-1} upon re-analysis, again over an order of magnitude lower. These and the additional examples listed in table 11 show that, for the determination of As, both the hydride and GFAAS techniques are subject to a wide range of variability.

The ICP and DCP spectrometers are only marginally useful tools for the analysis of As in the sample sets analyzed because of the low As concentrations in nearly all of these samples and the relatively poor sensitivity of these instruments for As. Samples having a solution As concentration less than 2 mg L^{-1} need to be analyzed by GFAAS or by hydride with a pre-reduction step, as recommended by Maest and Wing (1987). Because of the limited amount of plasma data, the ICP detection limit that is reported for As is a conservative estimate. ICP precision could not be determined accurately because of the low As concentrations compared to the ICP sensitivity for As. There is a significant spectral interference on the ICP As determination from Al, which is at least partly correctable. The interference ranges in this set of samples between 3% (Al/As ratios in the range of 10 to 20) and 32% (Al/As ratios in the range of 50 to 100) of the As concentration. The Al concentrations in solutions containing measurable As ranged from 10 mg L^{-1} to over 600 mg L^{-1}.

Table 11.--Analytical results for arsenic
[GFAAS, graphite-furnace atomic-absorption spectrometry]

Sample	Concentration, in milligrams per liter			
	Hydride generation method	GFAAS	Hydride generation method reruns	GFAAS reruns
82WA103	0.002	0.100	0.004, [1]0.126	
82WA125	0.001	0.022	0.0016	
82WA126	0.003	0.062		0.006
82WA141	0.004	0.013, 0.007		0.009
82WA146	0.001	0.0085, 0.0015		0.002
82WA156	0.001	0.022	0.0018	
82WA163	0.017	0.019, 0.040		0.020
82WA164	0.032	0.025, 0.069		0.067

[1]Analysis done on a separate subsample

Barium

Tables A-9 to A-12 of the Appendix list the sample code number, the SO_4 concentration, the ICP Ba concentration, the DCP Ba concentration, the Δ% value, compared with the DCP Ba concentration, calculated using the ICP Ba concentration, the barite saturation index (S.I.) calculated by WATEQ4F using ICP Ba data, and the barite S.I. calculated by WATEQ4F using DCP Ba data, in columns 1-7, respectively. The mean Δ% for the samples in table A-9 is -37.2; in table A-10, -28.0; in table A-11, +4.31; and in table A-12, +117. The overall mean of the absolute values of Δ% is 34.1. Tables A-9 to A-12 show that the average Δ% values cluster around mean values, which vary from one ICP analytical set to another. This initially suggested that the ICP values might be suspect. Torch positioning on the input slit of the ICP spectrometer using Mn may not necessarily be optimum for Ba. At this point it would be pure speculation, but if this is so, the Ba calibration would be subject to drifting, or time-instability, and the effect would be most pronounced at low levels. This is what appears to be denoted by the data. The standards, which were analyzed as unknowns every fourth solution, did not show such a trend.

The Δ% is plotted as a function of Ba concentration in figure 5, for all data. The solid symbols on figure 5 show that all Δ% values greater than +10 or less than -50 are for ICP or DCP determinations where the Ba concentration was less than 0.01 mg L^{-1} in the solution analyzed (samples 82WA165 and 82WA167 were diluted by a factor of 10 for analysis. Thus, their concentrations in the solutions analyzed were only one-tenth of the values shown on the plot). If these 7 concentrations are excluded, the remaining Δ% values are quite acceptable, considering that Ba is a trace constituent in this set of samples.

An alternative explanation for the systematic variation in Ba concentrations between techniques might be that kinetically controlled precipitation of barite has occurred after sample collection and during

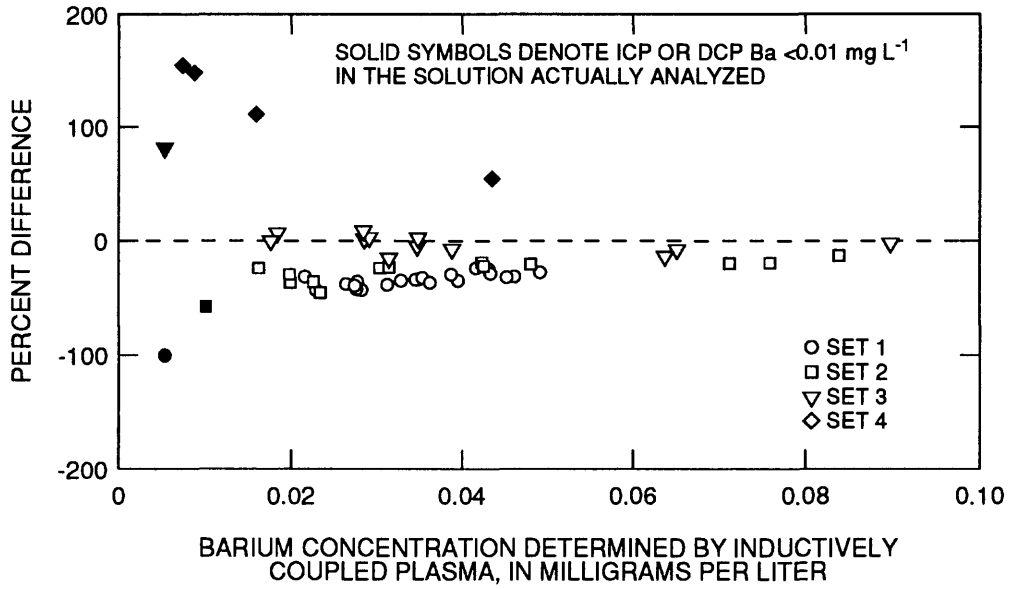

Figure 5. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for barium for all data.

membrane filter and immediately acidified to a pH of less than one. The change in solubility of barite between the *in situ* pH and a pH of one is not presently known. However, Ba should become more soluble as the pH is adjusted to this low value. In addition, the Ba concentrations show sufficient overlap between techniques and are uncertain enough that this possibility seems remote.

To further test the hypothesis that the ICP Ba concentrations may be in error, the complete set of analytical data was input to the equilibrium thermodynamic speciation modeling program WATEQ4F (Ball and others, 1987; Ball and Nordstrom, 1991) to calculate the saturation state (saturation index, S.I., or Log IAP/K) of the sample solutions with respect to the mineral barite ($BaSO_4$). Comparing barite S.I. values calculated by WATEQ4F using the DCP and ICP Ba concentrations reveals that the ICP S.I. values appear slightly closer to equilibrium, compared with the DCP S.I.'s, which are more oversaturated. Figure 6 is a plot of S.I. barite as a function of the common logarithm of the SO_4 concentration for all data. Figure 7 is a plot of S.I. barite as a function of pH for all data. The circles represent DCP Ba concentrations and the diamonds represent ICP concentrations. Barite S.I. values for the drainage of the main stem of Leviathan Creek (subset of data not shown separately) range between -0.81 undersaturated and +1.20 oversaturated using DCP Ba data, and between -0.97 and +1.01 using ICP Ba data. This difference may not be significant. However, the slight trend toward equilibrium when using ICP data in the calculations, combined with the agreement of S.I. values between the two data sets, indicates that the hypothesis that ICP Ba data are inferior to DCP data can be rejected. This conclusion is supported by the Ba concentrations obtained for standard reference water sample 71 by DCP (table 5) and standard reference water sample T97 by ICP (table 8), both of which are well within acceptable limits.

Notwithstanding the negative findings in the preceding paragraphs, which apply to samples having low levels of Ba in complex and concentrated matrices, both the ICP and DCP spectrometers are very useful tools for the analysis of Ba. For the analysis of acid mine waters, an operational detection limit is about 0.005 mg L^{-1} using either instrument.

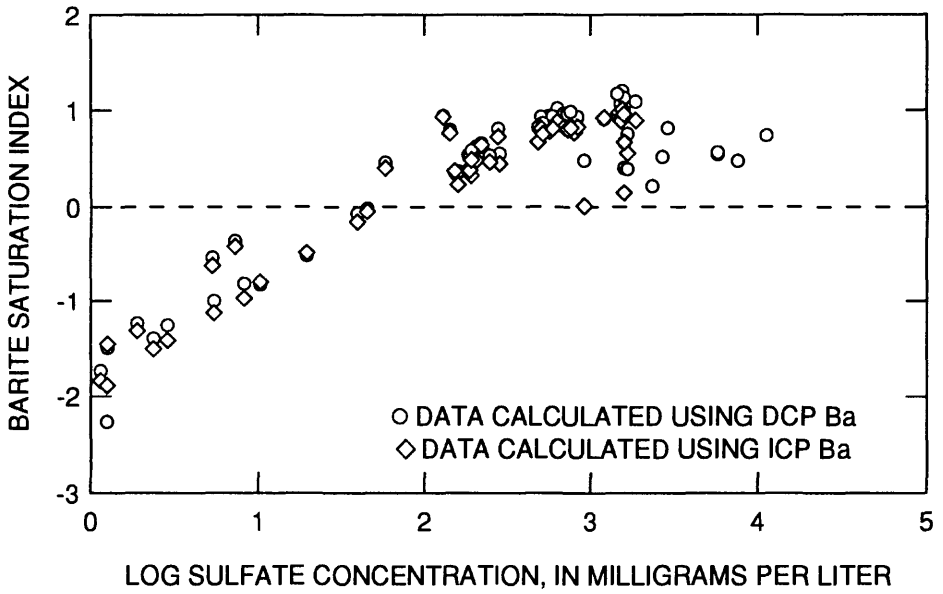

Figure 6. Relation between barite saturation index and the common logarithm of sulfate concentration for all data.

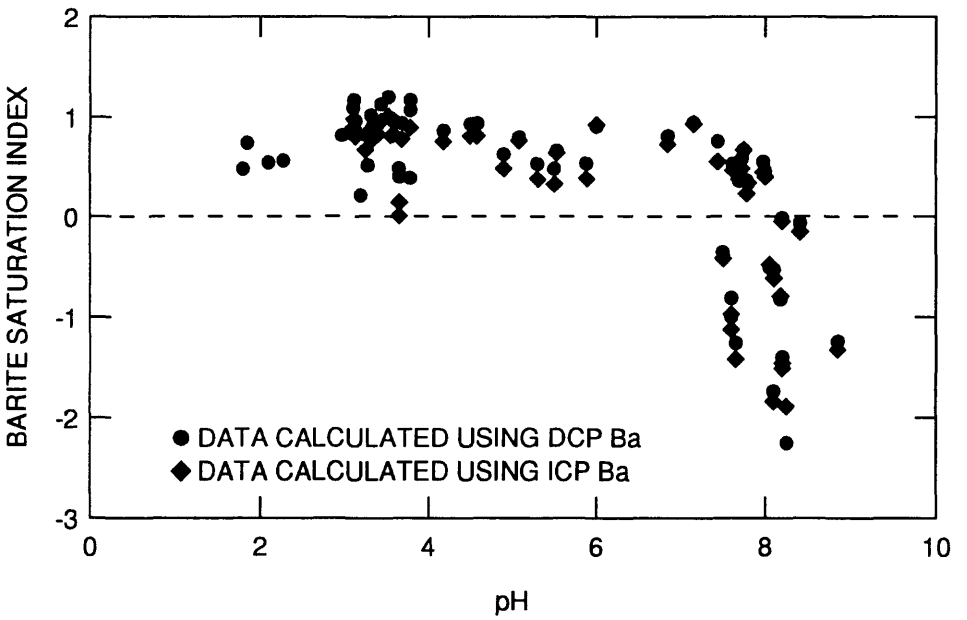

Figure 7. Relation between barite saturation index and pH for all data.

Tables A-13 to A-16 of the Appendix list the sample code number, the ICP Be concentration, the DCP Be concentration, and the Δ% value, compared with the ICP Be concentration, calculated using the DCP Be concentration, in columns 1-4, respectively. The mean of the Δ% values between the ICP and DCP is 36.6. These differences are primarily because of the extremely low levels at which Be occurs in this set of samples. The Be concentrations also appear to be negatively biased in table A-13, and positively biased in table A-16. Tables A-14 and A-15 have a total of only three values, all of which are similar. There are three instances of measurable Be by DCP and less-than-detection Be by ICP, all in table A-13, and encompassing DCP concentrations up to 0.003 mg L^{-1}.

The ICP and DCP determinations of Be are extremely accurate and precise. Relative standard deviation (RSD) data for the four ICP analytical sets show a RSD between three consecutive readings taken while analyzing a single solution of about 2% to less than 50% for blanks and samples equivalent to a blank in Be concentration. The 0.01 mg L^{-1} standard in dilute HNO_3 shows an accuracy to within 10-15% deviation from the "true" concentration, scarcely more than double the percentage deviation expected from the 0.1 mg L^{-1} top standard. Accuracy of the ICP for Be is further supported by the results of the analysis of standard reference water sample AMW2 (table 10), for which the Be estimate is well within the 95% confidence limit at a most probable concentration of 0.014 mg L^{-1}.

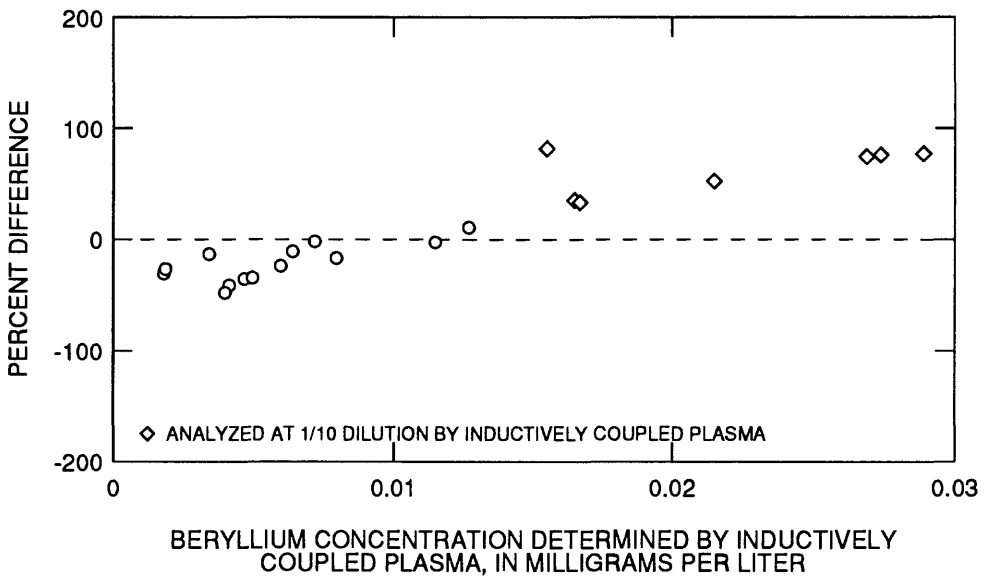

Figure 8. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for beryllium for all data.

Figure 8 is a graph of Δ% between ICP and DCP concentration estimates as a function of ICP Be concentration, for all data. The circles represent data for samples analyzed without dilution, and the diamonds represent data for samples diluted by a factor of 10 for analysis. The distribution of the diamonds indicates that the relatively high dissolved solids present in the samples of set four cause noticeable matrix problems, even when diluted by a factor of 10. If these data are ignored, the detection limit for Be by ICP appears to be less than 0.001 mg L^{-1} (fig. 8). This compares to an estimated DCP detection limit of about 0.002 mg L^{-1}.

The ICP and DCP spectrometers are both very useful tools for the analysis of Be. For the determination of Be in acid mine waters, the estimated detection limit is about 0.001 mg L^{-1}. There do not appear to be significant interferences on the ICP or DCP analysis of Be in acid mine water matrix containing high concentrations of Ca, Fe, SiO_2, Al, and Mg.

Boron

Tables A-17 to A-20 of the Appendix list the sample code number, the ferrozine Fe concentration, the ICP B concentration, the DCP B concentration, and the Δ% value, compared with the ICP B concentration, calculated using the DCP B concentration, in columns 1-5, respectively. For the ICP and DCP instruments used in this study, iron contributes a substantial interference to determination of B in these waters because of a spectral overlap (Ball and others, 1978), for which a correction technique was formulated by Ball and Nordstrom (1985, 1989). This interference from Fe is significant when using either B primary wavelength, even when using the higher dispersion echelle grating of the two present instruments, as compared with other spectrometer gratings used in ICP or DCP instruments. The interference is more pronounced at the 249.68 nm wavelength, because the strongest Fe line at 249.65 nm is closer to this B line than to the 249.77 nm line. It is because of this interference that the Fe concentration data are listed for reference. It was possible to calculate Δ% values in only 20 of the 63 samples, because of the low B concentrations in these waters. For the 20 comparisons, the mean Δ% value is 65.5. Of the remaining 43 samples in tables A-17 to A-20, there are 23 samples in which concentrations less than the detection limit were obtained by the ICP technique, whereas quantifiable values were obtained using the DCP technique. In table A-19, there are also two samples in which the ICP obtained a measurable concentration, while the DCP did not. This may be the result of an over- or undercorrection for either background or interelement spectral effects using one method or the other. Twenty-three of the 25 discordant readings occurred in the range, DCP B = 0.020 to 0.069 mg L^{-1}. The remaining two occurred at DCP B concentrations 0.164 and 0.354 mg L^{-1}. Also, there is usually very poor similarity in instances where Fe concentrations are very high. This indicates that the detection limit for B in acid mine water is considerably above that for standards in dilute acid. Results for analysis of standard reference water samples M102 (table 7) and T97 (table 8) place B estimates within ±6% of most probable values, well within 95% confidence limits.

The Δ% is plotted as a function of ICP B concentration in figure 9, for all data. The similarity of ICP to DCP determinations is generally poor at the low B levels occurring in these samples. The distribution of the diamonds indicates that the relatively high dissolved solids present in the samples of set 4 cause noticeable matrix problems, even when diluted by a factor of 10. Figure 9 also illustrates that the differences begin to scatter between 0.15 and 0.25 mg L^{-1}. This indicates that the ICP detection limit for B in these samples is about 0.15 mg L^{-1} rather than the 0.02 mg L^{-1} estimated using standards in dilute acid. This value varies as a function of the Fe concentration, from 0.02 mg L^{-1} in the absence of Fe to about 0.5 mg L^{-1} at Fe levels exceeding 2000 mg L^{-1}.

The ICP and DCP spectrometers may be excellent tools for the analysis of B, provided that the Fe/B ratio is not too high. The DCP spectrometer gave slightly better results, attributable to use of the more sensitive wavelength with that instrument. For this set of samples, the operational detection limit ranges from about 0.02 mg L^{-1} to about 0.5 mg L^{-1}, varying with the concomitant Fe concentration. In cases where matrices are particularly complex, special attention must be given to the fact that interelement interferences will have a significant effect on the accuracy and sensitivity of the determination.

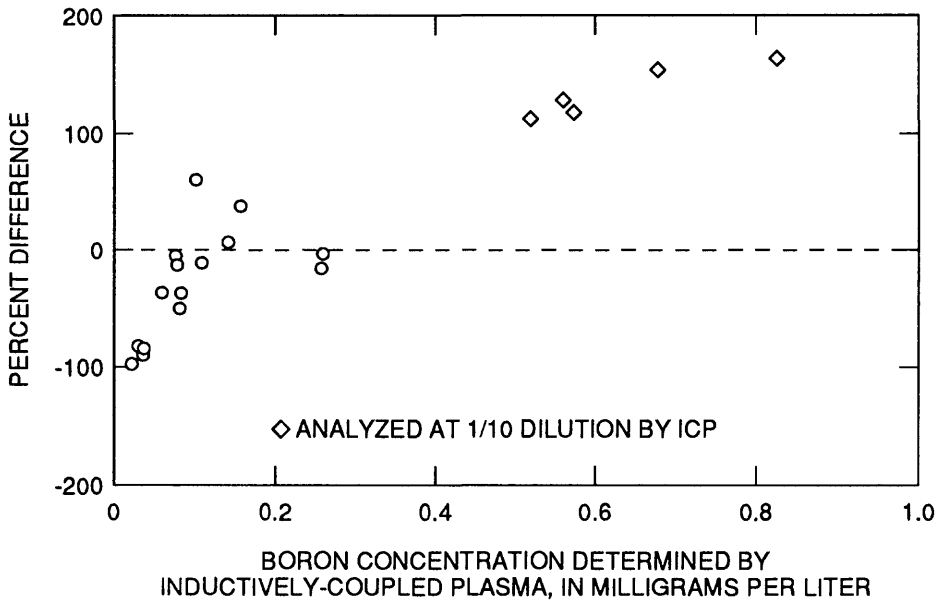

Figure 9. Relation between concentrations determined by inductively-coupled plasma (ICP) and direct current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for boron for all data

Cadmium

Tables A-21 to A-23 of the Appendix list the sample code number, the GFAAS Cd concentration, the Cd concentration determined by ICP without Fe and Al corrections, the Cd concentration determined by ICP with Al but without Fe correction, the Cd concentration determined by ICP with Al and Fe corrections, the Δ% value, compared with the Zeeman GFAAS Cd concentration, calculated using the ICP Cd concentration without Fe and Al correction, the Δ% value calculated using the ICP Cd concentration with Al but without Fe correction, and the Δ% value calculated using the ICP Cd concentration with Al and Fe corrections, in columns 1-8, respectively. Table A-24 of the Appendix lists the sample code number, the GFAAS Cd concentration, the Cd concentration determined by DCP, the Cd concentration determined by ICP without Fe and Al corrections, the Cd concentration determined by ICP with Al but without Fe correction, the Cd concentration determined by ICP with Al and Fe corrections, the Δ% value, compared with the Zeeman GFAAS concentration, calculated using the DCP concentration, the Δ% value calculated using the ICP concentration without Fe and Al correction, the Δ% value calculated using the ICP concentration with Al but without Fe correction, and the Δ% value calculated using the ICP concentration with Al and Fe corrections, in columns 1-10, respectively.

For the six samples (table A-24) for which GFAAS and DCP data can be compared, the mean Δ% for the comparisons is 20.4. Only two of the Cd concentrations are less than 0.02 mg L^{-1}. There are 37 samples (tables A-21 to A-24) for which GFAAS and fully corrected ICP data can be compared. The mean Δ% value for comparison of the GFAAS with ICP analyses is 63.1, but 33 of the Cd concentrations are less than 0.02 mg L^{-1}. The magnitudes of the Δ% values appear quite large, but were not unexpected considering the Cd levels being measured and the corrections applied. There are 14 samples in which concentrations less than the detection limit were obtained by one technique, whereas quantifiable values were obtained using the other technique. All are in the range, Cd = 1-3 ug L^{-1}. Analyses for standard reference water sample T97 (table 8) gives a Cd estimate 4.9% higher than the most probable

concentration and well within the 95% confidence limit. The estimate for standard reference water sample AMW2 (table 10) is 24% higher than the 95% confidence limit, clearly indicating difficulty in obtaining reliable Cd concentration estimates at low concentrations in complex matrices by ICP.

The GFAAS Cd concentrations are consistently significantly higher than the corresponding ICP Cd concentrations. Iron, Al, and Mg all were found by prior experiment to contribute spectral interferences to the ICP and DCP determination of Cd. The effect of Fe is the largest, followed by that of Al. The effect of Mg is virtually insignificant.

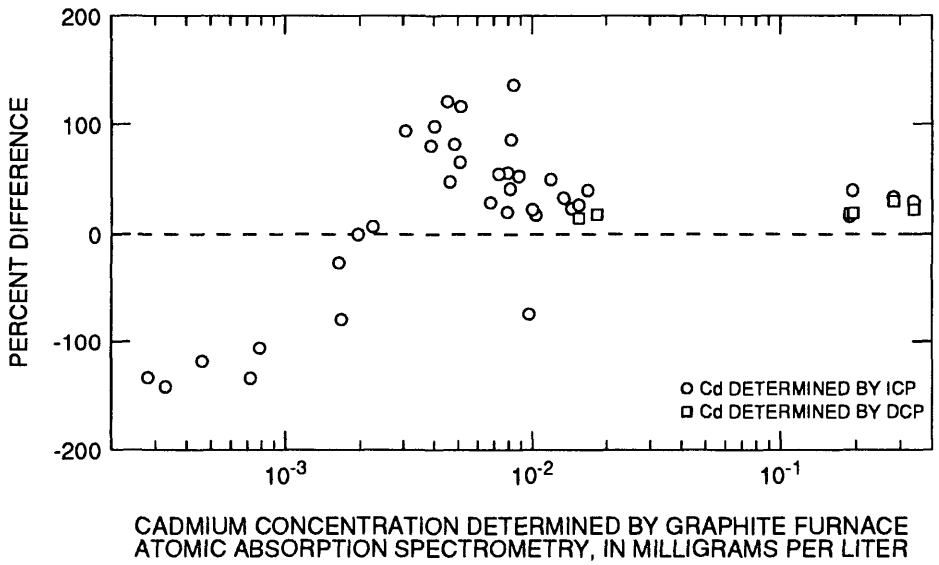

Figure 10. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, and GFAAS and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for cadmium for all data.

The Δ% from GFAAS Cd is plotted as a function of GFAAS Cd concentration in figures 10 and 11. Figure 10 shows all data for DCP and ICP Cd, with the squares denoting Δ% values calculated from DCP data. Figure 11 shows corrected (circles) and uncorrected (solid diamonds) ICP data in the range, Cd = 0 to 0.02 mg L^{-1}. Figure 11 indicates that there may be an overcorrection applied to the Cd concentrations for spectral interferences caused by Fe and Al. All but 7 concentrations (samples 82WA161-167, tables A-21 to A-24) were better without the Fe and Al corrections. Two of these samples were analyzed very near the previous detection limit, where only 1/10 dilutions were analyzed by ICP because of high solids content, where matrices are concentrated and complex. The remaining five are the final samples in analytical sets 1 and 3, when the ICP torch began to pulse and flicker, and subsequently extinguished. When Fe was less than 10 mg L^{-1} and Al was greater than 10 mg L^{-1}, comparison also was improved without the Al correction. Of the concentrations further improved without the Al correction, all had been in the Δ% range of ±10 without the Fe correction. Most of the remaining concentrations that compare poorly to GFAAS data are concentrations that are probably below the revised ICP detection limit. This implies that the interelement correction for the effect of Fe on the determination of Cd is not sufficiently accurate at the Fe and Cd concentrations normally found in acid mine water to justify decreasing the ICP detection limit below about 0.01 mg L^{-1}.

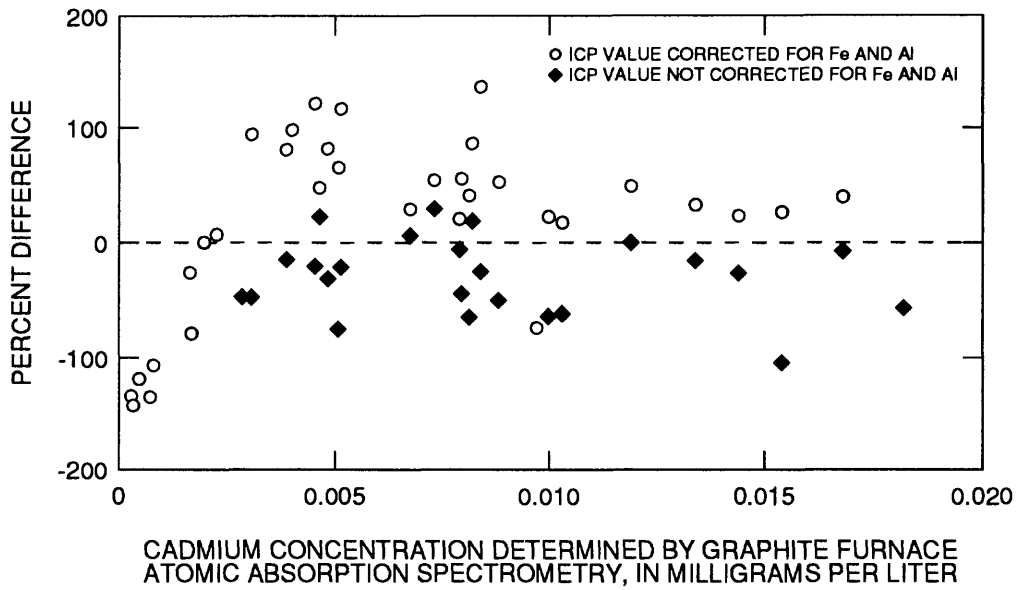

Figure 11. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for cadmium for 0 to 0.02 milligrams per liter.

Under extreme conditions with several spectral interferences per analyte in liquid-liquid solvent extraction circuit samples, a slight overcorrection for the calibration-subtraction method of spectral interference correction was observed (Johnson, 1983). In spite of these errors, however, concentration determinations were generally within two to three times the ideal detection limit or ±3% of the total background (expressed in units of apparent analyte concentration) present underneath the analyte wavelength during nebulization of the test solution (Johnson, 1983). Even though the spectral interference correction method was fairly sophisticated, indications were that more work needed to be done on the problem to perfect the method (Johnson, 1983).

The ICP spectrometer is a useful tool for the analysis of Cd. An operational detection limit for the determination of Cd in acid mine water of 0.005 to 0.01 mg L^{-1}, is more appropriate than the 0.001 mg L^{-1} concentration estimated using standards in dilute acid. The correction of Cd concentrations for the effects of Fe and Al needs to be evaluated and perhaps redetermined. If an improvement can be achieved in this area, the detection limit may be decreased to 0.005 mg L^{-1} or less. This problem does not exist if solution concentrations of Fe and Al are less than 10 mg L^{-1}.

Samples having Cd concentrations <0.02 mg L^{-1} are best analyzed by GFAAS. Above 0.02 mg L^{-1}, the ICP is expected to provide reliable results. Insufficient DCP analysis data points were available to assess the relative utility of this instrument at higher Cd concentrations.

Calcium

Tables A-25 to A-28 of the Appendix list the sample code number, the DCP Ca concentration, the ICP Ca concentration, the average of the DCP and ICP Ca concentrations, and the Δ% value,

compared with the ICP Ca concentration, calculated using the DCP Ca concentration, in columns 1-5, respectively. The graph of ICP-DCP Δ% as a function of ICP Ca concentration (fig. 12) illustrates that the concentrations determined by ICP and DCP are similar over a broad range of concentration. Thus, the accuracy of the determination does not appear to be a function of solution concentration over the 5 - 500 mg L^{-1} concentration range considered. In addition, this similarity indicates that, in the case of Ca, the ICP spectrometer could be standardized at a relatively low concentration, then used to qualitatively determine concentrations far in excess of this level with reasonable accuracy. ICP and DCP data for Ca in the Leviathan Mine samples were so similar in all but one case that they could be averaged. The one outlier (sample 82WA129), for which the ICP-DCP Δ% of 25.9 exceeded the ±15% level established as an indicator of good matching between methods, is doubtless a case where analysis of duplicates is indicated. The WATEQ4F speciated charge balance for this sample using the DCP concentration of 49.3 mg L^{-1} was -12.0%, whereas using the ICP concentration of 64.0 mg L^{-1} it was -2.1%. On a graph of Ca/SO_4 as a function of SO_4 (fig. 13), the 49.3 mg L^{-1} concentration is an obvious outlier, whereas 64.0 mg L^{-1} is not. Therefore, the DCP concentration was rejected, and the ICP concentration was substituted. Analyses for standard reference water samples M102 (table 7) and T97 (table 8) yield Ca estimates between -1.1% and +8.0% of the reported mean values, respectively, reinforcing the advisability of performing multiple determinations and averaging the results.

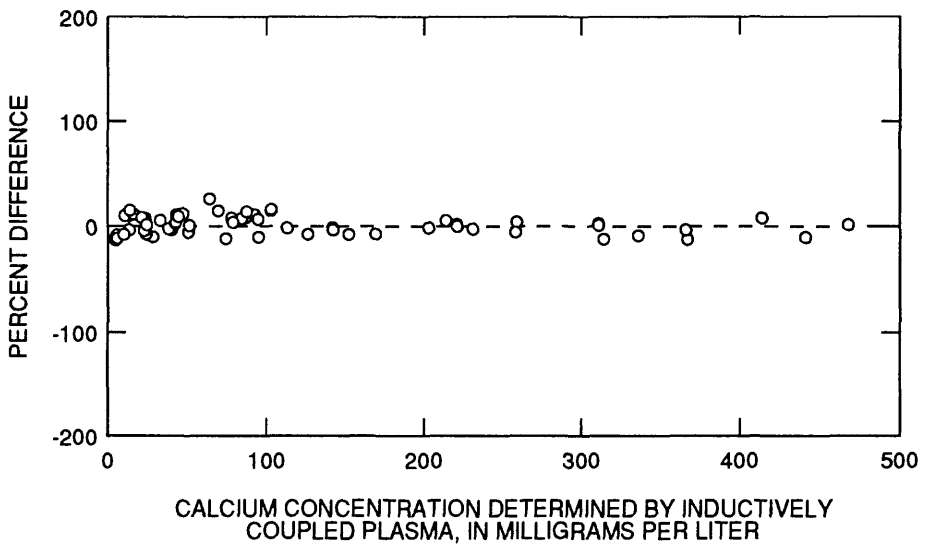

Figure 12. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for calcium for all data.

The ICP and DCP spectrometers are excellent tools for the analysis of Ca in a broad range of matrix and Ca concentrations. It was found by experiment that the ICP or DCP spectrometer could be standardized at a relatively low Ca concentration, for example 5 mg L^{-1}, then used to accurately determine Ca in solution at concentrations up to at least 500 mg L^{-1}. The authors are not recommending this as a standard analytical practice, simply stating that it happened to work in these two instances. Good analytical practice dictates that concentrations determined outside the range of standards need to be verified using conventional techniques.

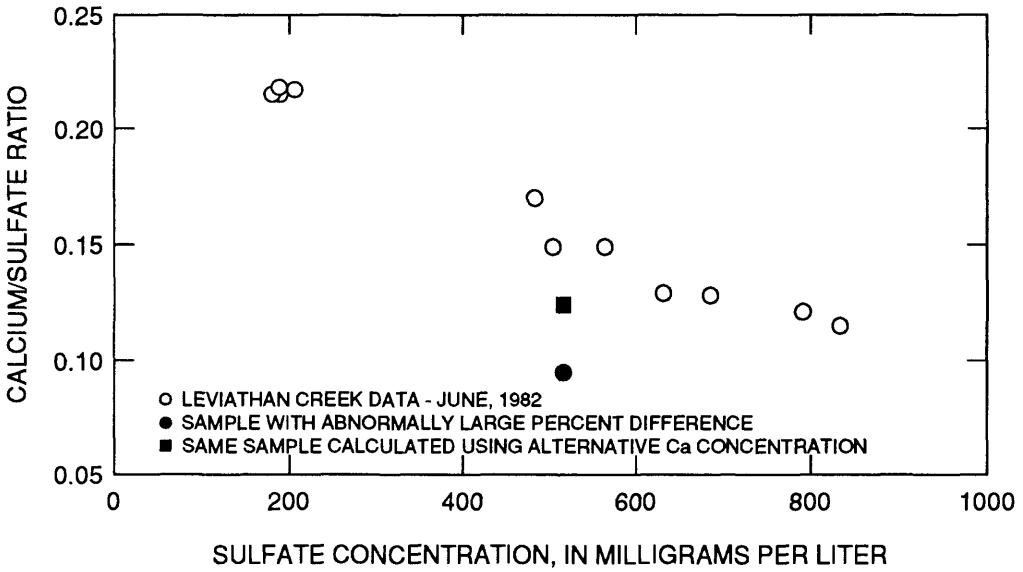

Figure 13. Relation between calcium/sulfate ratio and sulfate concentration for Leviathan Creek data for June 1982.

Chromium

Tables A-29 to A-32 of the Appendix list the sample code number, the GFAAS Cr concentration, the Cr concentration determined by ICP without corrections for interelement spectral effects, the Cr concentration determined by ICP with corrections for interelement spectral effects, the Cr concentration determined by DCP without corrections for interelement spectral effects, the Cr concentration determined by DCP with corrections for interelement spectral effects, the Δ% value, compared with the Zeeman GFAAS Cr concentration, calculated using the ICP Cr concentration without corrections for interelement spectral effects, the Δ% value calculated using the ICP Cr concentration with corrections for interelement spectral effects, the Δ% value calculated using the DCP Cr concentration without corrections for interelement spectral effects, and the Δ% value calculated using the DCP Cr concentration with corrections for interelement spectral effects, in columns 1-10, respectively. For corrected data, the absolute value of the mean Δ% from GFAAS for the analyses by DCP is 107; if the suggested revised detection limit of 0.03 mg L^{-1} is used, the mean becomes 22.7. For the analyses by ICP, the value is 71.9%; if the suggested revised detection limit of 0.01 mg L^{-1} is used, the mean becomes 43.0%. For uncorrected data, the absolute value of the mean Δ% for the analyses by DCP is 111; if the suggested revised detection limit of 0.03 mg L^{-1} is used, the mean becomes 47.3. For the analyses by ICP, the value is 65.3%; if the suggested revised detection limit of 0.01 mg L^{-1} is used, the mean becomes 57.8%. These large Δ% values occur because many GFAAS concentrations are much lower than the corresponding ICP and DCP concentrations. The GFAAS detection limit is 0.0001 mg L^{-1}, compared with the ICP or DCP detection limits of 0.01 and 0.03 mg L^{-1}, respectively, causing many of the lowest ICP and DCP concentrations to represent false positive values. This problem is evident in the standard reference water sample results (tables 5, 8, and 10), where Cr estimates at low levels in varying matrices show considerable scatter about mean values at low concentrations.

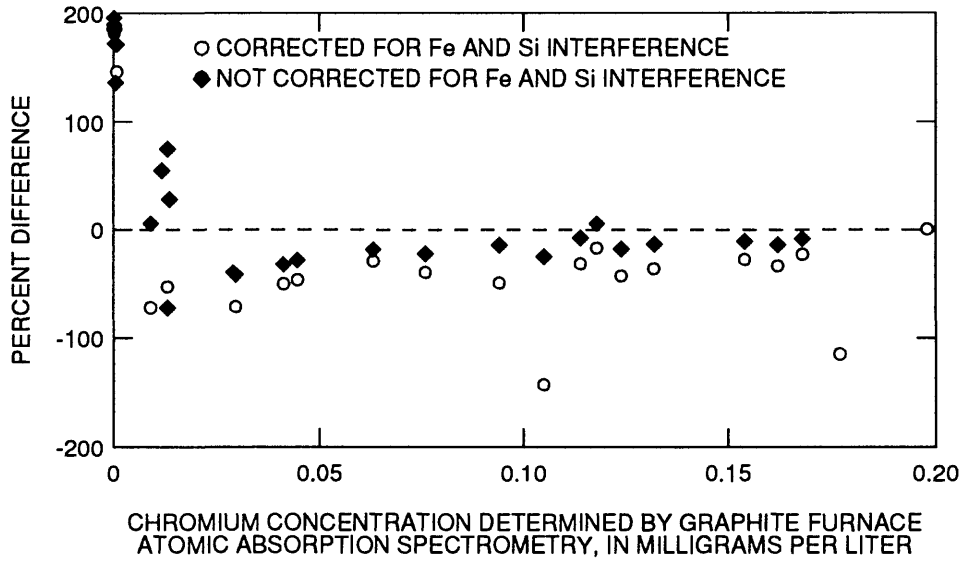

Figure 14. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for chromium for 0 to 0.2 milligrams per liter.

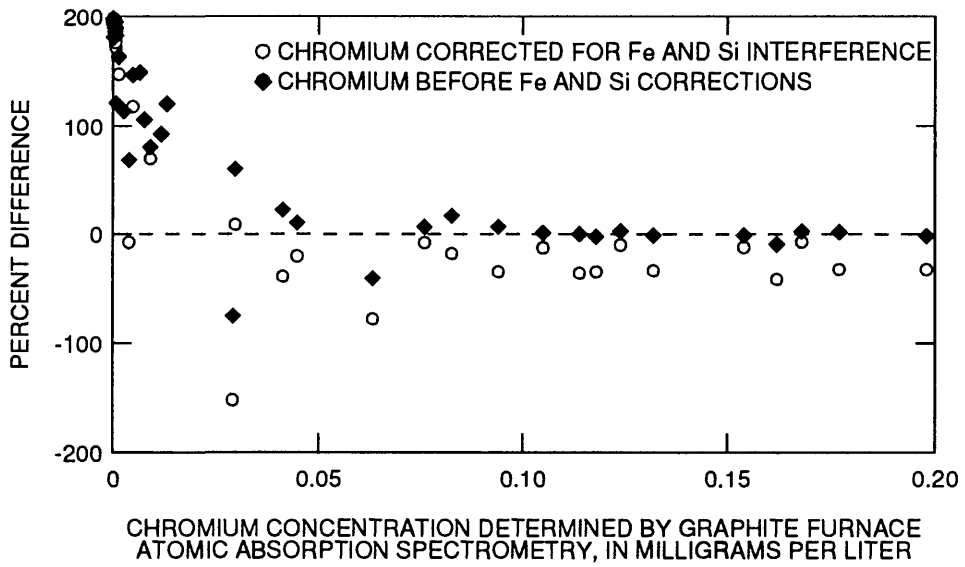

Figure 15. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for chromium for 0 to 0.2 milligrams per liter.

Figure 14 is a graph of Δ% between ICP and GFAAS as a function of GFAAS concentration, for corrected and uncorrected ICP data in the range, GFAAS Cr = 0 to 0.2 mg L^{-1}. The Δ% between GFAAS and DCP analyses is plotted as a function of GFAAS Cr concentration in figure 15, for corrected and uncorrected DCP data in the range, GFAAS Cr = 0 to 0.2 mg L^{-1}. Figures 14 and 15 show that the ICP and DCP determinations for Cr appear to be similar in their relation to the GFAAS data. These figures depict data that are quite scattered at the low end of the range shown, indicating that there is a considerable decrease in accuracy below 0.05 mg L^{-1} Cr using both techniques. The figures also indicate that the interelement corrections for Cr need revision, because the uncorrected plasma values seem to scatter less and to match the GFAAS concentrations better than the corrected concentrations. The ICP detection limit is about 0.01 mg L^{-1} (fig. 14). The one outlier at about 0.18 mg L^{-1} and -115% is a sample analyzed at a 1/10 dilution, where the Cr concentration in the solution analyzed was less than 0.02 mg L^{-1}. The ICP Cr concentrations are consistently 15-30% lower than GFAAS concentrations (fig. 14). The DCP detection limit is about 0.03 mg L^{-1} (fig. 15).

The ICP and DCP spectrometers are useful tools for the analysis of Cr. The ICP appears to be somewhat more sensitive than the DCP, at the respective wavelengths selected for ICP and DCP analysis. For this set of samples, an operational ICP detection limit is about 0.01 mg L^{-1}. Cr concentrations between 0.01 and 0.05 mg L^{-1} need to be determined by GFAAS, as do concentrations below 0.01 mg L^{-1}. There do not appear to be significant interferences on the ICP or DCP analysis of Cr in acid mine water matrix containing high concentrations of Ca, Fe, SiO_2, Al, and Mg. However, the possibility that complex and diverse matrices can have an adverse effect on this determination must not be ignored. Based on the preceding, the interelement corrections presently in place for this ICP instrument for the effect of Fe and Si on Cr, and the interelement corrections presently in place for this DCP instrument for the effect of Ca and Fe on Cr, need to be reevaluated and either redetermined or disregarded.

Cobalt

Tables A-33 to A-36 of the Appendix list the sample code number, the primary ICP Co concentration, the alternative ICP Co concentration, the primary DCP Co concentration, the alternative DCP Co concentration, the Zeeman GFAAS Co concentration, the Δ% value, compared with the primary ICP Co concentration, calculated using the primary DCP Co concentration, the Δ% value, compared with the alternative ICP Co concentration, calculated using the primary DCP Co concentration, the Δ% value, compared with the primary ICP Co concentration, calculated using the Zeeman GFAAS Co concentration, and the Δ% value, compared with the alternative ICP Co concentration, calculated using the Zeeman GFAAS Co concentration, in columns 1-10, respectively. Alternative concentration values, when present in the tables, are better matching values that were not selected manually (ICP) or by the computer (DCP) as "best values." The absolute value of the mean Δ% for the analyses was 11.2 by DCP and 14.9 by GFAAS, respectively. These differences appear to be because of several high percentage differences at lower Co concentration measurements between ICP and DCP. For example, the DCP concentrations are significantly higher for samples 82WA108, 143, 145, 150, 155, and 159, and significantly lower for samples 82WA111, 121, 126, and 153 in tables A-33 to A-36. In fact, there are 13 samples in which concentrations less than the detection limit were obtained by one technique, whereas measurable concentrations were obtained using another technique. In the case of the GFAAS concentrations, the difference is because GFAAS data exist only for samples containing less than 0.1 mg L^{-1} Co. For the remaining samples, the Co concentrations compare remarkably well. This indicates that both the DCP and the ICP are valuable tools for the analysis of Co, and that the 0.005 mg L^{-1} detection limit determined using standards in dilute acid might be too low for DCP analysis, and too high for the ICP. The most likely reason for this is a difference in sensitivity between the two analytical lines chosen for the two different instruments (table 2). In addition, there are a limited number of alternative ICP Co

concentrations that were rejected during the selection process (tables A-33 to A-36). Many of these match GFAAS data, presently believed to be the most accurate and precise values available for these samples, significantly better than their selected counterparts, suggesting that the computerized selection algorithm can make frequent errors, and therefore needs to be checked thoroughly and regularly.

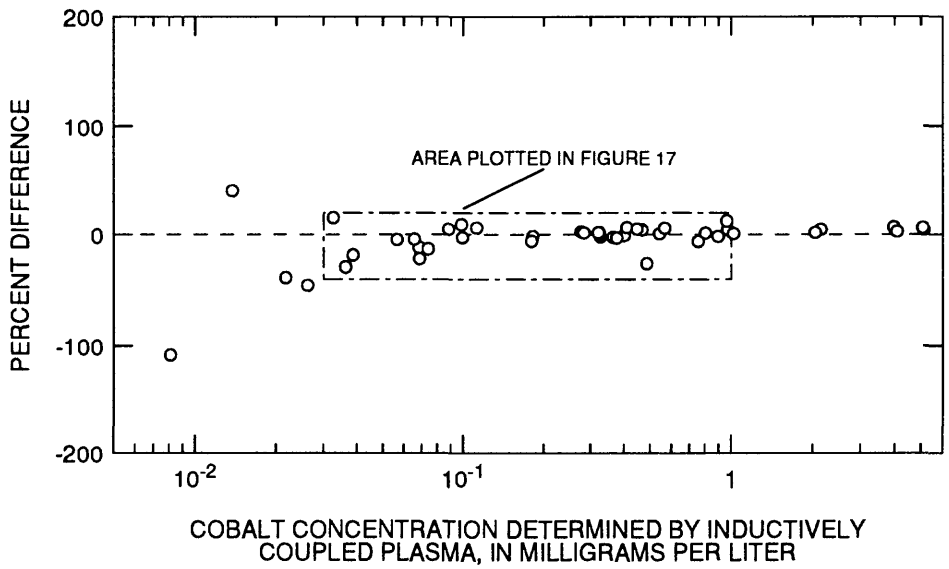

Figure 16. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for cobalt for all data.

The Δ% between ICP and DCP analyses is plotted as a function of Co concentration in figure 16 for all data. the same data for the range, Co = 0.03 to 1.0 mg L^{-1} are shown in figure 17. A comparison of ICP and GFAAS analyses for all data are shown in figure 18. The excellent matching of ICP and DCP concentrations above about 0.05 mg L^{-1} is apparent in figure 16. The two outliers, at 0.485 mg L^{-1} and -25.9%, and 0.963 mg L^{-1} and +12.6%, might be questionable. The DCP concentrations selected were from analysis of 1/10 dilutions (dilution data not shown), whereas concentrations obtained from analysis of the undiluted sample were 0.496 and 0.919 mg L^{-1}, respectively. The revised Δ% values would be -2.2 and +4.7, respectively. Detection limits by ICP and DCP can be estimated from figures 16 and 18. Figure 16 indicates a DCP limit of about 0.03 mg L^{-1} and figure 18 indicates an ICP limit of less than 0.01 mg L^{-1}. These detection limit estimates are not contradicted by evidence from standard reference water sample analyses, where a single DCP estimate is -7.9% different from the interlaboratory mean value (table 5), whereas two ICP estimates are -9.5 and 10% different from interlaboratory mean values (tables 8 and 10).

ICP Co concentrations are consistently lower than GFAAS concentrations (fig. 18). This relation, though statistically significant, may be misleading for two reasons. First, there are relatively few data points (14 out of a total sample set size of 63). Secondly, four samples have alternative ICP

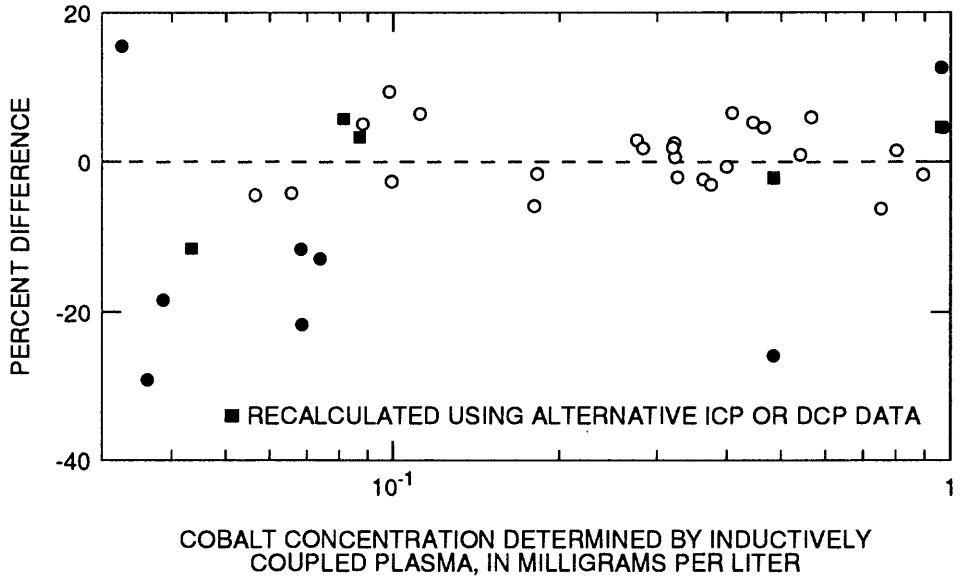

Figure 17. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for cobalt for 0.03 to 1.0 milligrams per liter.

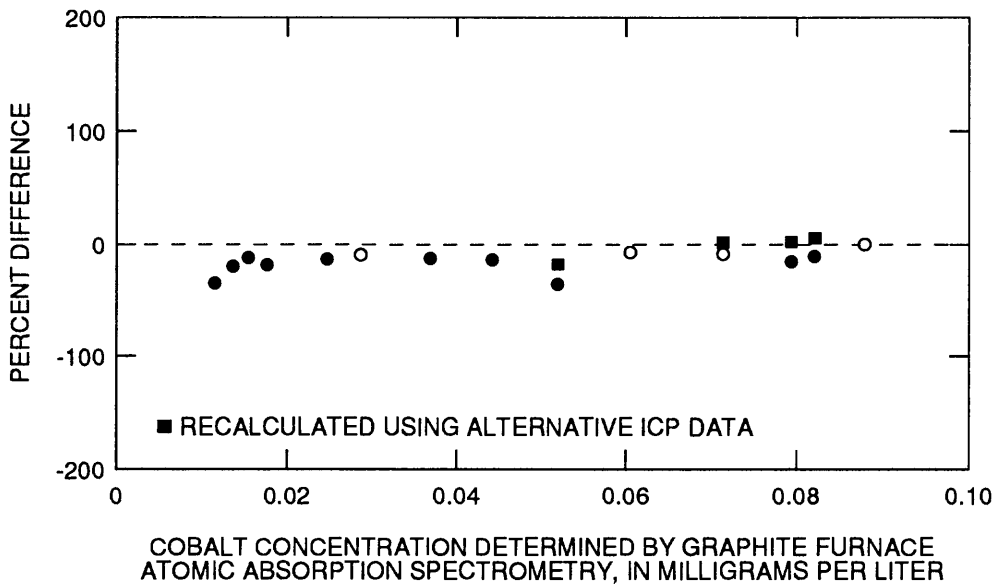

Figure 18. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for cobalt for 0 to 0.1 milligrams per liter.

concentrations that are higher than their GFAAS counterparts. Substituting these four values would make the relation between ICP and GFAAS Co concentrations more convincing because replacement of those ICP concentrations would move those four points more in line with all the others (fig. 18).

The ICP and DCP spectrometers are very useful tools for the analysis of Co. The DCP was less sensitive, probably because of the different wavelengths selected for ICP and DCP analysis. The operational ICP detection limit for the determination of Co in acid mine waters is about 0.002 mg L^{-1}. It may be possible to decrease this detection limit to an even lower concentration, provided that the torch unit can be made to operate optimally. There do not appear to be any significant interferences on the ICP analysis of Co in acid mine water matrix containing high concentrations of Ca, Fe, SiO_2, Al, and Mg.

Copper

Tables A-37 to A-40 of the Appendix list the sample code number, the ICP Cu concentration, the DCP cassette 1 Cu concentration, the DCP cassette 2 Cu concentration, the Zeeman GFAAS Cu concentration, the Δ% value, compared with the ICP Cu concentration, calculated using the DCP cassette 1 Cu concentration, the Δ% value calculated using the DCP cassette 2 Cu concentration, and the Δ% value calculated using the Zeeman GFAAS Cu concentration, in columns 1-8, respectively. The absolute value of the mean Δ% for the analyses by DCP Cassette 1 is 28.1; for the analyses by DCP Cassette 2, 32.4; and for the analyses by GFAAS, the concentration is 40.0. In the case of the DCP analyses the large differences for both cassettes are caused by a negative bias in the ICP concentrations as compared with the DCP concentrations. The DCP concentrations for the two cassettes are so similar that for publication in Ball and Nordstrom (1985) the two concentrations were averaged. In the case of the GFAAS concentrations, the large difference is caused by 12 very high Δ% values for the samples lowest in Cu and the samples with some of the most concentrated matrices. For the remaining samples, the ICP and GFAAS Cu concentrations compare very well, which indicates that either the Cu concentrations of most of the samples have changed significantly by a somewhat constant percentage since they were analyzed by DCP, or there is a positive bias in the DCP Cu determination.

The Δ% is plotted as a function of Cu concentration in figure 19 for all data for DCP Cassette 1. The comparison of ICP to GFAAS concentrations (fig. 20), shows a more normal distribution, reflecting the improved comparison of ICP to GFAAS data. Both figures exhibit a similar pattern of diverging Δ% values with decreasing Cu concentration, suggesting that the detection limit for Cu by ICP is nearer 0.05 mg L^{-1} than the 0.01 mg L^{-1} concentration determined using standards in dilute acid. A less sensitive Cu line was used in construction of the ICP simultaneous multielement slit plate, because geometry problems prevented use of the most sensitive wavelength. Thus, Cu estimates for standard reference water samples by DCP (table 5) are within 18% of the most probable value at Cu=0.0196 mg L^{-1}, and by ICP are only 1.2% different from the most probable value of 5.15 mg L^{-1} in standard reference water sample AMW2 (table 10).

As an explanation for the relatively poor similarity of ICP and DCP Cu concentrations, the analytical wavelengths chosen for the respective techniques have significantly different sensitivities and different potential for interferences. Ca, Mg, and Al all contribute positive interferences to the determination of Cu by ICP. The accuracy of the corrections applied to the raw Cu concentrations then determines the accuracy of the final values. Mg contributes an insignificant positive interference on the determination of Cu by DCP. The DCP is known to be more acutely subject to enhancements and suppressions because of solution concomitants than the ICP (Johnson, 1983; Johnson and others, 1979a, 1979b, 1980). If other, unaccounted, interferences are present in the DCP determination, they would cause the systematic bias apparent in the data of this experiment. This possibility is frequently strongly implied

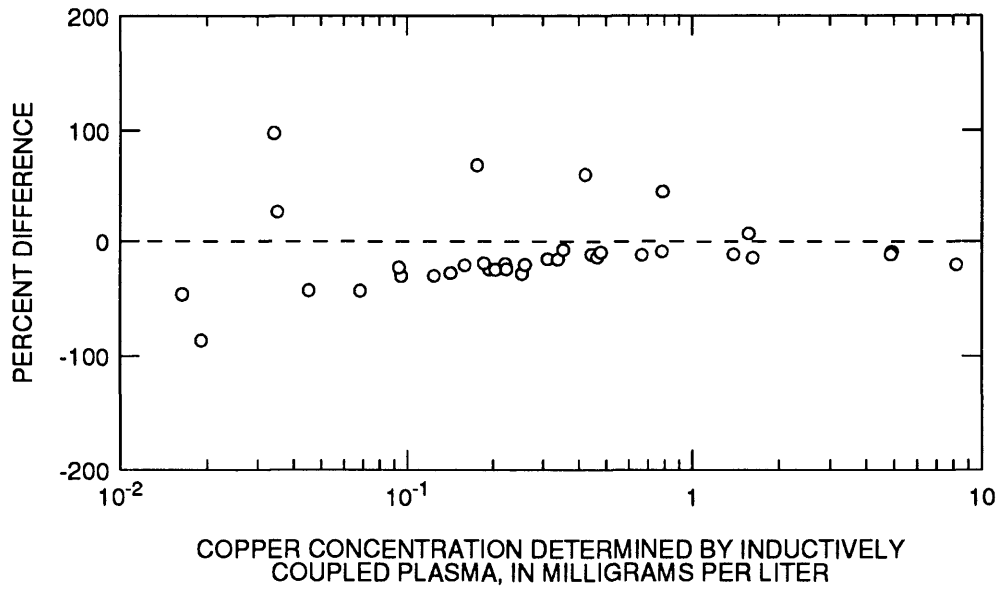

Figure 19. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for copper for all data.

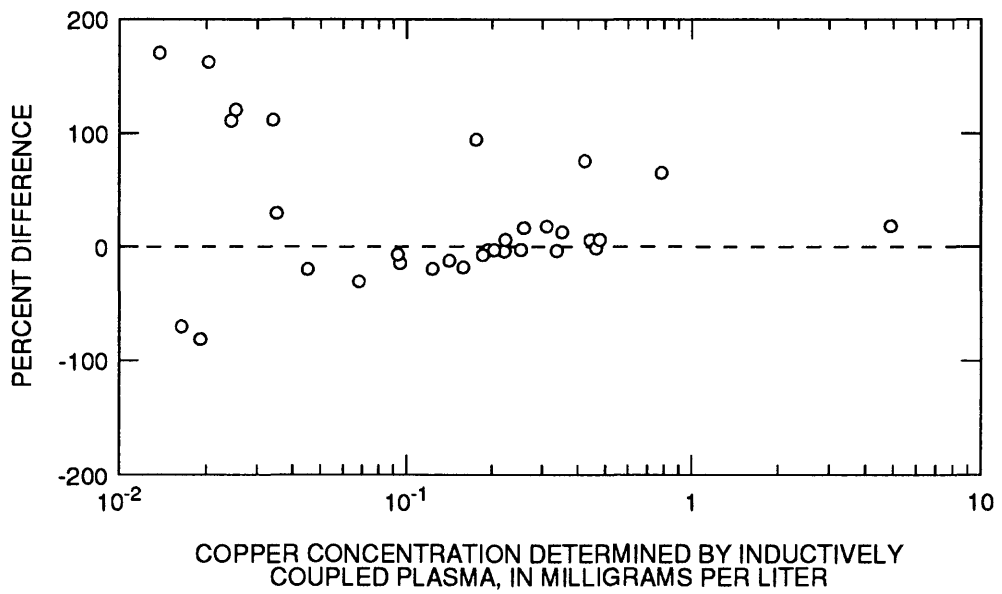

Figure 20. Relation between concentrations determined by inductively coupled plasma (ICP) and graphite furnace atomic absorption spectrometry, in percent difference, as a function of concentration determined by ICP for copper for all data.

in the data for more dilute analyses by DCP. On the basis of the analysis of a more concentrated aliquot, many samples should have yielded a similar Cu concentration in a more dilute analysis; however, values significantly less than those in the more concentrated analysis, or even less than detection, were frequently obtained. In addition, these values were frequently quite similar to concentrations obtained by ICP and/or GFAAS analysis. This is convincing evidence that an unaccounted interference by DCP analysis of the more concentrated solutions is being diluted out in the less concentrated analyses. A few examples from the data of table A-37 are shown in table 12.

Table 12.--Selected samples for which the use of alternative data improves the determination of copper
[DCP, direct-current plasma; ICP, inductively coupled plasma; GFAAS, graphite-furnace atomic-absorption spectrometry]

Sample Number	Copper concentration, in milligrams per liter			
	Mean DCP	Alternative[1] DCP	ICP	GFAAS
82WA107	0.0706	0.057	0.0453	0.055
82WA112	0.276	0.230	0.221	0.230
82WA113	0.326	0.315, <0.300	0.253	0.260
82WA115	0.355	0.304, <0.300	0.311	0.260
82WA116	0.401	0.323, <0.300	0.338	0.350
82WA120	0.515	0.470, <0.300	0.444	0.420
82WA122	0.184	0.126, 0.173	0.142	0.160
82WA124	0.529	0.501, 0.520	0.465	0.470
82WA131	0.542	0.466, <0.300	0.479	0.450
82WA152	0.249	0.168	0.194	0.200
82WA160	0.269	0.192	0.204	0.210
82WA161	0.331	0.243	0.259	0.220
82WA163	0.238	0.202	0.186	0.200
82WA164	0.287	0.210	0.223	0.210

[1]Alternative concentrations are those rejected by the computerized "best values" selection program in favor of the primary, or selected, value.

The DCP spectrometer, configured with the more sensitive analytical wavelength, was found to be much more useful for the analysis of these samples. The ICP spectrometer also would be useful for the analysis of Cu, if the problem with calibration instability could be alleviated. The recommended solution to this problem, however, is to configure the simultaneous ICP instrument with the more sensitive 324.75 nm wavelength. For this set of samples, the operational detection limit is about 0.05 mg L^{-1}. Significant lowering of this limit would be expected using the more sensitive Cu wavelength.

Iron

Tables A-41 to A-44 of the Appendix list the sample code number, the ferrozine Fe concentration from Ball and Nordstrom (1985), the ICP Fe concentration, the DCP cassette 1 Fe concentration, the DCP cassette 2 Fe concentration, the Δ% value, compared with the ferrozine Fe concentration, calculated using the ICP Fe concentration, the Δ% value calculated using the DCP cassette 1 Fe concentration, and the Δ%

value calculated using the DCP cassette 2 Fe concentration, in columns 1-8, respectively. Samples with ferrozine Fe concentrations less that 0.1 mg L^{-1} are included in the tables to establish an operational detection limit for the ICP determination. The following discussion refers only to those samples for which the ferrozine Fe concentration is greater that 0.1 mg L^{-1} and is based on the assumption that the ferrozine iron determinations are the most accurate. Zeeman-corrected GFAAS also can be used for the analysis of Fe. However, the samples were not analyzed using GFAAS because the ferrozine data set was believed to be of more than acceptable accuracy for the present purposes. There are 15 instances in which the ICP concentration is closest to the ferrozine value, 19 in which one or the other (Cassette 1 or Cassette 2) of the DCP concentrations is closest to the ferrozine value, and three in which Δ% values are equal for ICP and DCP. This comparison would suggest that the two plasma techniques are about equivalent in terms of accuracy. However, the mean Δ% is 4.8 for the ICP determinations, 10.3 for DCP cassette 1, and 8.5 for DCP cassette 2, which indicates that the ICP technique is about twice as accurate as the DCP technique for this determination.

Lack of DCP accuracy also is apparent in the standard reference water sample results (table 5), where Fe estimates at a most probable value of 0.112 are +56% and -19% of the most probable value for cassettes 1 and 2, respectively. For standard reference water samples AMW1 (table 9) and AMW2 (table 10), ICP Fe estimates appear to be of acceptable accuracy at the elevated concentrations in these samples. For the ICP determinations, there are only three instances in which the Δ% is greater than ±10. Of these, two of them are in the last four determinations done in analytical set 1, a point at which the torch was beginning to pulse and flicker, and eventually extinguished. The last four determinations in this set differ from the ferrozine data by about -9% or more. The third determination with a Δ% greater than ±10 is that for the most concentrated matrix and the highest Fe concentration of all the samples. It and the four samples discussed above were the only solutions in which an Fe concentration of greater than 200 mg L^{-1} was presented to the plasma. It is not presently known whether the deviation is because of degradation in linearity of the calibration at 40 times the concentration of the highest standard or a chemical or matrix interference. Results of analyses above an instrument's calibration range were not considered when assessing performance of the two instruments.

The Δ% is plotted as a function of ferrozine Fe concentration in figure 21, for all data. The similarity of ICP to ferrozine determinations is extremely good at all but the lowest Fe levels. The poor similarity at concentrations below 0.1 mg L^{-1} is because the ICP detection limit is about 100 times the ferrozine detection limit of about 0.0005 to 0.001 mg L^{-1}. The Δ% values (fig. 21) begin to scatter between about 0.05 and about 1.3 mg L^{-1}. This scatter indicates that the ICP detection limit for Fe in acid mine water is in this range rather than the 0.015 mg L^{-1} determined using standards in dilute acid. It is difficult to refine this estimate further because there were no samples in this set with ferrozine Fe concentrations between 0.0426 and 1.29 mg L^{-1}. A conclusion of concurrence between ICP, DCP, and ferrozine methods can be readily justified from the data, provided that only ferrozine Fe concentrations greater than 0.1 mg L^{-1} are used.

The ICP and DCP spectrometers are excellent tools for the analysis of Fe. An operational detection limit for the ICP spectrometer is 0.1 mg L^{-1} for this set of samples. The spectrometer could be calibrated at a concentration considerably below that expected in the samples, such as 5 mg L^{-1} in this case, then used for determinations in the range 0.1 to 200 mg L^{-1} with no significant loss of accuracy. This is a 3½ order-of-magnitude concentration range and a very broad range of matrix concentrations. The authors are not recommending this as a standard analytical practice, simply stating that it happened to work in the case of Fe for these two instruments. Good analytical practice dictates that concentrations determined outside the range of standards need to be verified using conventional techniques. In cases where matrices are particularly complex, special attention must be given to the possibility that matrix

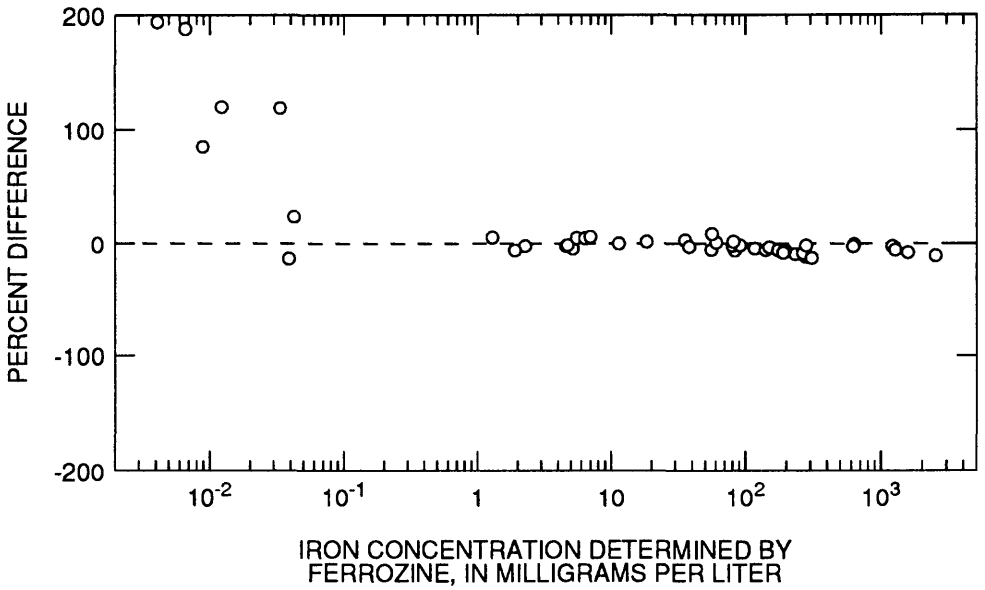

Figure 21. Relation between concentrations determined by inductively coupled plasma and ferrozine, in percent difference, as a function of concentration determined by ferrozine for iron for all data.

and/or inter-element interferences may be present.

Lead

For the purpose of this discussion, the Zeeman-corrected GFAAS Pb concentration estimates are assumed to be the most accurate, but only because the detection limit for the determination of Pb by GFAAS is about three orders of magnitude lower than that using either of the plasma techniques. While this is thought to be a reasonable assumption, the reader is reminded that this by itself does not assure that the Pb concentrations obtained using GFAAS are accurate estimates of the true Pb concentrations in these samples. Pb loss during the charring step of GFAAS analysis is prevented by adding a mixed matrix modifier to the sample in the graphite tube at analysis time. While this procedural modification is quite effective, it is not foolproof, and the mixed matrix modifier is unstable. Thus, results of acceptable accuracy and precision are by no means guaranteed. Tables A-45 to A-48 of the Appendix list the sample code number, the ICP Pb concentration, the DCP Pb concentration, the Zeeman GFAAS Pb concentration, the Δ% value, compared with the ICP Pb concentration, calculated using the DCP Pb concentration, and the Δ% value calculated using the Zeeman GFAAS Pb concentration, in columns 1-6, respectively. A blank field in the Δ% column indicates that no calculation was possible. There are 40 samples in which values less than the detection limit were obtained by the GFAAS technique. In 32 of these samples, measurable values were obtained using one or both plasma techniques. However, the Δ% values obtained for all the comparisons were not only very few, but were also very large. The best Δ% obtained was 45%, comparing ICP to DCP for sample 82WA169. The corresponding ICP to GFAAS Δ% value for that sample is 151.6%. The remaining data are even more scattered, making interpretation of the results for this element virtually impossible. For standard reference water sample 71 (table 5), the DCP concentration of 0.012 mg L^{-1} is only 9.1% different from the interlaboratory mean value of 0.0110 mg L^{-1}.

The ICP and DCP spectrometers are not useful tools for the analysis of Pb in the sample set analyzed because of the very low Pb concentrations in these samples. The ICP appears to be significantly better than the DCP, probably because of the respective wavelengths selected for ICP and DCP analysis. For this set of samples, an operational ICP detection limit is about 0.2-0.5 mg L^{-1}. Al contributes a substantial interference to the Pb determination, which is at least partially correctable. The interference ranges in this set of samples between 0 (no measurable Pb or less than 10 mg L^{-1} Al) and 98% (very high Al, very low but positive Pb) of the Pb concentration, for Al concentrations from fractional mg L^{-1} to upwards of 600 mg L^{-1}. Accuracy of Zeeman GFAAS results for Pb has not been verified. However, the Zeeman GFAAS results presently are judged to have accuracy and precision far superior to either ICP or DCP estimates at the Pb concentrations in this study.

Magnesium

The sample code number, the ICP Mg concentration and WATEQ4F charge balance, DCP concentration and WATEQ4F charge balance for undiluted, 1/10, 1/100, and 1/1000 dilutions, concentrations selected for inclusion in Ball and Nordstrom (1985), concentrations selected for WATEQ4F computations, charge balance calculated by WATEQ4F, and Δ% between the ICP and the DCP concentration selected for WATEQ4F computations are listed in table A-49 of the Appendix. Tables A-50 to A-52 of the Appendix list the sample code number, the ICP Mg concentration, the DCP Mg concentration for the undiluted sample, the DCP Mg concentration for the 1/10-diluted sample, the DCP Mg concentration for the 1/100-diluted sample, the DCP Mg concentration for the 1/1000-diluted sample, the Mg concentration published in Ball and Nordstrom (1985), the Mg concentration used for WATEQ4F computations, and the Δ% value, compared with the ICP Mg concentration, calculated using the DCP Mg concentration selected for WATEQ4F computations. Figures 22-24 show Δ% plotted against the ICP Mg concentration selected for WATEQ4F computations. Figure 22 shows all data. Figure 23 shows data for ICP analytical set 1, and figure 24 shows data for ICP analytical sets 2, 3, and 4. Data in set 1 (fig. 23) clearly are more different from zero than data in sets 2 through 4.

One sample (82WA119, table A-52) for which a difference of 23.4% was calculated using the Ball and Nordstrom (1985) Mg value becomes -4.3% when recalculated using the DCP Mg concentration of 99.1 mg L^{-1} selected for use in WATEQ4F computations. There were an additional 10 samples where a DCP Mg concentration not initially selected by the computerized best-values selection program was substituted later when running WATEQ4F computations. Eight of these 11 alternative selections compare to the ICP data better than the original computer-selected Mg values.

The data in tables A-49 to A-52 and the graphs (figs. 22-24) indicate that the DCP and ICP spectrometers are reliable tools for the analysis of Mg. The slight tendency toward modality of the data between analytical sets indicates that for maximum accuracy and precision of the results, duplicate analyses need to be done. Standard reference water sample results (tables 6, 7, and 8) also suggest that accuracy and precision can be maximized by performing several determinations, preferably at different dilutions of the sample. The comparability of the ICP and DCP concentrations over a broad range of concentration indicates that accuracy of the determination is not a function of solution concentration over the concentration range considered here (ICP range = 1.29 - 112 mg L^{-1}). This adherence to a linear calibration also indicates that the spectrometer could be standardized at a relatively low Mg concentration, for example 20 mg L^{-1}, and then used to determine Mg present in the analyte solution at concentrations up to at least 120 mg L^{-1}. Once again, the authors are not recommending this as a routine analytical practice, simply stating that it worked in this case. Under the calibration conditions used here, the data suggest that the ICP detection limit is about 0.5 mg L^{-1}. If necessary, this limit could very likely be improved considerably, as the sensitivity of both plasma instruments for this element is very good.

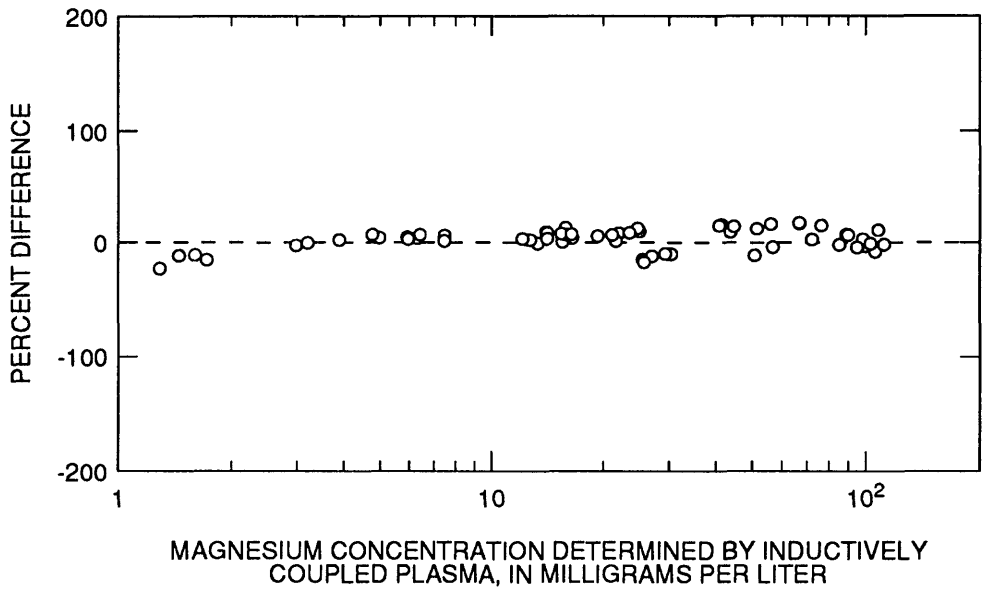

Figure 22. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for magnesium for all data.

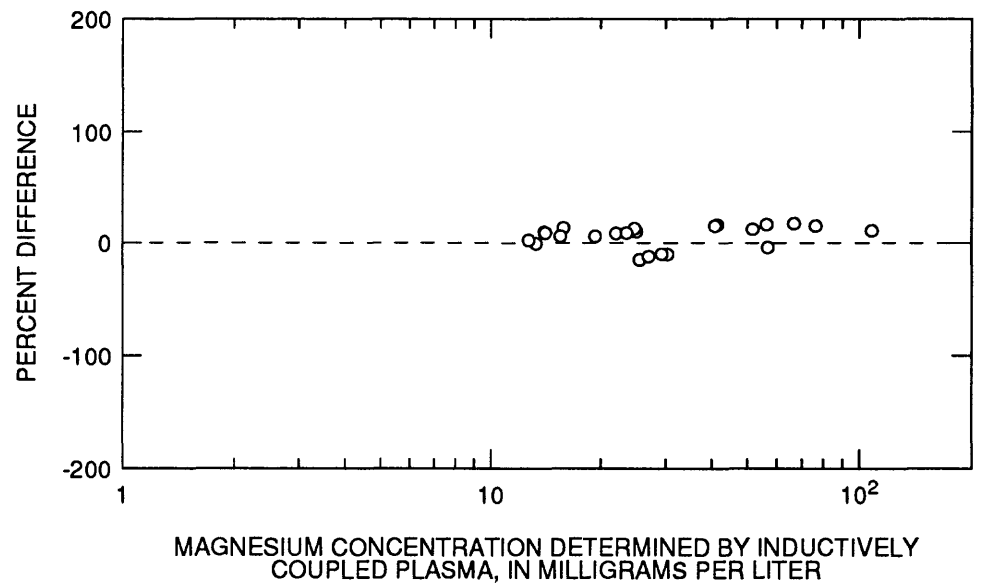

Figure 23. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for magnesium for data in analytical set 1.

The mean of the ICP concentration and the DCP concentration selected for publication in Ball and Nordstrom (1985) was taken as the best estimate of solution Mg concentration, except for samples 82WA118, 119, 132, 165, 167, 168, and 169, for which the 1/100 dilution DCP concentration and the ICP concentration were averaged. These values are presented in table 13.

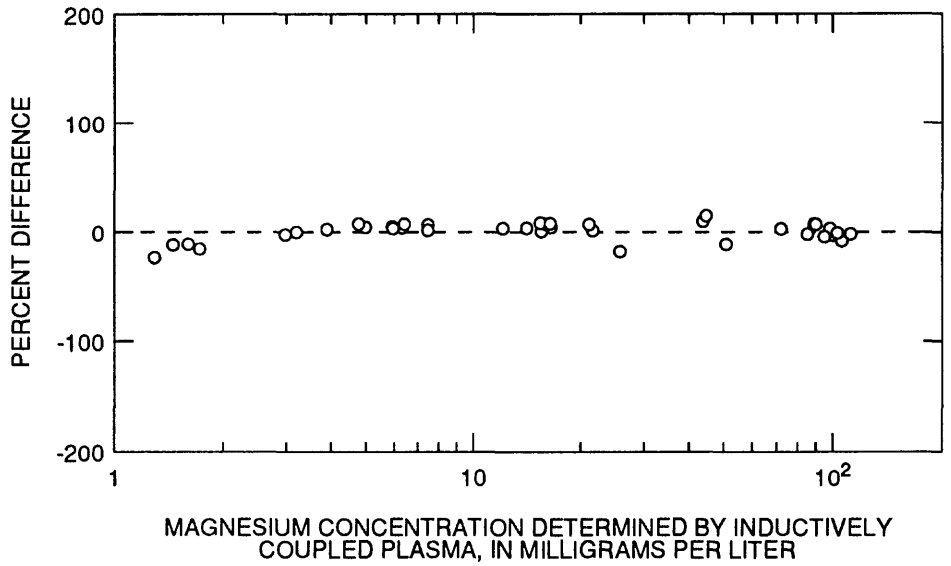

Figure 24. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for magnesium for data in analytical sets 2, 3, and 4.

Table 13.--Best estimates of magnesium concentrations, in milligrams per liter
[All concentrations are the average of the inductively coupled plasma value and the direct-current plasma value selected for publication in Ball and Nordstrom (1985), except as noted]

Sample Number	Concentration	Sample Number	Concentration	Sample Number	Concentration	Sample Number	Concentration
82WA104	13.4	82WA149	38.3	82WA114	7.24	82WA153	5.86
82WA106	12.6	82WA151	37.9	82WA117	3.21	82WA154	4.88
82WA107	13.4	82WA152	61.5	82WA121	25.1	82WA156	96.9
82WA109	13.5	82WA155	22.5	82WA123	6.18	82WA158	104
82WA110	23.6	82WA157	102	82WA125	106	82WA159	11.9
82WA112	23.8	82WA160	61.3	82WA126	13.9	82WA162	71.1
82WA113	24.2	82WA161	70.9	82WA127	95.7	82WA166	7.41
82WA115	25.2	82WA163	51.8	82WA128	108	82WA170	4.61
82WA116	28.5	82WA164	48.5	82WA141	3.85	82WA118	[1]53.8
82WA120	14.9	82WA100	1.54	82WA142	3.02	82WA119	[1]97.0
82WA122	21.1	82WA101	1.46	82WA143	15.5	82WA132	[1]86.1
82WA124	53.1	82WA102	1.70	82WA144	16.2	82WA165	[1]43.2
82WA129	18.8	82WA103	1.87	82WA146	14.8	82WA167	[1]88.0
82WA130	23.2	82WA105	15.5	82WA147	6.19	82WA168	[1]89.4
82WA131	27.0	82WA108	5.78	82WA148	15.8	82WA169	[1]42.2
82WA145	15.1	82WA111	21.5	82WA150	20.4		

[1]Concentration is average of inductively coupled plasma and 1/100 direct-current plasma.

Manganese

Tables A-53 to A-56 of the Appendix list the sample code number, ICP Mn concentration, the primary (Ball and Nordstrom, 1985) DCP Mn concentration, the alternative DCP Mn concentration, the Zeeman GFAAS Mn concentration, the Δ% value, compared with the ICP Mn concentration, calculated using the primary DCP Mn concentration, the Δ% value calculated using the alternative DCP Mn concentration, and the Δ% value calculated using the Zeeman GFAAS Mn concentration, in columns 1-8, respectively. A blank field indicates that no calculation was possible. The mean Δ% values are 6.0% for the primary Ball and Nordstrom (1985) DCP data, 8.6% for the alternative (more dilute analyses) DCP data, and 30.8% for the GFAAS data. There are only three samples for which data exist for both ICP and GFAAS. One has a Δ% of 66.7%; the other two are more than acceptable, compared to GFAAS data.

The Δ% is plotted as a function of ICP Mn concentration in figure 25, for all data. Concentrations determined by ICP and DCP are similar at all levels. It is apparent that the differences begin to scatter between 0.02 and 0.8 mg L^{-1} (fig. 25). There are insufficient data in this figure to determine accurately what an operational detection limit in acid mine effluent might be. In table A-54, there are six samples in which concentrations less than the detection limit were obtained by the ICP technique, whereas measurable concentrations were obtained using the DCP or the GFAAS technique. These discordant values, in the range 0.012 to 0.035 mg L^{-1}, raise the estimated ICP detection limit to about 0.02 mg L^{-1}. The literature detection limit (table 2) is 0.0014 mg L^{-1}.

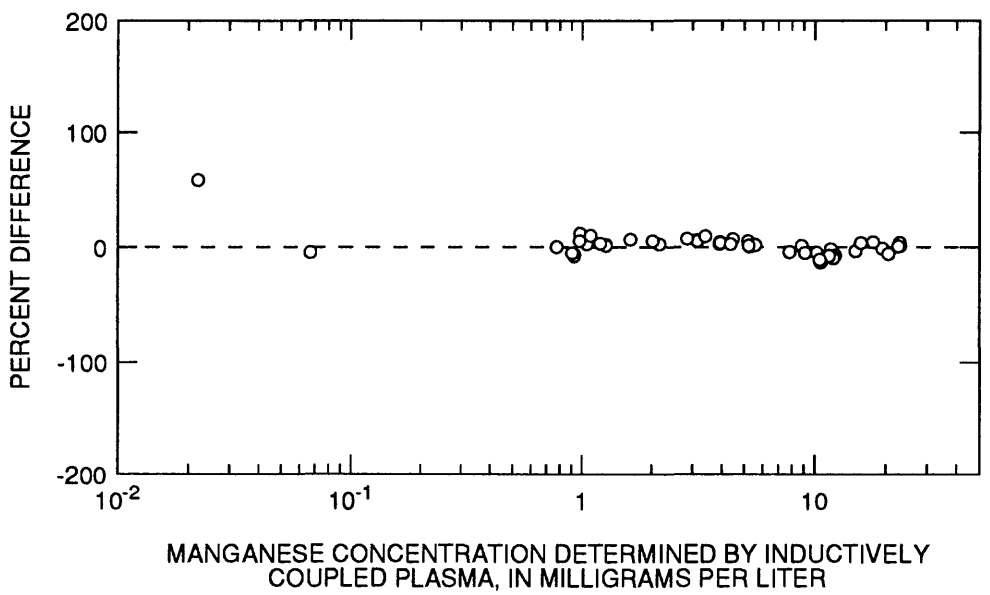

Figure 25. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for manganese for all data.

The range ±5% in the data in figure 25 encompasses results that are virtually indistinguishable from each other. Therefore, a conclusion of concurrence between ICP and DCP methods can be readily justified from the data, provided that only Mn concentrations greater than 0.02 mg L^{-1} are used.

The DCP and ICP spectrometers are excellent tools for the analysis of Mn, using an operational detection limit of 0.02 mg L^{-1} for this set of samples. Standard reference water sample results (tables 5, 9, and 10) indicate that Mn can be determined by ICP or DCP with accuracy well within acceptable limits in a broad range of sample matrices. In cases where matrices are particularly complex, special attention needs to be given to the possibility that matrix and/or interelement interferences may be present.

Molybdenum

Tables A-57 to A-60 of the Appendix list the sample code number, the ICP Mo concentration, the DCP Mo concentration, and the Δ% value, compared with the ICP Mo concentration, calculated using the DCP Mo concentration, in columns 1-4, respectively. A blank field in the Δ% column indicates that no calculation was possible. The absolute value of the mean Δ% for the analyses by DCP is 119.5%. Detection limits are poor for the 202.03 nm line, and there is a serious background interference due to Al recombination-continuum. The apparent levels of Mo in these waters are too low for determination by conventional ICP (Fries, T. L., written commun., April, 1991). The determination of Mo using GFAAS is extremely difficult, and was not attempted for this study.

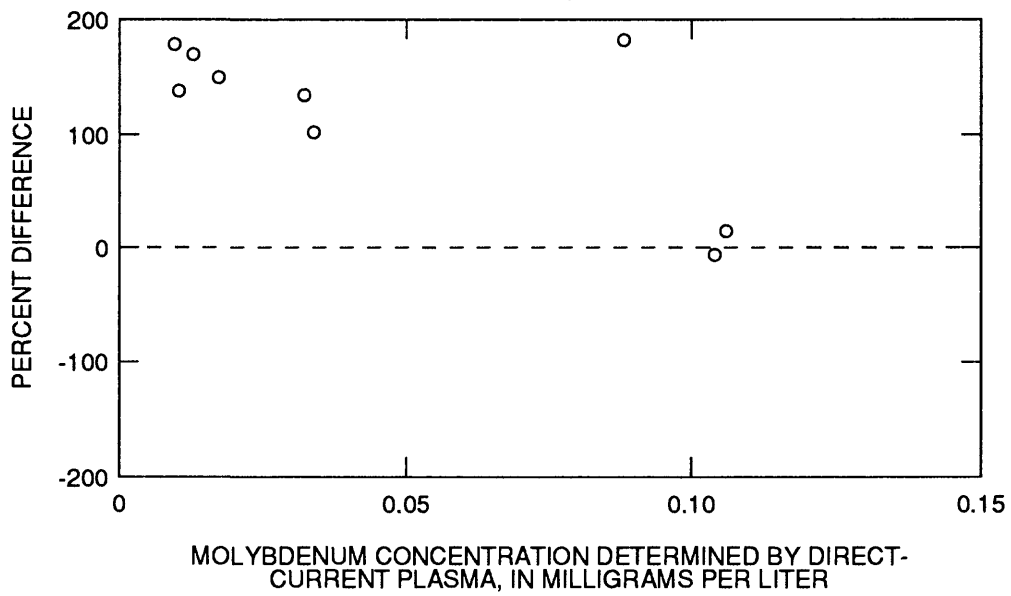

Figure 26. Relation between concentrations determined by inductively coupled plasma and direct-current plasma (DCP) spectrometry, in percent difference, as a function of concentration determined by DCP for molybdenum for all data.

A graph of Δ% between ICP and DCP analyses as a function of DCP Mo concentration is shown in figure 26, which shows all data. There are few data points (fig. 26) on which to base any interpretations or conclusions. The DCP detection limit was estimated at about 0.003 mg L^{-1}. There are 53 samples for which values less than the detection limit were obtained by one technique, whereas measurable concentrations were obtained using the other technique. These discordant values encompass

DCP concentrations as high as 0.123 mg L^{-1}. Standard reference water sample results (table 5) underscore the lack of sensitivity of the ICP for this determination.

The ICP spectrometer was not useful for the analysis of Mo at the concentrations present in the 1982 Leviathan samples. Consequently, it was not possible to determine whether there were significant interferences on the ICP analysis of Mo in acid mine water matrix containing high concentrations of Ca, Fe, SiO_2, Al, and Mg. Further investigation of the ICP analysis for Mo will be necessary before this element can be determined routinely.

Nickel

Tables A-61 to A-64 of the Appendix list the sample code number, the ICP Ni concentration, the DCP Ni concentration, the Zeeman GFAAS Ni concentration, the Δ% value, compared with the ICP Ni concentration, calculated using the DCP Ni concentration, and the Δ% value calculated using the Zeeman GFAAS Ni concentration, in columns 1-6, respectively. A blank field in the Δ% column indicates that no calculation was possible. The mean of the absolute values of the percent differences for the analyses by DCP is 10.6%; for the analyses by GFAAS, the mean of the absolute values is 23.6%. For the individual DCP analyses, this difference appears to be caused by several very large Δ% values for Ni concentrations at the low end of the measurable range, namely samples 82WA108, 111, 144, 150, and 158. Of the remaining 43 DCP determinations for which a Δ% value could be calculated, all have Δ% values under ±20%, and 31 of them have Δ% values less than 10%. Many of the 15 samples for which no calculation was possible gave ICP Ni concentrations less than 0.004 mg L^{-1}, and gave measurable concentrations by DCP coupled with less-than-detection concentrations by GFAAS. Differences between ICP and GFAAS concentrations are due primarily to results for samples 82WA114 and 82WA144. Four samples with Ni concentrations above 0.1 mg L^{-1} (82WA120, 128, 145, and 166) have GFAAS Ni concentrations significantly different from the ICP and DCP concentrations, that usually match each other much better in this range. The standard reference water sample results indicate that there is excellent accuracy for the determination of Ni at the 0.25 mg L^{-1} level (table 10) and that both the ICP and DCP give acceptable results at concentrations approaching the detection limit (tables 5 and 8).

The Δ% between ICP and DCP analyses is plotted as a function of DCP Ni concentration in figure 27, for all data. Figure 28 is a plot of data for comparison of ICP and GFAAS analyses, for all data. The ICP and DCP determinations for Ni (fig. 27) are similar. Figure 28 is likewise comparable, but data are scattered in this lower range, suggesting that accuracy may be decreased using one technique or the other below 0.2 mg L^{-1} Ni. ICP detection limits by can be estimated by examining figures 27 and 28. In an earlier experiment on the GFAAS determination of Ni, the DCP detection limit was estimated at about 0.02-0.03 mg L^{-1}. The distribution of Δ% values in figures 27 and 28 indicates an ICP detection limit of approximately 0.004 mg L^{-1}.

The ICP spectrometer is a very useful tool for the analysis of Ni, and appears to be somewhat better than the DCP, whose performance was only slightly poorer. This difference may be related to the use of two different Ni wavelengths in the two plasma instruments. These two wavelengths may have different sensitivity and interference characteristics. An operational ICP detection limit for this set of samples is about 0.003 mg L^{-1}. Ni concentrations below about 0.02 mg L^{-1} need to be determined by GFAAS, if possible. Fe contributes a small spectral interference to the determination of Ni using the 231.60 nm line. For this set of samples, the interference amounted to 0.2 to 2.2% of the Ni concentrations, for Fe concentrations from several mg L^{-1} to about 2,500 mg L^{-1}. Otherwise, there do not appear to be any other interferences on the ICP determination of Ni in acid mine water matrix containing

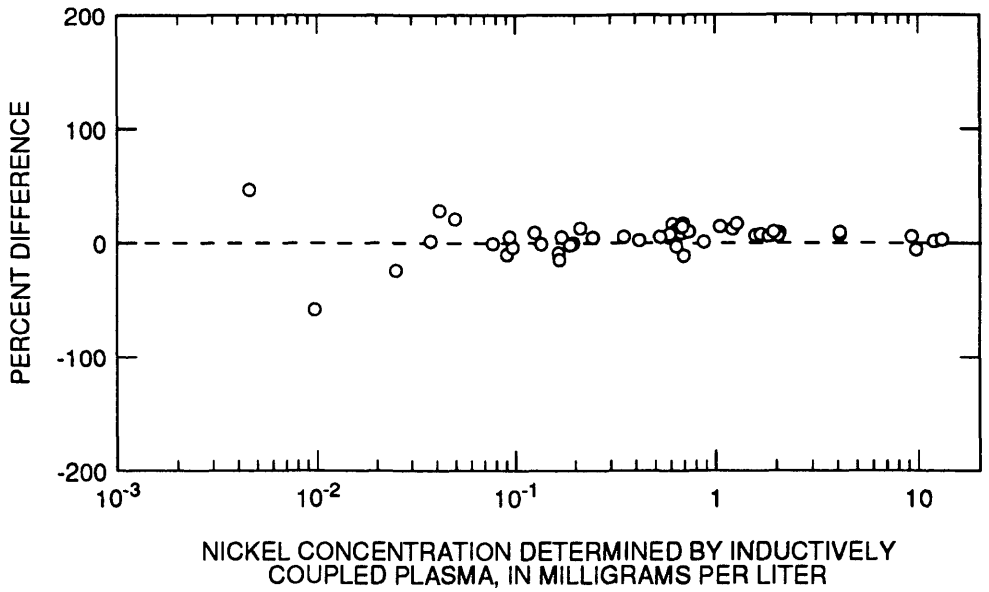

Figure 27. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for nickel for all data.

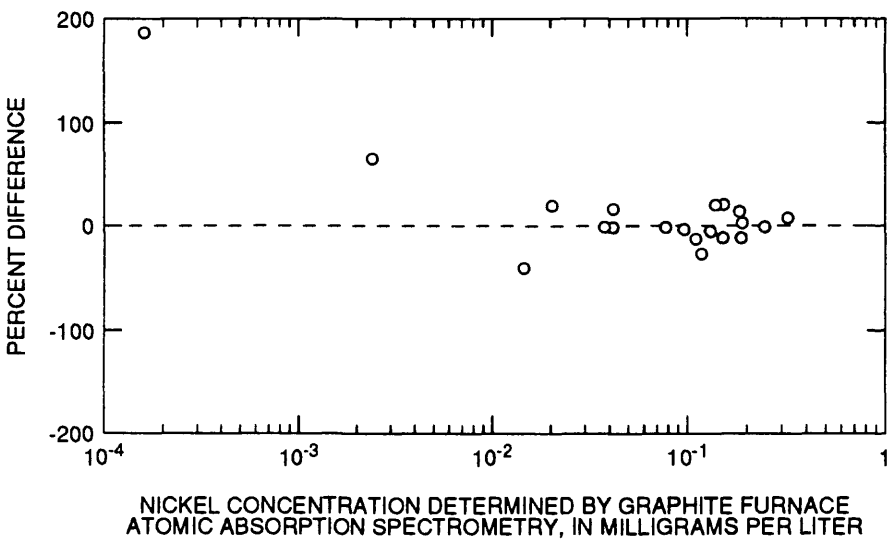

Figure 28. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for nickel for all data.

high concentrations of Ca, Fe, SiO_2, Al, and Mg. However, the possibility that complex and diverse matrices might have an adverse effect on this determination should not be ignored.

Silica

Although the constituent actually measured is Si, it is conventional to report concentration values in terms of SiO_2. Since concentrations are reported as SiO_2 the following discussion refers to Si as SiO_2. Tables A-65 to A-68 of the Appendix list the sample code number, the ICP SiO_2 concentration, the undiluted DCP SiO_2 concentration, the 1/10-diluted DCP SiO_2 concentration, the 1/100-diluted DCP SiO_2 concentration, the Δ% value, compared with the ICP SiO_2 concentration, calculated using the undiluted DCP SiO_2 concentration, the Δ% value calculated using the 1/10-diluted DCP SiO_2 concentration, and the Δ% value calculated using the 1/100-diluted DCP SiO_2 concentration, in columns 1-8, respectively. A blank field in the Δ% column indicates that no calculation was possible. The Δ% is plotted as a function of SiO_2 concentration in figure 29. Many of the differences are above 10%. When examined in more detail, there is a strong correlation between Δ% and the DCP dilution from which the DCP SiO_2 concentration was selected. Thirty-one values were selected from the undiluted DCP analyses, and all 31 have Δ% values of +8.3% or greater. Of the 32 values selected from the 1/10 diluted DCP analyses, only 11 of them have Δ% values greater than 10. Of these 11, 10 of them were from the very end of two sets, 1 and 4. As mentioned earlier, all of the ICP analytical runs were abbreviated by the torch becoming unstable and extinguishing itself prematurely. Near the end of a run, since the torch was getting ready to go out it may have been operating in an unstable manner, resulting in burning off of the quartz bonnet, causing the Si background to fluctuate.

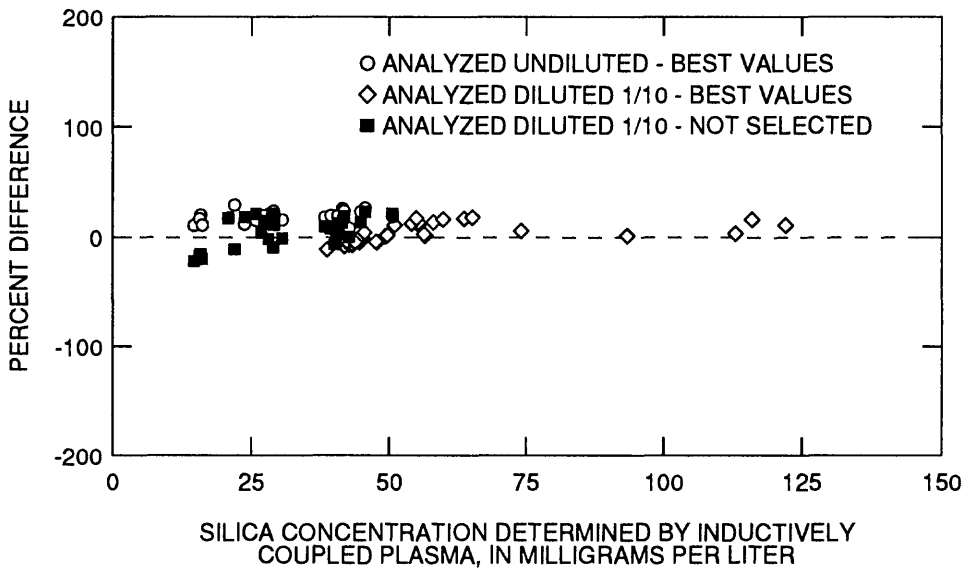

Figure 29. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for silica for all data.

The overall range of the scatter in the ICP results is unacceptably high. Therefore it cannot be determined whether the ICP spectrometer can reliably determine SiO_2 in this range of matrix and SiO_2 concentrations, because of the poor operation of the ICP torch. Consequently, there is insufficient data to confirm the reliability of the ICP technique. Therefore, the DCP values were retained, the DCP detection limit was reassessed, and the DCP concentrations were revised. Table 14 contains a list of proposed revisions to the Leviathan master data set.

Table 14.--Best estimates of silica concentrations, in milligrams per liter

Sample No	Old Value	New Value
82WA108	35.3	42.6
82WA109	35.7	42.6
82WA111	22.7	25.6
82WA112	35.2	36.4
82WA117	39.3	42.6
82WA121	24.9	31.7
82WA123	26.1	30.8
82WA126	22.8	28.5
82WA128	16.3	24.4
82WA143	34.9	36.2
82WA145	33.6	37.9
82WA146	32.0	35.7
82WA147	32.9	34.4
82WA148	32.3	36.4
82WA149	33.0	36.9
82WA150	24.6	23.2
82WA151	31.9	34.8
82WA153	24.3	26.0
82WA154	22.3	23.4
82WA155	34.4	37.5
82WA156	33.5	35.7
82WA159	35.5	39.0
82WA162	22.8	25.0
82WA170	41.8	40.8

Sodium and Potassium

Tables A-69 to A-72 of the Appendix list the sample code number, the DCP Na concentration, the ICP Na concentration, the flame AAS (using an ionization suppressing buffer) Na concentration, the Δ% value, compared with the ICP Na concentration, calculated using the DCP Na concentration, and the Δ% value calculated using the flame AAS Na concentration, in columns 1-6, respectively. Tables A-73 to A-76 of the Appendix list the sample code number, the DCP K concentration, the ICP K concentration, the flame AAS (using an ionization suppressing buffer) K concentration, the Δ% value, compared with the ICP K concentration, calculated using the DCP K concentration, and the Δ% value calculated using the flame AAS K concentration, in columns 1-6, respectively. It is apparent from the tables that there are major differences in reported Na and K concentrations as a function of the technique used. At the present time, the flame AAS concentrations, where present, are believed to be the most accurate estimates of the true Na and K concentrations, followed by the DCP values. The ICP concentrations are believed to be the least accurate. This conclusion appears to be refuted by the standard reference water sample results (tables 6, 7, and 8), that show ICP and DCP Na and K concentrations are equal to or greater than the most probable values. One caution that needs to be observed in this case is that none of these three standard reference water samples are acid mine water. It may well be possible to obtain more accurate estimates

of Na and K concentrations in solutions where they are major constituents, which is what they are in standard reference water samples 72, M102, and T97.

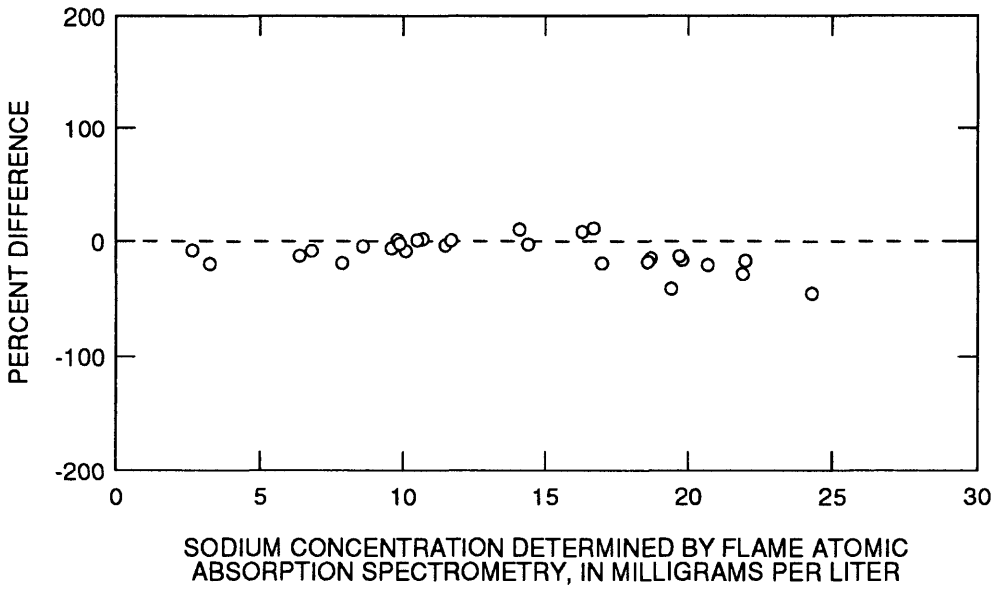

Figure 30. Relation between concentrations determined by flame atomic absorption spectrometry (AAS) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by flame AAS for sodium for all data.

The Δ% values are plotted as a function of Na concentration in figure 30. The same relation for K is shown in figure 31. These plots and from the data in tables A-69 to A-76 show that the similarity of flame AAS, ICP, and DCP determinations is rather poor, especially considering the Na levels in these samples. This is most likely caused by three problems: 1) There appears to be a substantial Ca interference in the ICP determination of Na. Note, however, that other investigators have observed no such interference (Fries, T. L., written commun., April, 1991). This raises the possibility that the Ca solutions used to quantify this assumed interference may have been contaminated with Na; 2) DCP Na determinations in the most concentrated samples were imprecise because of the concentrated matrix; 3) The ICP determinations were done using torch parameters that were quite far from optimum for the determination of alkali metals using ICP. This condition negates the advantage gained by using a special long-wavelength photomultiplier tube for the K channel of the simultaneous ICP unit. The K levels in these samples are frequently quite low; the detection limit was not determined but may well be higher than the preset 0.3 mg L^{-1} level. At the time of analysis, the ICP torch was not operating up to specifications and would not stay lit at the low power and coolant flow settings recommended by the manufacturer for the determination of alkali metals. The overall range of the scatter is unacceptably high. Therefore a conclusion of concurrence between methods cannot be justified from the data.

The ICP spectrometer is not well suited for the analysis of Na and K in this range of matrix and Na and K concentrations, using the multielement compromise torch power and entrance slit alignment settings used in this study. The power and argon flow parameters deemed appropriate for the analysis of alkali metals were not used at the time of this study, because of the improper functioning of the torch, mentioned previously. ICP or DCP concentration estimates need to be verified using other analytical

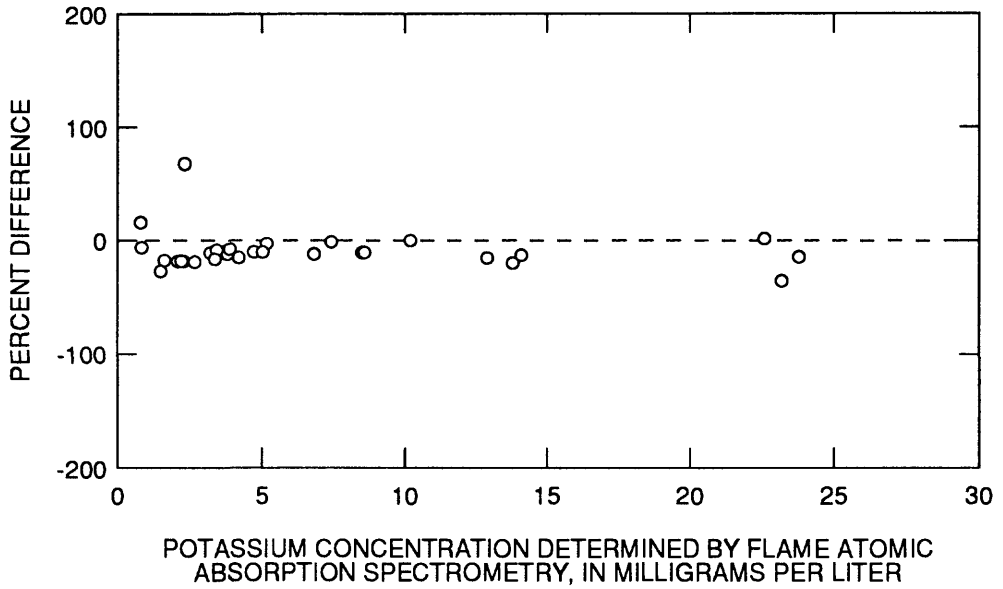

Figure 31. Relation between concentrations determined by flame atomic absorption spectrometry (AAS) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by flame AAS for potassium for all data.

techniques, such as flame atomic-absorption spectrometry or flame emission, before release or other use of the data.

Strontium

Tables A-77 to A-80 of the Appendix list the sample code number, the ICP Sr concentration, the undiluted DCP Sr concentration, the 1/10-diluted DCP Sr concentration, the 1/100-diluted DCP Sr concentration, the Δ% value, compared with the ICP Sr concentration, calculated using the undiluted DCP Sr concentration, the Δ% value calculated using the 1/10-diluted DCP Sr concentration, and the Δ% value calculated using the 1/100-diluted DCP Sr concentration, in columns 1-8, respectively. A blank field indicates that no calculation was possible. The overall mean Δ% is 6.73 for the undiluted samples; 4.81 for the 1/10 dilutions; and 18.9 for the 1/100 dilutions. The overall mean Δ% is 5.45 for the DCP values selected for publication in Ball and Nordstrom (1985); this includes DCP analyses done at both no dilution and at 1/10 dilution. For individual samples, most of the differences between ICP and DCP larger than 10% appear to occur when comparing the ICP concentration to the DCP undiluted determination. If the DCP detection limit were decreased from 0.005 to 0.001 mg L^{-1}, all but four 1/10 dilution concentrations would be automatically selected by the data reduction program, eliminating or dramatically decreasing all but six of the Δ% values larger than 10. The only remaining differences larger than 10% are for 82WA104 (decreased from 23.2 to 11.0%), and 82WA118, 119, 125, 156, and 169 (unaffected by the modification). The fact that three of the last five outliers (82WA118, 119, and 169) are for the highly concentrated samples, and that the remaining two are for the same sampling site, which, coincidentally, is a concentrated seep of unique chemical makeup, indicates that one technique or the other may be sensitive to variations in sample matrix, or to a concomitant interferent.

Standard reference water sample results are very interesting. For the acid mine water samples (tables 9 and 10), Δ% values for ICP determinations are both negative. This indicates that there may be

a matrix effect on Sr emission, such as emission enhancement by concomitant elements in the solution, or suppression in the acid mine water matrix. The evidence of this report is not sufficient to make a more definitive statement on this subject, but there is a clear need for additional investigation.
In contrast, Δ% values for the more "normal" surface water types such as those in tables 5 to 8 range from +11.9 to +34.4 for Sr concentrations of 0.077 to 1.34 mg L^{-1}.

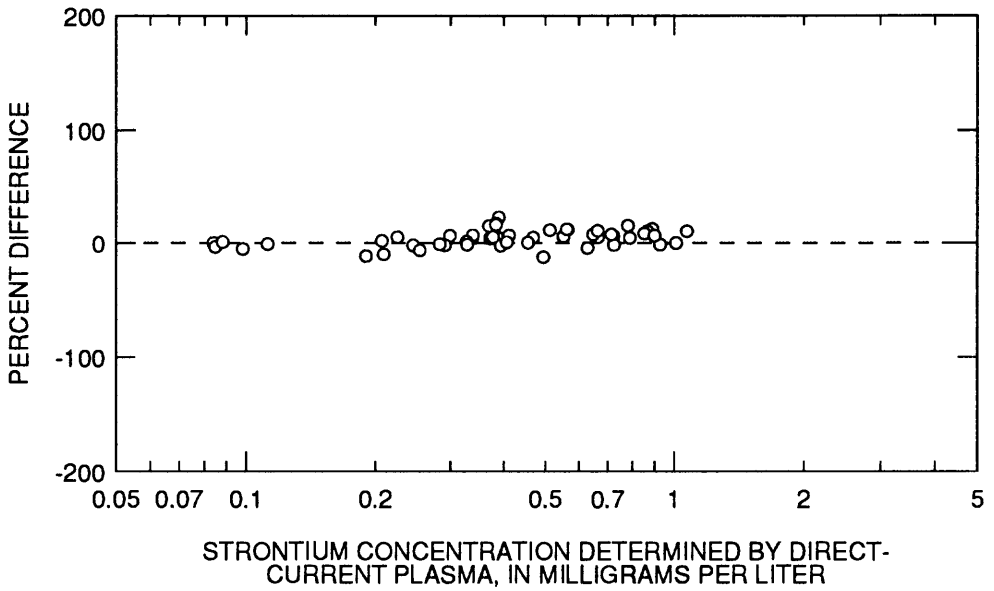

Figure 32. Relation between concentrations determined by inductively coupled plasma and direct-current plasma (DCP) spectrometry, in percent difference, for all data, as a function of undiluted DCP Sr concentration.

The Δ% is plotted as a function of Sr concentration in figure 32, for all data for the DCP undiluted analyses. Figure 33 is a plot of the same parameters for the DCP 1/10 dilutions; and figure 34 is a plot of the same parameters for the DCP 1/100 dilutions. Figure 35 is a plot of Δ% calculated using the concentrations selected for publication in Ball and Nordstrom (1985). Figure 33 shows somewhat less scatter than the other three plots, reflecting the improved overall mean Δ% value calculated. This is more evident if the four most concentrated samples and the two "unique seep" samples are removed from consideration. The data in figure 34 clearly indicate a trend wherein the Sr concentrations measured using DCP tend to drop off dramatically below about 1.50 mg L^{-1} on the plot (the concentration in the solution presented to the spectrometer for analysis was ≤0.015 mg L^{-1}), when compared either to ICP data or to DCP data from more concentrated analyses. This may reflect either systematic errors in making dilutions or decreased accuracy and precision related to making determinations at these low solution Sr concentrations. Using the data shown in figure 33, there is, overall, virtually no tendency of the points to begin scattering as the concentration goes lower, even at the lowest concentrations in this sample set. This indicates that the detection limits for both ICP and DCP are considerably below the lowest Sr concentration measured, about 0.08 mg L^{-1}. The DCP detection limit of 0.005 mg L^{-1} was set quite conservatively, as Sr concentrations in dilute acid could be detected as low as 0.0005 mg L^{-1}.

The ICP spectrometer is a very useful tool for the analysis of Sr. An operational ICP detection limit for this set of samples is about of 0.002 mg L^{-1}. This may be decreased when samples having even

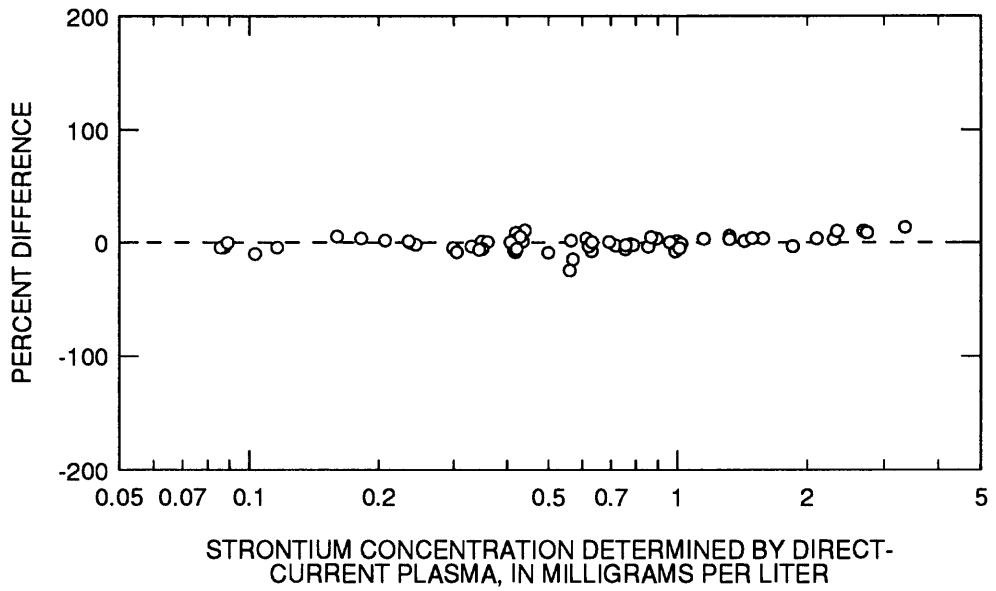

Figure 33. Relation between concentrations determined by inductively coupled plasma and direct-current plasma (DCP) spectrometry, in percent difference, for all data, as a function of 1/10 diluted DCP Sr concentration.

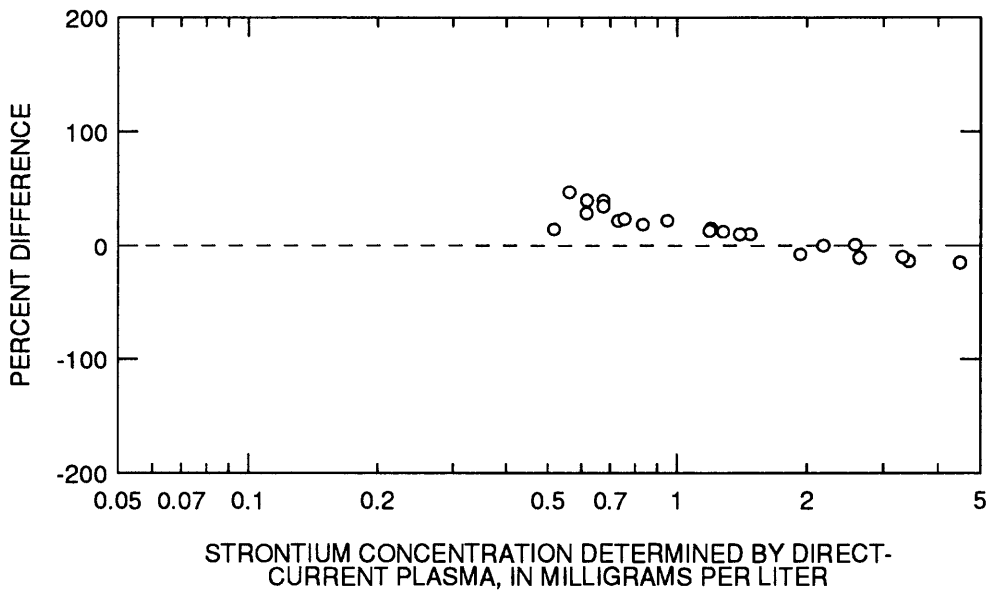

Figure 34. Relation between concentrations determined by inductively coupled plasma and direct-current plasma (DCP) spectrometry, in percent difference, for all data, as a function of 1/100 diluted DCP Sr concentration.

lower concentrations of Sr are encountered. In cases where matrices are particularly complex, special attention is required because both matrix and interelement interferences may be present.

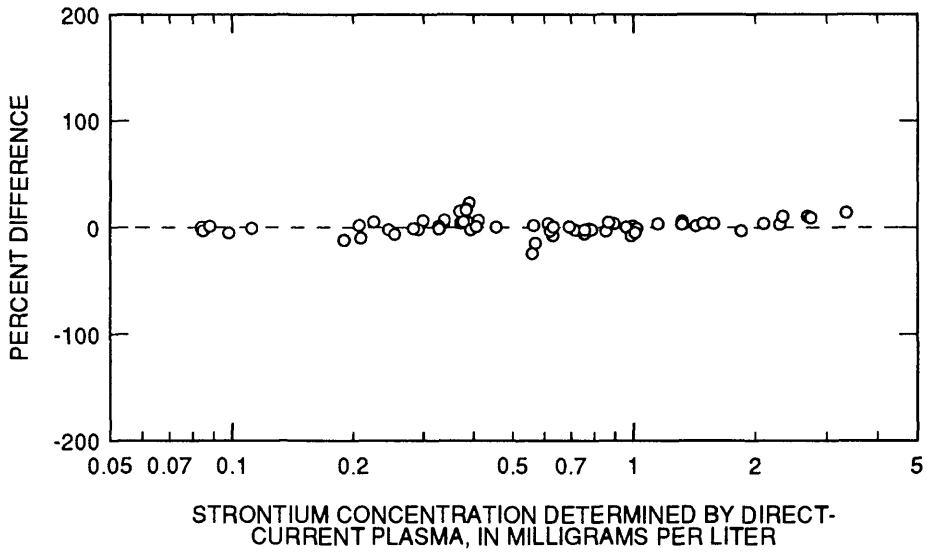

Figure 35. Relation between concentrations determined by inductively coupled plasma and direct-current plasma (DCP) spectrometry, in percent difference, for all data, as a function of DCP Sr concentrations from Ball and Nordstrom (1985).

After re-evaluation of the available data for Sr it has been determined that the Sr detection limit by DCP can be decreased from 0.005 mg L^{-1} to 0.001 mg L^{-1}, and that the mean of the DCP and ICP concentrations can be used, except in the case of samples 82WA125 and 82WA156, where only the DCP concentrations are used.

Vanadium

Tables A-81 to A-84 of the Appendix list the sample code number, the ICP V concentration, the DCP V concentration, the Zeeman GFAAS V concentration, the Δ% value, compared with the ICP V concentration, calculated using the DCP V concentration, and the Δ% value calculated using the Zeeman GFAAS V concentration, in columns 1-6, respectively. A blank field in the Δ% column indicates that no calculation was possible. There are 39 samples in which concentrations greater than the detection limit were obtained by the ICP or DCP technique, whereas concentrations less than the detection limit were obtained using the GFAAS technique. There are four samples in which concentrations less than the detection limit were obtained by the ICP or DCP technique, whereas measurable values were obtained using the GFAAS technique. This indicates that these two instruments have roughly equivalent ability to measure V in these samples. There were 23 Δ% calculations comparing ICP to GFAAS, out of a total of 63 samples in the set, with a mean Δ% value of 69.2%, and 24 comparing ICP to DCP, with a mean Δ% value of 54.7%. Only two standard reference water samples list V as a constituent (M102 and T97). Vanadium is present in these two samples at levels well below either the ICP or DCP detection limit and was not detected using either technique.

Mg and Al interfere on the ICP determination of V. The Al interference amounts to a maximum of only 2% of the V concentration, but the Mg interference can be substantial, depending on the relative concentrations of V and Mg. In the more dilute samples, that usually contain a high Mg/V ratio, the

correction is up to 100% of the V concentration, whereas in the more concentrated samples, where the Mg/V ratio is much smaller, the correction is only a few percent of the total V present.

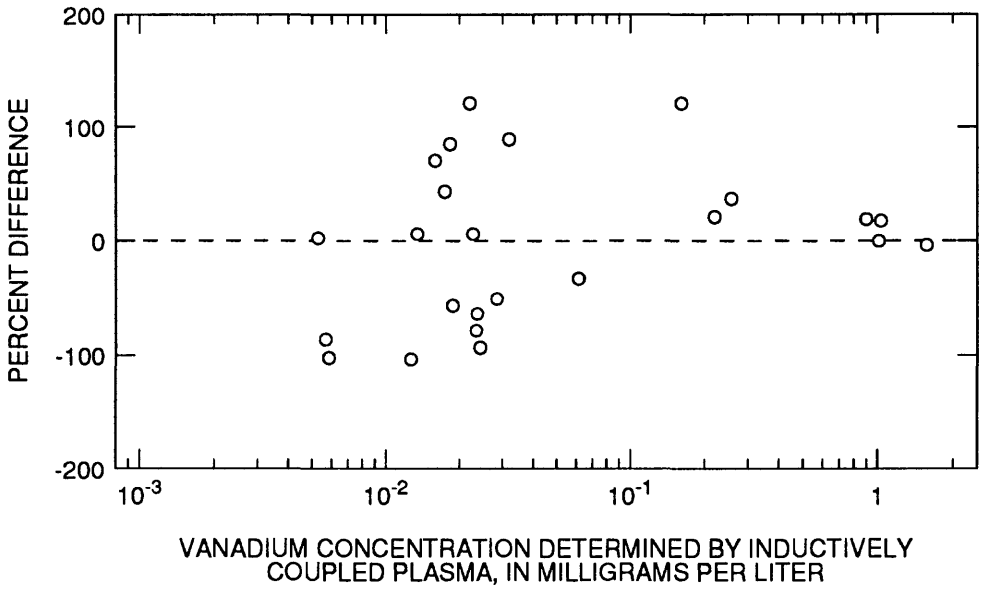

Figure 36. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for vanadium for all data.

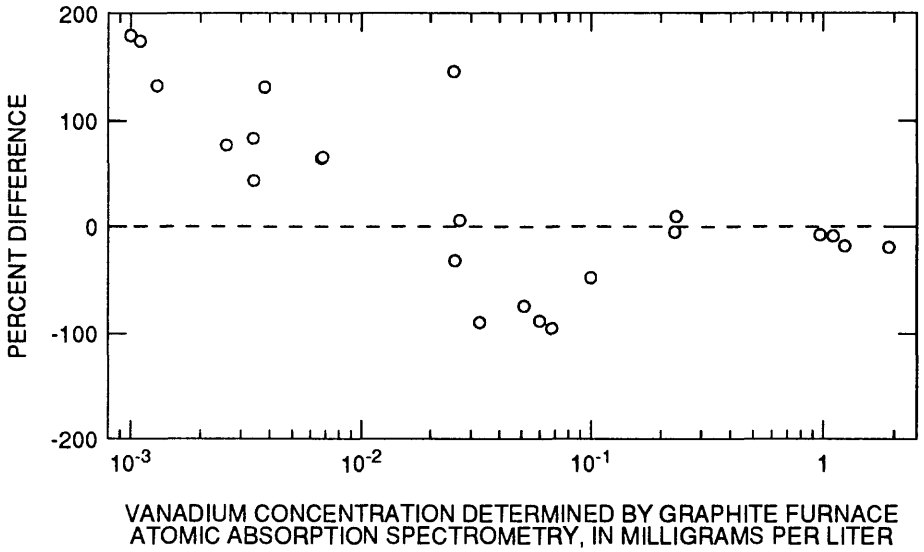

Figure 37. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for vanadium for all data.

Figure 36 shows the Δ% for all data, ICP to DCP, as a function of DCP V concentration. Figure 37 is an analogous plot comparing ICP to GFAAS data. It is apparent (figs. 36 and 37) that Δ% values begin to scatter significantly below 0.1 mg L^{-1} V, and are fairly close to zero above that concentration.

From these two figures, an ICP detection limit of roughly 0.075 mg L^{-1} can be estimated. This compares with an estimate for the DCP while performing GFAAS determinations of 0.03-0.04 mg L^{-1}.

The ICP spectrometer is only a marginally useful tool for the analysis of V in the sample set analyzed, because of the very low V concentrations in these samples and the relatively lower sensitivities of the ICP and DCP for V. Consequently, all plasma data were rejected in favor of the GFAAS concentrations. The DCP appears to be significantly more sensitive than the ICP, whose performance was substantially poorer, at least using the 310.23 nm and 437.92 nm wavelengths selected for ICP and DCP analysis, respectively. An operational ICP detection limit for this set of samples is about 0.075 mg L^{-1}. For samples containing less that about 0.25 mg L^{-1} V, determinations need to be done by GFAAS to obtain precision and accuracy within acceptable limits. Mg contributes a substantial interference to the V determination that is at least partially correctable. The interference ranges in this set of samples between 0 (no measurable V or less than 10 mg L^{-1} Mg) and 100% (very high Mg, very low but positive V) of the V concentration for Mg concentrations from less than 2 mg L^{-1} to over 110 mg L^{-1}. The uncertainty in this correction will have a substantial effect on the detection limit for the determination (Fries, T. L., written commun., April, 1991).

Zinc

Tables A-85 to A-88 of the Appendix list the sample code number, the ICP Zn concentration, the DCP cassette 1 Zn concentration, the DCP cassette 2 Zn concentration, the Zeeman GFAAS Zn concentration, the Δ% value, compared with the ICP Zn concentration, calculated using the DCP cassette

1 Zn concentration, the Δ% value calculated using the DCP cassette 2 Zn concentration, and the Δ% value calculated using the Zeeman GFAAS Zn concentration, in columns 1-8, respectively. A blank field in the Δ% column indicates that no calculation was possible. The absolute value of the mean Δ% for the analyses by DCP Cassette 1 is 14.6; for the analyses by DCP Cassette 2, 21.9; and for the analyses by GFAAS, the value is 28.2. These differences appear to be due to anomalously high values caused by contamination of many of the individual aliquots split out for analysis (for extreme examples, see the results for 82WA110, 128, and 166). In the case of the GFAAS values, the Δ% values apparently are somewhat large, but considering the levels measured, they were not unexpected. The evidence from the standard reference water sample analyses strongly supports the hypothesis of widely scattered estimates at very low Zn concentrations (tables 5 and 8) and excellent agreement with given values at extremely high Zn concentrations (tables 9 and 10).

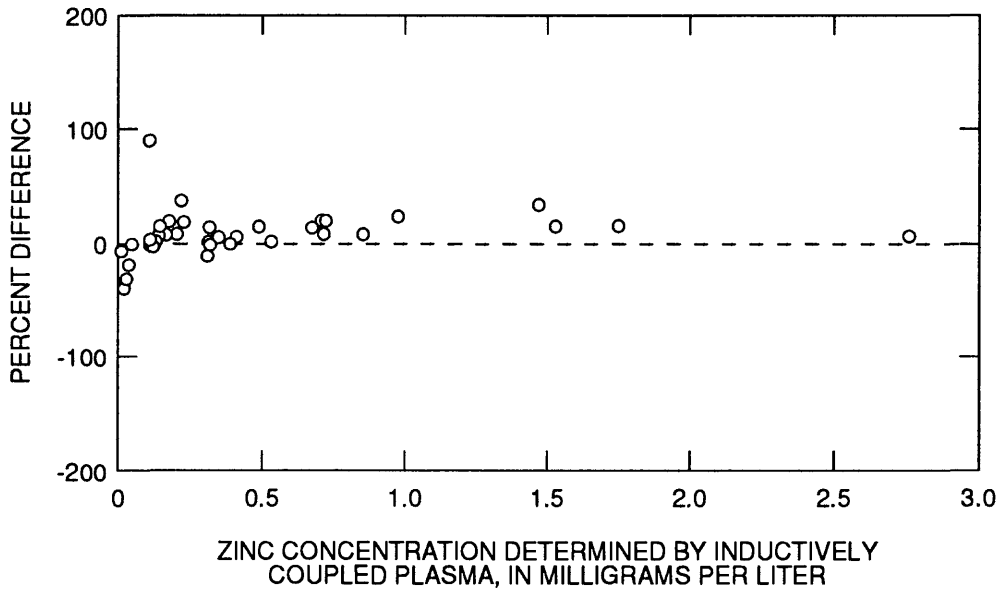

Figure 38. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for zinc for all cassette 1 data.

The Δ% is plotted as a function of Zn concentration in figures 38 and 39, for all data for DCP Cassette 1 and Cassette 2, respectively. Figure 40 shows the GFAAS data. Figures 38 and 39 are remarkably similar in appearance, as they should be. Figure 40 exhibits a pattern of limited divergence of Δ% values with decreasing Zn concentration. This pattern indicates that the detection limit for Zn by ICP potentially could be extremely low because of high sensitivity of the ICP for Zn, but is limited to a much higher concentration by the ubiquitous presence of Zn contaminants in the usual laboratory environment. This is illustrated by the Δ% value near 100 at a GFAAS concentration of about 0.04 mg L^{-1} (fig. 40). The detection limit is very roughly estimated to be around 0.005 to 0.02 mg L^{-1}, rather than the value of 0.002 or 0.006 mg L^{-1} determined previously using standards in dilute acid, or the sub-ug L^{-1} range alluded to by the distribution in figure 40. This was somewhat unexpected, but the difficulty of controlling Zn contamination has proven to be a formidable problem.

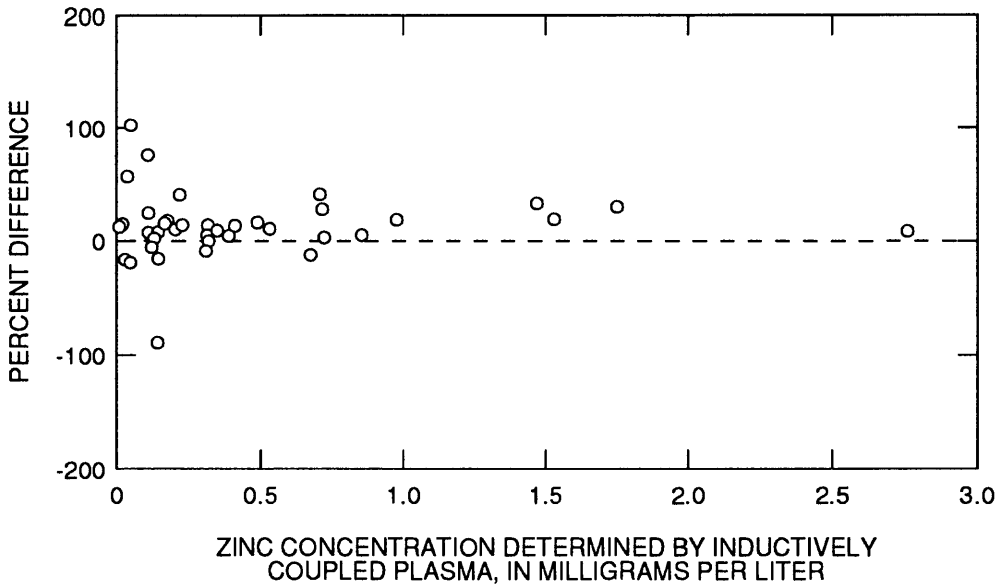

Figure 39. Relation between concentrations determined by inductively coupled plasma (ICP) and direct-current plasma spectrometry, in percent difference, as a function of concentration determined by ICP for zinc for all cassette 2 data.

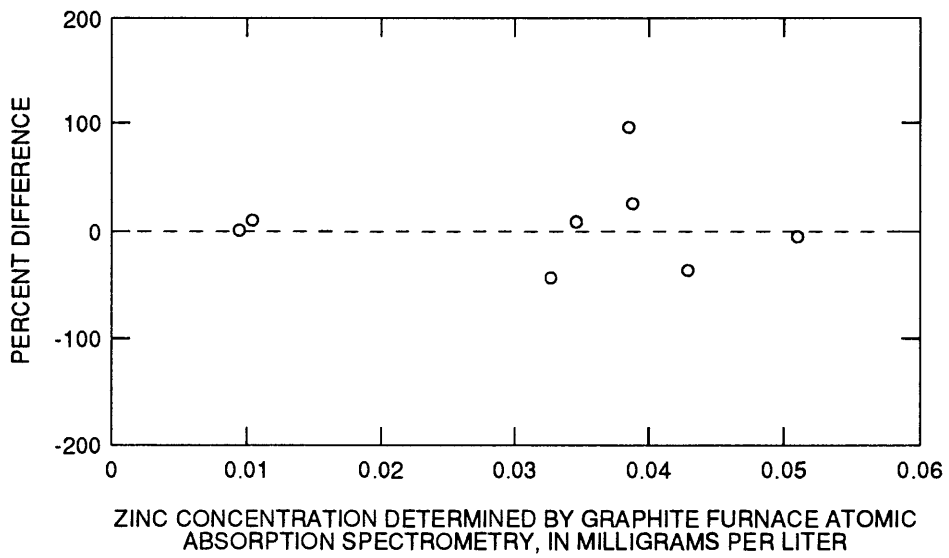

Figure 40. Relation between concentrations determined by graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma spectrometry, in percent difference, as a function of concentration determined by GFAAS for zinc for all data.

As an explanation for the relatively poor similarity of some ICP and DCP Zn concentrations, the ICP calibration for Zn appears to be rather sensitive, and torch positioning on the input slit of the ICP spectrometer using Mn may not necessarily be optimum for Zn. Mg contributes a positive interference to the determination of Zn by ICP. The accuracy of the corrections applied to the raw Zn values then

determines the accuracy of the final concentrations. Si and Fe contribute small interferences, and Mg contributes a substantial interference on the determination of Zn by DCP. This possibility is sometimes apparent in the data for more dilute analyses by DCP. Based on the analysis of a more concentrated aliquot, many samples ought to have yielded a similar Zn concentration in a more dilute sample aliquot; however, concentrations significantly less than those in the more concentrated analysis, or even less than detection, were frequently obtained. In addition, these concentrations were sometimes quite similar to concentrations obtained by ICP and/or GFAAS analysis. This indicates that an unaccounted source of inaccuracy, most likely high, drifting background in the DCP analysis of the more concentrated analyses, is sometimes absent in the analyses of less concentrated samples (dynamic background correction was not done during DCP analysis). A few examples from the data in tables A-85 to A-88 are shown in table 15.

Table 15.--Best estimates of zinc concentraitns, in milligrams per liter
[DCP, direct-current plasma; ICP, inductively coupled plasma]

	Zinc concentration, in milligrams per liter		
	Mean	Alternative[1]	
Sample Number	DCP mg L^{-1}	DCP mg L^{-1}	ICP mg L^{-1}
82WA110	0.147	0.223	0.219
82WA129	0.371	0.194	0.142
82WA118	1.290	1.420	1.750
82WA169	1.040	1.290	1.470

[1]Alternative concentrations are those rejected by the computerized "best values" selection program in favor of the primary, or selected, concentration.

The ICP spectrometer is potentially a useful tool for the analysis of Zn, provided that problems with Zn contamination of sample aliquots can be alleviated somewhat. An operational detection limit for this set of samples is about 0.01 mg L^{-1}. Significant lowering of this limit will probably only be achieved if a "clean room" environment can be used for processing of samples to be analyzed for Zn. Samples with Zn concentrations below 0.05 mg L^{-1} appear to be best analyzed by GFAAS. For concentrations exceeding 0.05 mg L^{-1}, samples may be analyzed by ICP or DCP. However, because of the high possibility of random contamination samples need to be analyzed in at least duplicate, with samples having poor statistics reanalyzed additional times until such problems are resolved. Outliers excluded from the Leviathan data compilation because they have almost certainly been contaminated are listed in table 16.

Table 16.--Sources of zinc values excluded from averaging calculations because of contamination

82WA110	ICP	82WA124	ICP	82WA128	ICP	82WA157	DCP2
82WA115	ICP	82WA125	ICP	82WA129	DCP2	82WA168	DCP1
82WA118	ICP	82WA127	ICP	82WA132	ICP	82WA169	ICP

SUMMARY AND CONCLUSIONS

Three primary techniques have been used to analyze samples collected from an area of acid mine drainage. The techniques are inductively-coupled plasma and direct-current plasma spectrometry and Zeeman graphite-furnace atomic-absorption spectrometry. Three secondary techniques, flame atomic-absorption spectrometry, hydride-generation atomic-absorption spectrometry, and visible spectrometry, also were used for specific elements. Results of determinations using these techniques were compared with one another for the purpose of determining what analytical strategy and techniques were appropriate for each of the constituents considered.

Of the techniques employed in this study, flame atomic-absorption spectrometry was judged best for Na and K. Hydride-generation atomic-absorption spectrometry was judged best for As. Colorimetric determination using ferrozine as the color agent was judged most accurate, precise, and sensitive for Fe. Cd, Mo, Pb, and V concentrations were too low in this set of samples to make a qualitative determination between the ICP and DCP instruments. Of the remaining elements, Ba, Be, Ca, Cr, Mg, Mn, Sr, and Zn, the ICP and DCP instruments have roughly equivalent sensitivity, precision, and detection limit. Co and Ni were better determined by ICP; Al, B, Cu, and Si were better determined by DCP, at the respective wavelengths selected. The ICP and DCP detection limits are typically 0.001 to 0.5 milligrams per liter in acid mine waters. At metal (not including B and Si) concentrations below these limits, graphite-furnace atomic-absorption spectrometry is the method of choice because of its relatively greater sensitivity and specificity.

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APPENDIX: TABLES OF ANALYTICAL DATA

Table A-1. Results of analyses for aluminum in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[mg L^{-1}, milligrams per liter; µg L^{-1}, micrograms per liter; DCP, direct-current plasma spectrometry; ICP, inductively coupled plasma spectrometry; GFAAS, graphite-furnace atomic-absorption spectrometry; flame AAS, flame atomic-absorption spectrometry; Δ%, percent difference in concentration; Log IAP/K, common logarithm of quotient of ion activity product and equilibrium constant]

Sample Number	Concentration (mg L^{-1})				ICP-primary DCP (Δ%)	ICP-alternative DCP (Δ%)	GFAAS-primary DCP (Δ%)
	Primary DCP	Dilute DCP	ICP	GFAAS			
82WA104	0.32	0.36	0.08	0.48	-120	-127	40.0
82WA106	0.14	0.21	<0.01	0.202			36.3
82WA107	0.48	0.48	0.42	0.73	-13.3	-13.3	41.3
82WA109	4.78	5.03	5.06	5.27	5.7	[1]**0.6**	9.8
82WA110	18.5	18.8	19.8		6.8	5.2	
82WA112	19.8	19.5	20.5		3.5	5.0	
82WA113	26.5	29.0	28.8		8.3	**-0.7**	
82WA115	29.8	<10.0	32.2		7.7		
82WA116	32.9	35.0	37.5		13.1	**6.9**	
82WA120	21.5	26.4	24.4		12.6	-7.9	
82WA122	15.3	15.9	16.0		4.5	0.6	
82WA124	29.8	27.2	29.8		0.0	9.1	
82WA129	17.1	20.1	21.7		23.7	**7.7**	
82WA130	14.3	14.8	15.0		4.8	1.3	
82WA131	35.6	35.4	39.9		11.4	12.0	
82WA145	0.06	0.12	<0.01	0.107			56.3
82WA149	19.7	13.5	19.9		1.0	38.3	
82WA151	18.4	11.3	18.8		2.2	49.8	
82WA152	44.4	43.9	45.0		1.3	2.5	
82WA155	6.50		7.18	7.37	9.9		12.5
82WA157	51.2	61.2	54.7		6.6	-11.2	
82WA160	45.5	46.9	47.8		4.9	1.9	
82WA161	50.9	58.2	58.1		13.2	**-0.2**	
82WA163	44.0	44.3	46.9		6.4	5.7	
82WA164	53.6	61.7	55.6		3.7	-10.4	

[1]**Bold** indicates improvement of ≥5 in Δ% when alternative DCP Al concentration is used in the calculation.

Table A-2. Results of analyses for aluminum in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-primary DCP (Δ%)	ICP-alternative DCP (Δ%)	GFAAS-primary DCP (Δ%)
	Primary DCP	Dilute DCP	ICP	GFAAS			
82WA100	0.04	<0.10	0.06	0.039	40.0		-2.5
82WA101	0.04	<0.10	<0.01	0.042			4.9
82WA102	0.05	<0.10	<0.01	0.047			-6.2
82WA103	0.06	<0.10	0.02	0.068	-100		12.5
82WA105	0.03	0.10	<0.01	0.0068			-126.1
82WA108	0.03	0.11	<0.01	0.045			40.0
82WA111	0.09	0.29	0.03	0.109	-100	-163	19.1
82WA114	0.12	0.14	0.03	0.195	-120	-129	47.6
82WA117	<0.01	<0.10	<0.01	0.0177			
82WA121	0.10	0.12	<0.01	0.038			-89.9
82WA123	0.02	<0.10	<0.01	0.0065			-101.9
82WA125	73.2	51.3	74.6		1.9	37.0	
82WA126	0.12	0.24	<0.01	0.134			11.0
82WA127	46.8	48.8	52.7		11.9	7.7	
82WA128	0.37	1.09	0.54	0.222	37.4	-67.5	-50.0

Table A-3. Results of analyses for aluminum in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-primary DCP (Δ%)	ICP-alternative DCP (Δ%)	GFAAS-primary DCP (Δ%)
	Primary DCP	Dilute DCP	ICP	GFAAS			
82WA141	0.02	0.16	<0.01	0.043			73.0
82WA142	0.04	0.18	<0.01	0.059			38.4
82WA143	0.14	0.21	0.46	0.519	107	[1]**74.6**	115.0
82WA144	0.03	<0.10	<0.01	0.0085			-111.7
82WA146	0.05	<0.10	0.01	0.036	-133		-32.6
82WA147	0.02	0.18	0.06	0.0101	100	-100	-65.8
82WA148	0.39	0.51	0.39	0.62	0.0	-26.7	45.5
82WA150	0.10	0.33	<0.01	0.088			-12.8
82WA153	0.02	0.14	<0.01	0.001			-181.0
82WA154	0.02	0.23	<0.01	0.002			-163.6
82WA156	57.4	70.6	58.8		2.4	-18.2	
82WA158	0.12	1.04	0.45	0.100	116	-79.2	-18.2
82WA159	0.04	<0.10	<0.01	0.016			-85.7
82WA162	0.28	1.01	0.48	0.45	52.6	-71.1	46.6
82WA166	2.18	2.51	2.13	2.35	-2.3	-16.4	7.5
82WA170	<0.01	0.19	0.05	0.146		-117	

[1]**Bold** indicates improvement of ≥5 in Δ% when alternative DCP Al concentration is used in the calculation.

Table A-4. Results of analyses for aluminum in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-primary DCP (Δ%)	ICP-alternative DCP (Δ%)	GFAAS-primary DCP (Δ%)
	Primary DCP	Dilute DCP	ICP	GFAAS			
82WA118	426	469	438		2.8	-6.8	
82WA119	624	620	623		-0.2	0.5	
82WA132	309	310	355		13.9	13.5	
82WA165	52.3	45.1	51.0		-2.5	12.3	
82WA167	113	101	108		-4.5	6.7	
82WA168	111	127	103		-7.5	-20.9	
82WA169	416	451	399		-4.2	-12.2	

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-5. Results of analyses for arsenic in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				DCP-hydride (Δ%)	ICP-hydride (Δ%)	GFAAS-hydride (Δ%)
	Hydride	DCP	ICP	GFAAS			
82WA104	0.001	<0.360	<0.300	0.0036			113.0
82WA106	0.003	<0.360	<0.300	0.010			107.7
82WA107	0.003	<0.360	<0.300	0.013			125.0
82WA109	0.005	<0.360	<0.300	0.014			94.7
82WA110	0.010	<0.360	<0.300	0.0251			86.0
82WA112	0.31	0.666	<0.300	0.39	73.0		22.9
82WA113	0.37	0.482	<0.300	0.53	26.3		35.6
82WA115	0.92	1.01	<0.300	1.11	9.3		18.7
82WA116	0.88	1.26	<0.300	1.43	35.5		47.6
82WA120	0.002	<0.360	<0.300	0.014			150.0
82WA122	0.005	0.415	<0.300	0.0143	195.2		96.4
82WA124	0.001	0.394	<0.300	0.0035	199.0		111.1
82WA129	0.005	0.478	<0.300	0.010	195.9		66.7
82WA130	0.005	0.391	<0.300	0.0089	194.9		56.1
82WA131	1.4	1.51	0.718	1.58	7.6	-64.4	12.1
82WA145	0.001	<0.360	<0.300	0.0052			135.5
82WA149	0.0082	<0.360	<0.300	0.014			52.3
82WA151	0.0070	<0.360	<0.300	0.017			83.3
82WA152	0.019	<0.360	<0.300	0.038			66.7
82WA155	0.021	<0.360	<0.300	0.039			60.0
82WA157	0.012	<0.360	<0.300	0.021			54.5
82WA160	0.032	0.386	<0.300	0.035	169.4		9.0
82WA161	0.032	<0.360	<0.300	0.046			35.9
82WA163	0.017	<0.360	<0.300	0.019			11.1
82WA164	0.032	<0.360	<0.300	0.025			-24.6

Table A-6. Results of analyses for arsenic in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration ($mg\ L^{-1}$)				DCP-hydride (Δ%)	ICP-hydride (Δ%)	GFAAS-hydride (Δ%)
	Hydride	DCP	ICP	GFAAS			
82WA100	0.003	<0.360	<0.300	0.010			107.7
82WA101	0.002	<0.360	<0.300	0.012			142.9
82WA102	0.002	<0.360	<0.300	0.008			120.0
82WA103	0.002	<0.360	<0.300	0.100			192.2
82WA105	0.003	<0.360	<0.300	0.0033			9.5
82WA108	0.001	<0.360	<0.300	0.002			66.7
82WA111	0.003	<0.360	<0.300	0.002			-40.0
82WA114	0.005	<0.360	<0.300	0.059			168.8
82WA117	0.003	<0.360	<0.300	0.0054			57.1
82WA121	0.001	0.526	<0.300	0.0026	199.2		88.9
82WA123	0.003	<0.360	<0.300	0.0079			89.9
82WA125	0.001	0.530	<0.300	0.022	199.2		182.6
82WA126	0.003	<0.360	<0.300	0.062			181.5
82WA127	0.0080	<0.360	0.323	0.044		190.3	138.5
82WA128	0.002	<0.360	<0.300	0.005			85.7

Table A-7. Results of analyses for arsenic in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				DCP-hydride (Δ%)	ICP-hydride (Δ%)	GFAAS-hydride (Δ%)
	Hydride	DCP	ICP	GFAAS			
82WA141	0.004	<0.360	<0.300	0.013			105.9
82WA142	0.004	<0.360	<0.300	0.0077			63.2
82WA143	0.001	<0.360	<0.300	0.0029			97.4
82WA144	0.002	<0.360	<0.300	0.0042			71.0
82WA146	0.001	<0.360	<0.300	0.0085			157.9
82WA147	0.002	<0.360	<0.300	0.0035			54.5
82WA148	0.003	<0.360	<0.300	0.0057			62.1
82WA150	0.004	<0.360	<0.300	0.0052			26.1
82WA153	0.001	<0.360	<0.300	0.0024			82.4
82WA154	0.0009	<0.360	<0.300	0.006			147.8
82WA156	0.001	<0.360	0.408	0.022		199.0	182.6
82WA158	0.0008	<0.360	<0.300	0.007			159.0
82WA159	0.001	<0.360	<0.300	0.013			171.4
82WA162	0.005	<0.360	<0.300	0.0078			43.8
82WA166	0.001	<0.360	<0.300	0.012			169.2
82WA170	0.0007	<0.360	<0.300	0.013			179.6

Table A-8. Results of analyses for arsenic in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				DCP-hydride (Δ%)	ICP-hydride (Δ%)	GFAAS-hydride (Δ%)
	Hydride	DCP	ICP	GFAAS			
82WA118	30.	37.6	43.5	40.	22.5	36.7	28.6
82WA119	40.	39.6	40.4	41.	-1.0	1.0	2.5
82WA132	27.	26.3	24.6	27.1	-2.6	-9.3	0.4
82WA165	0.021	<0.360	<3.00	0.025			17.4
82WA167	0.53	1.14	<3.00	0.51	73.1		-3.8
82WA168	0.42	0.549	<3.00	0.44	26.6		4.7
82WA169	34.	32.6	33.1	31.7	-4.2	-2.7	-7.0

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-9. Results of analyses for barium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Sulfate (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)	Log IAP/K barite	
		ICP barium	DCP barium[1]		ICP	DCP
82WA104	189	32.8	46.7	-35.0	0.327	0.481
82WA106	180	34.8	49.0	-33.9	0.388	0.537
82WA107	188	34.5	48.7	-34.1	0.378	0.528
82WA109	206	35.3	49.0	-32.5	0.485	0.627
82WA110	483	39.5	56.3	-35.1	0.671	0.825
82WA112	564	36.2	52.5	-36.8	0.780	0.942
82WA113	631	46.1	63.3	-31.4	0.880	1.02
82WA115	686	45.2	62.4	-32.0	0.826	0.966
82WA116	790	38.7	52.1	-29.5	0.771	0.900
82WA120	680	<5.00	<5.00			
82WA122	504	49.1	64.9	-27.7	0.812	0.933
82WA124	912	5.32	16.0	-100.2	0.007	0.485
82WA129	517	43.1	55.4	-25.0	0.757	0.866
82WA130	530	43.3	57.8	-28.7	0.811	0.937
82WA131	833	41.6	53.0	-24.1	0.830	0.936
82WA145	158	21.6	29.7	-31.6	0.230	0.369
82WA149	723	27.7	39.8	-35.9	0.805	0.963
82WA151	764	26.4	38.8	-38.0	0.820	0.987
82WA152	1,480	28.2	43.8	-43.3	0.978	1.17
82WA155	364	<5.00	<5.00			
82WA157	1,670	<5.00	9.02			0.392
82WA160	1,550	27.6	42.5	-42.5	1.01	1.20
82WA161	1,870	22.9	35.6	-43.4	0.897	1.09
82WA163	1,520	27.4	40.9	-39.5	0.894	1.07
82WA164	1,570	31.2	46.1	-38.6	0.960	1.13

[1]DCP values are from Ball and Nordstrom (1985).

Table A-10. Results of analyses for barium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Sulfate (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)	Log IAP/K barite	
		ICP barium	DCP barium[1]		ICP	DCP
82WA100	2.36	12.7	16.2	-24.2	-1.51	-1.40
82WA101	2.86	13.7	19.9	-36.9	-1.42	-1.26
82WA102	5.41	14.7	19.8	-29.6	-1.13	-1.00
82WA103	8.17	15.7	22.6	-36.0	-0.972	-0.814
82WA105	38.9	39.1	48.0	-20.4	-0.157	-0.068
82WA108	1.89	35.0	42.3	-18.9	-1.32	-1.24
82WA111	283	23.8	30.3	-24.0	0.446	0.551
82WA114	57.2	73.6	83.9	-13.1	0.403	0.460
82WA117	5.30	58.4	71.2	-19.8	-0.622	-0.536
82WA121	276	62.5	75.9	-19.4	0.727	0.811
82WA123	1.14	24.9	31.4	-23.1	-1.84	-1.74
82WA125	2,340	<5.00	5.66			0.212
82WA126	190	34.0	42.5	-22.2	0.487	0.584
82WA127	1,600	5.55	10.1	-58.1	0.144	0.404
82WA128	1,650	14.7	23.4	-45.7	0.555	0.757

[1]DCP values are from Ball and Nordstrom (1985).

Table A-11. Results of analyses for barium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Sulfate (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)	Log IAP/K barite	
		ICP barium	DCP barium[1]		ICP	DCP
82WA141	19.7	19.7	18.4	6.8	-0.485	-0.515
82WA142	10.2	19.7	18.4	6.8	-0.796	-0.826
82WA143	156	29.0	28.5	1.7	0.343	0.336
82WA144	44.7	36.1	38.8	-7.2	-0.051	-0.019
82WA146	152	30.0	29.1	3.0	0.373	0.360
82WA147	1.26	31.0	28.4	8.8	-1.46	-1.50
82WA148	219	33.1	34.7	-4.7	0.641	0.661
82WA150	245	26.9	31.4	-15.4	0.465	0.532
82WA153	1.25	12.6	5.32	81.3	-1.89	-2.26
82WA154	1.27	<5.00	<5.00			
82WA156	2,030	<5.00	<5.00			
82WA158	1,580	17.6	17.6	0.0	0.670	0.670
82WA159	130	88.0	89.8	-2.0	0.934	0.943
82WA162	1,200	35.7	34.8	2.6	0.923	0.912
82WA166	143	60.3	65.1	-7.7	0.766	0.799
82WA170	7.21	55.6	63.7	-13.6	-0.422	-0.363

[1]DCP values are from Ball and Nordstrom (1985).

Table A-12. Results of analyses for barium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Sulfate (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)	Log IAP/K barite	
		ICP barium	DCP barium[2]		ICP	DCP
82WA118	7,540	57.9	7.35	154.9	1.38	0.481
82WA119	11,200	<50.0	12.5			0.741
82WA132	5,730	<50.0	12.0			0.545
82WA165	1,450	76.0	43.5	54.4	1.41	1.17
82WA167	2,880	55.7	15.9	111.2	1.36	0.819
82WA168	2,810	<50.0	8.36			0.518
82WA169	5,690	58.9	8.74	148.3	1.39	0.563

[1]Samples in Table A-12 were diluted 1/10 for ICP analysis.
[2]DCP values are from Ball and Nordstrom (1985).

Table A-13. Results of analyses for beryllium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})		ICP-DCP (Δ%)
	ICP	DCP[1]	
82WA104	<1.00	<2.00	
82WA106	<1.00	<2.00	
82WA107	<1.00	<2.00	
82WA109	<1.00	<2.00	
82WA110	<1.00	<2.00	
82WA112	<1.00	2.67	
82WA113	<1.00	<2.00	
82WA115	1.31	<2.00	
82WA116	1.79	2.44	-30.7
82WA120	3.40	3.89	-13.4
82WA122	<1.00	<2.00	
82WA124	6.38	7.12	-11.0
82WA129	<1.00	<2.00	
82WA130	<1.00	<2.00	
82WA131	1.85	2.42	-26.7
82WA145	<1.00	<2.00	
82WA149	<1.00	3.07	
82WA151	<1.00	2.74	
82WA152	4.11	6.25	-41.3
82WA155	<1.00	<2.00	
82WA157	7.94	9.40	-16.8
82WA160	4.65	6.65	-35.4
82WA161	5.96	7.56	-23.7
82WA163	3.96	6.45	-47.8
82WA164	4.94	7.00	-34.5

[1]DCP values are from Ball and Nordstrom (1985).

Table A-14. Results of analyses for beryllium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP[1]	ICP-DCP (Δ%)
82WA100	<1.00	<2.00	
82WA101	<1.00	<2.00	
82WA102	<1.00	<2.00	
82WA103	<1.00	<2.00	
82WA105	<1.00	<2.00	
82WA108	<1.00	<2.00	
82WA111	<1.00	<2.00	
82WA114	<1.00	<2.00	
82WA117	<1.00	<2.00	
82WA121	<1.00	<2.00	
82WA123	<1.00	<2.00	
82WA125	12.7	11.4	10.8
82WA126	<1.00	<2.00	
82WA127	7.17	7.31	-1.9
82WA128	<1.00	<2.00	

[1]DCP values are from Ball and Nordstrom (1985).

Table A-15. Results of analyses for beryllium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP[1]	ICP-DCP (Δ%)
82WA141	<1.00	<2.00	
82WA142	<1.00	<2.00	
82WA143	<1.00	<2.00	
82WA144	<1.00	<2.00	
82WA146	<1.00	<2.00	
82WA147	<1.00	<2.00	
82WA148	<1.00	<2.00	
82WA150	<1.00	<2.00	
82WA153	<1.00	<2.00	
82WA154	<1.00	<2.00	
82WA156	11.5	11.8	-2.6
82WA158	<1.00	<2.00	
82WA159	<1.00	<2.00	
82WA162	1.06	<2.00	
82WA166	<1.00	<2.00	
82WA170	<1.00	<2.00	

[1]DCP values are from Ball and Nordstrom (1985).

Table A-16. Results of analyses for beryllium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP[2]	ICP-DCP (Δ%)
82WA118	28.9	12.7	77.9
82WA119	27.4	12.2	76.8
82WA132	26.9	12.2	75.2
82WA165	15.5	6.46	82.3
82WA167	16.5	11.5	35.7
82WA168	16.7	11.9	33.6
82WA169	21.5	12.5	52.9

[1]Samples in this set were diluted 1/10 for ICP analysis.
[2]DCP values are from Ball and Nordstrom (1985).

Table A-17. Results of analyses for boron in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Ferrozine iron (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)
		ICP boron	DCP boron	
82WA104	4.59	<20	20	
82WA106	5.17	<20	<20	
82WA107	5.52	<20	<20	
82WA109	4.72	<20	<20	
82WA110	18.4	<20	22	
82WA112	55.7	<20	30	
82WA113	83.3	<20	26	
82WA115	117	<20	28	
82WA116	141	<20	49	
82WA120	60.6	81	136	-50.7
82WA122	80.0	<20	33	
82WA124	2.27	36	95	-90.1
82WA129	91.1	<20	44	
82WA130	81.3	<20	43	
82WA131	150	<20	47	
82WA145	0.0033	<20	<20	
82WA149	35.5	<20	33	
82WA151	56.2	<20	35	
82WA152	174	22	64	-97.7
82WA155	0.0336	<20	37	
82WA157	1.29	83	121	-37.3
82WA160	233	<20	69	
82WA161	277	30	72	-82.4
82WA163	266	37	91	-84.4
82WA164	308	59	86	-37.2

Table A-18. Results of analyses for boron in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Ferrozine iron (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)
		ICP boron	DCP boron	
82WA100	0.0207	<20	25	
82WA101	0.0239	<20	23	
82WA102	0.0394	<20	25	
82WA103	0.0087	<20	22	
82WA105	0.0242	<20	<20	
82WA108	0.0099	<20	<20	
82WA111	0.0207	<20	25	
82WA114	0.0091	<20	<20	
82WA117	0.0088	<20	<20	
82WA121	6.38	<20	27	
82WA123	0.0569	<20	<20	
82WA125	196	257	302	-16.1
82WA126	0.0154	<20	22	
82WA127	1.90	141	132	6.6
82WA128	0.0056	108	121	-11.4

Table A-19. Results of analyses for boron in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Ferrozine iron (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)
		ICP boron	DCP boron	
82WA141	0.0089	76	80	-5.1
82WA142	0.0426	78	89	-13.2
82WA143	0.0066	<20	<20	
82WA144	0.0389	<20	<20	
82WA146	0.0091	<20	<20	
82WA147	0.0110	<20	<20	
82WA148	7.00	<20	<20	
82WA150	0.0123	<20	<20	
82WA153	0.0058	<20	<20	
82WA154	0.0040	<20	<20	
82WA156	190	259	268	-3.4
82WA158	0.0124	156	106	38.2
82WA159	0.0127	69	<20	
82WA162	38.1	101	54	60.6
82WA166	11.4	51	<20	
82WA170	0.0041	<20	<20	

Table A-20. Results of analyses for boron in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Ferrozine iron (mg L^{-1})	Concentration (µg L^{-1})		ICP-DCP (Δ%)
		ICP boron	DCP boron	
82WA118	1570	560	122	128.4
82WA119	2510	<200	354	
82WA132	1210	<200	164	
82WA165	280	826	83	163.5
82WA167	631	573	148	117.9
82WA168	621	519	145	112.7
82WA169	1270	678	89	153.6

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-21. Results of analyses for cadmium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After Al correction ICP	After Al and Fe correction ICP	GFAAS-uncorrected ICP (Δ%)	GFAAS-Al corrected ICP (Δ%)	GFAAS-Al and Fe corrected ICP (Δ%)
82WA104	2.01	<1.00	[1]<1.00	[1]<1.00			
82WA106	2.16	<1.00	[1]<1.00	[1]<1.00			
82WA107	2.25	2.10	[1]2.10	[1]2.10	6.9	6.9	6.9
82WA109	4.01	1.37	[1]1.37	[1]1.37	98.1	98.1	98.1
82WA110	7.90	8.38	7.74	6.43	-5.9	[2]**2.0**	20.5
82WA112	8.20	6.79	6.15	3.25	**18.8**	28.6	86.5
82WA113	11.9	11.9	11.1	7.18	**0.0**	7.0	49.5
82WA115	13.4	15.6	14.8	9.61	-15.2	**-9.9**	32.9
82WA116	16.8	18.1	17.1	11.2	-7.4	**-1.8**	40.0
82WA120	2.84	4.58	3.85	<1.00	-46.9	**-30.2**	
82WA122	4.54	5.59	5.05	1.12	-20.7	**-10.6**	120.8
82WA124	4.64	3.71	2.86	[1]2.86	**22.3**	47.5	47.5
82WA129	5.14	6.38	5.71	1.36	-21.5	**-10.5**	116.3
82WA130	4.83	6.63	6.11	2.02	-31.4	**-23.4**	82.0
82WA131	14.4	18.8	17.7	11.4	-26.5	**-20.6**	23.3
82WA145	0.24	<1.00	[1]<1.00	[1]<1.00			
82WA149	3.88	4.48	3.84	1.65	-14.4	**1.0**	80.7
82WA151	3.06	4.96	4.35	1.10	-47.4	**-34.8**	94.2
82WA152	7.95	12.5	11.4	4.49	-44.5	**-35.7**	55.6
82WA155	1.96	1.96	[1]1.96	[1]1.96	0.0	0.0	0.0
82WA157	6.74	6.34	5.02	[1]5.02	6.1	29.3	29.3
82WA160	8.82	14.7	13.6	5.15	-50.0	**-42.6**	52.5
82WA161	10.3	19.5	18.1	8.64	-61.7	-54.9	**17.5**
82WA163	8.13	15.9	14.7	5.35	-64.7	-57.6	**41.2**
82WA164	9.98	19.4	18.1	7.96	-64.1	-57.8	**22.5**

[1]No correction was made for this interferent.
[2]**Bold** indicates the smallest ICP Δ% value.

Table A-22. Results of analyses for cadmium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After Al correction ICP	After Al and Fe correction ICP	GFAAS-uncorrected ICP (Δ%)	GFAAS-Al corrected ICP (Δ%)	GFAAS-Al and Fe corrected ICP (Δ%)
82WA101	1.21	<1.00	[1]<1.00	[1]<1.00			
82WA102	0.30	<1.00	[1]<1.00	[1]<1.00			
82WA103	0.62	<1.00	[1]<1.00	[1]<1.00			
82WA105	0.15	<1.00	[1]<1.00	[1]<1.00			
82WA108	0.18	<1.00	[1]<1.00	[1]<1.00			
82WA111	0.42	<1.00	[1]<1.00	[1]<1.00			
82WA114	0.06	<1.00	[1]<1.00	[1]<1.00			
82WA117	0.08	<1.00	[1]<1.00	[1]<1.00			
82WA121	0.31	<1.00	[1]<1.00	[1]<1.00			
82WA123	2.41	<1.00	[1]<1.00	[1]<1.00			
82WA125	8.40	10.8	9.19	1.59	-25.0	[2]**-9.0**	136.3
82WA126	0.79	2.58	[1]2.58	[1]2.58	-106.2	-106.2	-106.2
82WA127	7.31	5.45	4.18	[1]4.18	**29.2**	54.5	54.5
82WA128	1.26	<1.00	[1]<1.00	[1]<1.00			

[1]No correction was made for this interferent.
[2]**Bold** indicates the smallest ICP Δ% value.

Table A-23. Results of analyses for cadmium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After Al correction ICP	After Al and Fe correction ICP	GFAAS-uncorrected ICP (Δ%)	GFAAS-Al corrected ICP (Δ%)	GFAAS-Al and Fe corrected ICP (Δ%)
82WA141	0.09	<1.00	[1]<1.00	[1]<1.00			
82WA142	0.09	<1.00	[1]<1.00	[1]<1.00			
82WA143	0.28			1.41			-133.7
82WA144	0.07	<1.00	[1]<1.00	[1]<1.00			
82WA146	0.21	<1.00	[1]<1.00	[1]<1.00			
82WA147	0.08	<1.00	[1]<1.00	[1]<1.00			
82WA148	1.64			2.13			-25.0
82WA150	0.13	<1.00	[1]<1.00	[1]<1.00			
82WA153	<0.05			1.01			
82WA154	<0.05	<1.00	[1]<1.00	[1]<1.00			
82WA156	5.08	11.2	9.85	2.58	-75.2	[2]**-63.9**	65.3
82WA158	0.33			1.95			-142.1
82WA159	<0.05			2.07			
82WA162	0.72		5.89	3.68		-156.4	**-134.5**
82WA166	1.68		4.78	3.88		-96.0	**-79.1**
82WA170	0.46			1.80			-118.6

[1]No correction was made for this interferent.
[2]**Bold** indicates the smallest ICP Δ% value.

Table A-24. Results of analyses for cadmium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	DCP	Uncorrected ICP	After Al correction ICP	After Al and Fe correction ICP	GFAAS-DCP (Δ%)	GFAAS-uncorrected ICP (Δ%)	GFAAS-Al corrected ICP (Δ%)	GFAAS-Al & Fe corrected ICP (Δ%)
82WA118	282	209	275	264	201	29.7	[2]**2.5**	6.6	33.5
82WA119	338	271	353	339	251	22.0	-4.3	**-0.3**	29.5
82WA132	188	156	223	214	160	18.6	-17.0	**-12.9**	16.1
82WA165	9.71	<10.0		38.7	21.1			-119.8	**-73.9**
82WA167	15.4	13.3	48.9	44.9	11.8	14.6	-104.2	-97.8	**26.5**
82WA168	18.2	15.2	32.6	28.6	<10.0	18.0	-56.7	**-44.4**	
82WA169	194	160	195	184	130	19.2	**-0.5**	5.3	39.5

[1]Samples in this set were diluted 1/10 for ICP analysis.
[2]**Bold** indicates the smallest ICP Δ% value.

Table A-25. Results of analyses for calcium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Mean	ICP-DCP (Δ%)
82WA104	41.3	39.9	40.6	-3.4
82WA106	39.1	38.1	38.6	-2.6
82WA107	38.8	43.2	41.0	10.7
82WA109	42.1	47.3	44.7	11.6
82WA110	76.8	87.6	82.2	13.1
82WA112	80.5	87.1	83.8	7.9
82WA113	78.6	84.5	81.6	7.2
82WA115	83.2	92.6	87.9	10.7
82WA116	89.0	103	96.0	14.6
82WA120	60.2	69.5	64.9	14.3
82WA122	72.1	77.8	75.0	7.6
82WA124	203	214	209	5.3
82WA129	49.3	64.0	56.7	25.9
82WA130	76.5	87.5	82.0	13.5
82WA131	87.9	103	95.5	15.8
82WA145	41.3	42.4	41.9	2.6
82WA149	144	142	143	-1.4
82WA151	147	142	145	-3.5
82WA152	217	221	219	1.8
82WA155	88.9	94.8	91.9	6.4
82WA157	384	414	399	7.5
82WA160	221	221	221	0.0
82WA161	249	259	254	3.9
82WA163	206	203	205	-1.5
82WA164	182	169	176	-7.4

Table A-26. Results of analyses for calcium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})			ICP-DCP (Δ%)
	DCP	ICP	Mean	
82WA100	5.61	5.09	5.35	-9.7
82WA101	5.57	4.88	5.23	-13.2
82WA102	5.94	5.46	5.70	-8.4
82WA103	6.58	5.86	6.22	-11.6
82WA105	31.2	28.2	29.7	-10.1
82WA108	13.9	13.4	13.7	-3.7
82WA111	83.2	74.1	78.7	-11.6
82WA114	25.9	24.0	25.0	-7.6
82WA117	10.8	9.97	10.4	-8.0
82WA121	105	94.7	99.9	-10.3
82WA123	23.6	22.6	23.1	-4.3
82WA125	416	367	392	-12.5
82WA126	53.4	50.5	52.0	-5.6
82WA127	368	336	352	-9.1
82WA128	489	441	465	-10.3

Table A-27. Results of analyses for calcium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Mean	ICP-DCP (Δ%)
82WA141	11.9	13.1	12.5	9.6
82WA142	9.81	10.8	10.3	9.6
82WA143	39.4	43.5	41.5	9.9
82WA144	31.3	33.0	32.2	5.3
82WA146	41.2	42.8	42.0	3.8
82WA147	14.5	16.2	15.4	11.1
82WA148	51.0	51.3	51.2	0.6
82WA150	76.0	78.8	77.4	3.6
82WA153	22.0	23.6	22.8	7.0
82WA154	19.8	21.4	20.6	7.8
82WA156	379	366	373	-3.5
82WA158	462	468	465	1.3
82WA159	40.6	44.4	42.5	8.9
82WA162	354	314	334	-12.0
82WA166	24.1	24.4	24.3	1.2
82WA170	12.0	13.9	13.0	14.7

Table A-28. Results of analyses for calcium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})			ICP-DCP (Δ%)
	DCP	ICP	Mean	
82WA118	136	126	131	-7.6
82WA119	273	258	266	-5.6
82WA132	237	231	234	-2.6
82WA165	165	152	158	-8.0
82WA167	303	311	307	2.6
82WA168	308	311	310	1.0
82WA169	115	113	114	-1.7

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-29. Results of analyses for chromium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After correction ICP	Uncorrected DCP	After correction DCP	Uncorrected ICP-GFAAS (Δ%)	After correction ICP-GFAAS (Δ%)	Uncorrected DCP-GFAAS (Δ%)	After correction DCP-GFAAS (Δ%)
82WA104	0.1	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA106	0.2	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA107	0.3	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA109	2.7	<3.0	[1]<3.0	9.84	<3.0			113.9	
82WA110	44.7	33.5	27.7	49.6	36.5	-28.6	-47.0	10.4	-20.2
82WA112	63.2	52.4	46.9	41.9	27.8	-18.7	-29.6	-40.5	-77.8
82WA113	105	81.0	17.7	106	92.4	-25.8	-142.3	0.9	-12.8
82WA115	124	103	80.2	127	112	-18.5	-42.9	2.4	-10.2
82WA116	154	137	116	152	136	-11.7	-28.1	-1.3	-12.4
82WA120	76.0	60.4	50.6	81.0	70.1	-22.9	-40.1	6.4	-8.1
82WA122	13.0	6.1	<3.0	<3.0	[1]<3.0	-72.5			
82WA124	5.3	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA129	29.0	19.3	<3.0	13.2	3.94	-40.2		-74.9	-152.2
82WA130	13.5	18.0	<3.0	<3.0	[1]<3.0	28.6			
82WA131	168	154	133	172	156	-8.7	-23.3	2.4	-7.4
82WA145	0.1	<3.0	[1]<3.0	15.7	8.56			197.5	195.4
82WA149	29.6	19.3	14.0	55.4	32.3	-42.1	-71.6	60.7	8.7
82WA151	41.3	29.7	24.6	51.8	27.9	-32.7	-50.7	22.6	-38.7
82WA152	114	105	82.6	114	79.7	-8.2	-31.9	0.0	-35.4
82WA155	0.7	<3.0	[1]<3.0	23.8	9.14			188.6	171.5
82WA157	7.6	<3.0	[1]<3.0	24.7	<3.0			105.9	
82WA160	132	115	91.2	130	94.5	-13.8	-36.6	-1.5	-33.1
82WA161	162	140	115	147	107	-14.6	-33.9	-9.7	-40.9
82WA163	94.1	80.9	56.8	101	66.6	-15.1	-49.4	7.1	-34.2
82WA164	118	125	99.1	115	83.3	5.8	-17.4	-2.6	-34.5

[1]No interelement interference correction was made for this analyte.

Table A-30. Results of analyses for chromium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After correction ICP	Uncorrected DCP	After correction DCP	Uncorrected ICP-GFAAS (Δ%)	After correction ICP-GFAAS (Δ%)	Uncorrected DCP-GFAAS (Δ%)	After correction DCP-GFAAS (Δ%)
82WA100	0.3	<3.0	[1]<3.0	20.2	[1]20.2			194.1	194.1
82WA101	0.3	<3.0	[1]<3.0	19.5	[1]19.5			193.9	193.9
82WA102	0.3	<3.0	[1]<3.0	29.4	[1]29.4			196.0	196.0
82WA103	0.1	<3.0	[1]<3.0	25.1	[1]25.1			198.4	198.4
82WA105	0.2	5.5	<3.0	3.9	<3.0	186.0		180.5	
82WA108	9.0	9.5	4.2	21.1	18.7	5.8	-72.5	80.4	70.0
82WA111	0.1	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA114	1.4	<3.0	[1]<3.0	13.8	9.3			163.2	147.4
82WA117	0.3	<3.0	[1]<3.0	14.5	12.6			191.9	190.7
82WA121	0.2	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA123	0.8	<3.0	[1]<3.0	3.3	<3.0		121.2		
82WA125	13	28.6	7.6	52.4	<3.0	75.0	-52.9	120.5	
82WA126	0.2	<3.0	[1]<3.0	<3.0	[1]<3.0				
82WA127	6.5	<3.0	[1]<3.0	44.6	<3.0			149.1	
82WA128	0.7	<3.0	[1]<3.0	50.2	<3.0			194.5	

[1]No interelement interference correction was made for this analyte.

Table A-31. Results of analyses for chromium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After correction ICP	Uncorrected DCP	After correction DCP	Uncorrected ICP-GFAAS (Δ%)	After correction ICP-GFAAS (Δ%)	Uncorrected DCP-GFAAS (Δ%)	After correction DCP-GFAAS (Δ%)
82WA141	0.3	<3.0	[1]<3.0	17.3	15.2			193.2	192.3
82WA142	0.2	7.3	4.1	17.4	[1]17.4	189.3	181.5	195.5	195.5
82WA143	0.6	<3.0	[1]<3.0	21.9	15.1			189.3	184.7
82WA144	0.4	5.2	<3.0	14.7	9.3	171.6		189.4	183.5
82WA146	0.6	<3.0	[1]<3.0	22.8	15.7			189.7	185.3
82WA147	0.3	<3.0	[1]<3.0	24.0	21.4			195.1	194.5
82WA148	0.8	10.3	5.1	<3.0	[1]<3.0	171.2	145.9		
82WA150	4.8	<3.0	[1]<3.0	31.3	18.6			146.8	117.9
82WA153	0.2	<3.0	[1]<3.0	26.3	23.5			197.0	196.6
82WA154	0.7	<3.0	[1]<3.0	15.2	11.8			182.4	177.6
82WA156	11.6	20.5	<3.0	31.5	<3.0	55.5		92.3	
82WA158	0.3	7.5	[1]7.5	20.4	<3.0	184.7	184.7	194.2	
82WA159	0.6	3.2	<3.0	16.4	9.4	136.0		185.9	176.0
82WA162	0.3	<3.0	[1]<3.0	30.1	<3.0			196.1	
82WA166	3.9	<3.0	[1]<3.0	8.0	3.6			68.4	-7.7
82WA170	0.2	17.4	4.9	12.2	10.1	195.5	184.2	193.5	192.2

[1]No interelement interference correction was made for this analyte.

Table A-32. Results of analyses for chromium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) GFAAS	Uncorrected ICP	After correction ICP	Uncorrected DCP	After correction DCP	Uncorrected ICP-GFAAS (Δ%)	After correction ICP-GFAAS (Δ%)	Uncorrected DCP-GFAAS (Δ%)	After correction DCP-GFAAS (Δ%)
82WA118		2540	2390	2620	2580				
82WA119		3840	3670	3530	3500				
82WA132		2180	2020	1990	1930				
82WA165	82.6	<30.0	[2]<30.0	97.9	69.1			17.0	-17.8
82WA167	198	199	[2]199	194	143	0.5	0.5	-2.0	-32.3
82WA168	177	47.9	[2]47.9	180	128	-114.8	-114.8	1.7	-32.1
82WA169		2320	2160	2300	2270				

[1]Samples in this set were diluted 1/10 for ICP analysis.
[2]No interelement interference correction was made for this analyte.

Table A-33. Results of analyses for cobalt in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})					Primary ICP-DCP (Δ%)	Alternative ICP-DCP (Δ%)	Primary ICP-GFAAS (Δ%)	Alternative ICP-GFAAS (Δ%)
	Primary ICP	Alternative ICP	Primary DCP	Alternative DCP	GFAAS				
82WA104	68.3	81.3	76.7		79.4	-11.6	5.8	-15.0	2.4
82WA106	73.9	86.9	84.1		82.1	-12.9	3.3	-10.5	5.7
82WA107	88.1		83.7		87.9	5.1		0.2	
82WA109	112		105			6.5			
82WA110	276		268			2.9			
82WA112	283		278			1.8			
82WA113	400		403			-0.7			
82WA115	466		445			4.6			
82WA116	541		536			0.9			
82WA120	99.3		102			-2.7			
82WA122	326		333			-2.1			
82WA124	182		185			-1.6			
82WA129	363		372			-2.4			
82WA130	323		321			0.6			
82WA131	566		533			6.0			
82WA145	36.2	43.3	48.6		51.9	-29.2	-11.5	-35.6	-18.1
82WA149	322		314			2.5			
82WA151	320		314			1.9			
82WA152	753		801	744		-6.2	1.2		
82WA155	26.1		41.4		28.6	-45.3		-9.1	
82WA157	409		383			6.6			
82WA160	802		790			1.5			
82WA161	970		926			4.6			
82WA163	894		909			-1.7			
82WA164	1020		1010			1.0			

Table A-34. Results of analyses for cobalt in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})					Primary ICP-DCP (Δ%)	Primary ICP-Alternative DCP (Δ%)	Primary ICP-GFAAS (Δ%)	Alternative ICP-GFAAS (Δ%)
	Primary ICP	Alternative ICP	Primary DCP	Alternative DCP	GFAAS				
82WA100	<5.0		17.1		<1.0				
82WA101	<5.0		15.6		<1.0				
82WA102	<5.0		24.1		1.0				
82WA103	<5.0		19.8		1.6				
82WA105	<5.0		<5.0		<1.0				
82WA108	21.7		32.1		24.7	-38.7		-12.9	
82WA111	14.7		<5.0		17.6			-18.0	
82WA114	<5.0		6.3		<1.0				
82WA117	<5.0		10.7		<1.0				
82WA121	32.6		27.9		36.9	15.5		-12.4	
82WA123	<5.0		<5.0		1.2				
82WA125	485		629	496		-25.9	-2.2		
82WA126	13.7		9.1		15.4	40.4		-11.7	
82WA127	375		387			-3.1			
82WA128	68.6		85.3			-21.7			

Table A-35. Results of analyses for cobalt in samples with pH from 5.08 to 8.25 [except sample 82WA155 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})					Primary ICP-DCP (Δ%)	Alternative ICP-DCP (Δ%)	Primary ICP-GFAAS (Δ%)	Alternative ICP-GFAAS (Δ%)
	Primary ICP	Alternative ICP	Primary DCP	Alternative DCP	GFAAS				
82WA141	<5.0		13.8		1.8				
82WA142	<5.0		12.3		<1.0				
82WA143	38.6		46.4		44.2	-18.4		-13.5	
82WA144	<5.0		<5.0		<1.0				
82WA146	56.4		59.0		60.5	-4.5		-7.0	
82WA147	<5.0		15.6		<1.0				
82WA148	98.4		89.6			9.4			
82WA150	8.1		27.3		11.5	-108.5		-34.7	
82WA153	<5.0		11.8		<1.0				
82WA154	<5.0		<5.0		<1.0				
82WA156	446		423			5.3			
82WA158	11.2		<5.0		13.6			-19.4	
82WA159	<5.0		8.8		<1.0				
82WA162	180		191			-5.9			
82WA166	65.6	72.9	68.4		71.4	-4.2		-8.5	2.1
82WA170	<5.0		<5.0		<1.0				

Table A-36. Results of analyses for cobalt in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})					Primary ICP-DCP (Δ%)	Primary ICP-Alternative DCP (Δ%)	Primary ICP-GFAAS (Δ%)	Alternative ICP-GFAAS (Δ%)
	Primary ICP	Alternative ICP	Primary DCP	Alternative DCP	GFAAS				
82WA118	5110		4870			4.8			
82WA119	5070		4750			6.5			
82WA132	3970		3700			7.0			
82WA165	963		849	919		12.6	4.7		
82WA167	2140		2040			4.8			
82WA168	2040		2000			2.0			
82WA169	4080		3960			3.0			

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-37. Results of analyses for copper in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA104	19.1	48.1	53.2	45	-86.3	-94.3	-80.8
82WA106	<10.0	44.4	45.6	38			
82WA107	45.3	70.2	70.9	55	-43.1	-44.1	-19.3
82WA109	68.3	106	105	93	-43.3	-42.4	-30.6
82WA110	222	278	236	230	-22.4	-6.1	-3.5
82WA112	221	270	282	230	-20.0	-24.3	-4.0
82WA113	253	338	313	260	-28.8	-21.2	-2.7
82WA115	311	364	345	260	-15.7	-10.4	17.9
82WA116	338	397	405	350	-16.1	-18.0	-3.5
82WA120	444	499	531	420	-11.7	-17.8	5.6
82WA122	142	188	180	160	-27.9	-23.6	-11.9
82WA124	465	536	522	470	-14.2	-11.6	-1.1
82WA129	159	197	202	190	-21.3	-23.8	-17.8
82WA130	124	169	164	150	-30.7	-27.8	-19.0
82WA131	479	528	559	450	-9.7	-15.4	6.2
82WA145	16.4	26.4	24.5	34	-46.7	-39.6	-69.8
82WA149	95.2	130	135	110	-30.9	-34.6	-14.4
82WA151	93.4	118	123	100	-23.3	-27.4	-6.8
82WA152	194	249	248	200	-24.8	-24.4	-3.0
82WA155	353	380	373	310	-7.4	-5.5	13.0
82WA157	782	852	930		-8.6	-17.3	
82WA160	204	263	275	210	-25.3	-29.6	-2.9
82WA161	259	319	343	220	-20.8	-27.9	16.3
82WA163	186	226	249	200	-19.4	-29.0	-7.3
82WA164	223	286	288	210	-24.8	-25.4	6.0

Table A-38. Results of analyses for copper in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	<10.0	<10.0	<3.0	1.7			
82WA101	<10.0	<10.0	<3.0	<0.5			
82WA102	<10.0	<10.0	<3.0	1.8			
82WA103	<10.0	<10.0	<3.0	1.8			
82WA105	<10.0	<10.0	<3.0	1.8			
82WA108	<10.0	<10.0	<3.0	1.0			
82WA111	<10.0	13.6	13.8	12			
82WA114	<10.0	<10.0	<3.0	1.8			
82WA117	<10.0	<10.0	<3.0	1.4			
82WA121	<10.0	<10.0	<3.0	0.7			
82WA123	<10.0	<10.0	<3.0	1.1			
82WA125	1620	1870	1950		-14.3	-18.5	
82WA126	25.3	<10.0	5.4	6.3		129.6	120.3
82WA127	666	750	771		-11.9	-14.6	
82WA128	34.1	11.7	14.2	9.6	97.8	82.4	112.1

Table A-39. Results of analyses for copper in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA141	<10.0	<10.0	<3.0	1.1			
82WA142	<10.0	<10.0	<3.0	0.9			
82WA143	<10.0	<10.0	<3.0	1.7			
82WA144	<10.0	<10.0	<3.0	1.4			
82WA146	<10.0	<10.0	<3.0	1.7			
82WA147	<10.0	<10.0	<3.0	2.0			
82WA148	<10.0	19.8	20.6	17			
82WA150	<10.0	<10.0	<3.0	1.5			
82WA153	20.3	<10.0	<3.0	2.1			162.5
82WA154	13.8	<10.0	<3.0	1.1			170.5
82WA156	1390	1560	1560		-11.5	-11.5	
82WA158	24.4	<10.0	7.7	7.0		104.0	110.8
82WA159	<10.0	<10.0	<3.0	0.7			
82WA162	36.0	<10.0	<3.0	<0.5			
82WA166	35.1	26.7	27.3	26	27.2	25.0	29.8
82WA170	<10.0	<10.0	<3.0	<0.5			

Table A-40. Results of analyses for copper in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA118	4910	5390	5250	4100	-9.3	-6.7	18.0
82WA119	8180	10100	9180		-21.0	-11.5	
82WA132	4870	5470	5380		-11.6	-10.0	
82WA165	422	225	234	190	60.9	57.3	75.8
82WA167	176	85.3	85.5	63	69.4	69.2	94.6
82WA168	787	495	498	400	45.6	45.0	65.2
82WA169	1570	1460	1490		7.3	5.2	

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-41. Results of analyses for iron in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-ferrozine (Δ%)	Cassette 1 DCP-ferrozine (Δ%)	Cassette 2 DCP-ferrozine (Δ%)
	Ferrozine	ICP	Cassette 1 DCP	Cassette 2 DCP			
82WA104	4.59	4.49	3.98	5.13	-2.2	-14.2	11.1
82WA106	5.17	4.94	4.29	5.62	-4.5	-18.6	8.3
82WA107	5.52	5.79	4.66	6.20	4.8	-16.9	11.6
82WA109	4.72	4.65	3.48	4.74	-1.5	-30.2	0.4
82WA110	18.4	18.7	17.4	19.4	1.6	-5.6	5.3
82WA112	55.7	52.7	48.3	52.1	-5.5	-14.2	-6.7
82WA113	83.3	78.3	72.4	78.5	-6.2	-14.0	-5.9
82WA115	117	112	106	112	-4.4	-9.9	-4.4
82WA116	141	133	120	137	-5.8	-16.1	-2.9
82WA120	60.6	61.1	53.8	62.6	0.8	-11.9	3.2
82WA122	80.0	78.4	70.0	78.3	-2.0	-13.3	-2.1
82WA124	2.27	2.22	2.32	2.40	-2.2	2.2	5.6
82WA129	91.1	89.6	68.3	88.6	-1.7	-28.6	-2.8
82WA130	81.3	82.6	69.4	79.2	1.6	-15.8	-2.6
82WA131	150	145	138	148	-3.4	-8.3	-1.3
82WA145	0.0033	<0.015	<0.015	<0.02			
82WA149	35.5	36.5	35.3	32.4	2.8	-0.6	-9.1
82WA151	56.2	61.1	58.2	53.8	8.4	3.5	-4.4
82WA152	174	164	158	185	-5.9	-9.6	6.1
82WA155	0.0336	0.133	<0.015	<0.02	119		
82WA157	1.29	1.36	1.96	1.68	5.3	41.2	26.3
82WA160	233	212	216	256	-9.4	-7.6	9.4
82WA161	277	247	277	216	-11.5	0.0	-24.7
82WA163	266	244	231	275	-8.6	-14.1	3.3
82WA164	308	271	278	265	-12.8	-10.2	-15.0

Table A-42. Results of analyses for iron in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration ($mg\ L^{-1}$)				ICP-ferrozine (Δ%)	Cassette 1 DCP-ferrozine (Δ%)	Cassette 2 DCP-ferrozine (Δ%)
	Ferrozine	ICP	Cassette 1 DCP	Cassette 2 DCP			
82WA100	0.0207	<0.015	<0.015	<0.02			
82WA101	0.0239	<0.015	<0.015	<0.02			
82WA102	0.0394	<0.015	0.032	<0.02		-20.7	
82WA103	0.0087	<0.015	0.028	<0.02		105.2	
82WA105	0.0242	<0.015	<0.015	<0.02			
82WA108	0.0099	<0.015	0.126	0.034		170.9	109.8
82WA111	0.0207	<0.015	<0.015	<0.02			
82WA114	0.0091	<0.015	<0.015	<0.02			
82WA117	0.0088	<0.015	<0.015	<0.02			
82WA121	6.38	6.68	6.39	6.85	4.6	0.2	7.1
82WA123	0.0569	<0.015	<0.015	<0.02			
82WA125	196	185	200	198	-5.8	2.0	1.0
82WA126	0.0154	<0.015	<0.015	<0.02			
82WA127	1.90	1.79	2.11	2.18	-6.0	10.5	13.7
82WA128	0.0056	<0.015	<0.015	0.099			178.6

Table A-43. Results of analyses for iron in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-ferrozine (Δ%)	Cassette 1 DCP-ferrozine (Δ%)	Cassette 2 DCP-ferrozine (Δ%)
	Ferrozine	ICP	Cassette 1 DCP	Cassette 2 DCP			
82WA141	0.0089	0.022	<0.015	0.822	84.8		195.7
82WA142	0.0426	0.054	0.026	0.853	23.6	-48.4	181.0
82WA143	0.0066	0.214	<0.015	<0.02	188		
82WA144	0.0389	0.034	<0.015	<0.02	-13.4		
82WA146	0.0091	<0.015	<0.015	<0.02			
82WA147	0.0110	<0.015	<0.015	0.939			195.4
82WA148	7.00	7.42	6.91	7.47	5.8	-1.3	6.5
82WA150	0.0123	0.049	<0.015	0.042	120		109.4
82WA153	0.0058	<0.015	<0.015	<0.02			
82WA154	0.0040	<0.015	<0.015	<0.02			
82WA156	190	175	193	220	-8.2	1.6	14.6
82WA158	0.0124	<0.015	<0.015	<0.02			
82WA159	0.0127	<0.015	<0.015	<0.02			
82WA162	38.1	37.0	38.0	36.6	-2.9	-0.3	-4.0
82WA166	11.4	11.4	10.9	11.4	0.0	-4.5	0.0
82WA170	0.0041	0.263	0.307	0.339	194	194.7	195.2

Table A-44. Results of analyses for iron in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-ferrozine (Δ%)	Cassette 1 DCP-ferrozine (Δ%)	Cassette 2 DCP-ferrozine (Δ%)
	Ferrozine	ICP	Cassette 1 DCP	Cassette 2 DCP			
82WA118	1570	1450	1660	1230	-7.9	5.6	-24.3
82WA119	2510	2260	2050	3120	-10.5	-20.2	21.7
82WA132	1210	1180	1190	1260	-2.5	-1.7	4.0
82WA165	280	275	231	215	-1.8	-19.2	-26.3
82WA167	631	626	621	713	-0.8	-1.6	12.2
82WA168	621	605	627	643	-2.6	1.0	3.5
82WA169	1270	1200	1230	1310	-5.7	-3.2	3.1

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-45. Results of analyses for lead in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA104	<20.0	<20.0	<0.5		
82WA106	<20.0	<20.0	<0.5		
82WA107	<20.0	<20.0	<0.5		
82WA109	<20.0	<20.0	<0.5		
82WA110	<20.0	82.2	<0.5		
82WA112	<20.0	27.2	0.9		
82WA113	<20.0	98.1	<0.5		
82WA115	<20.0	87.5	1.9		
82WA116	<20.0	103	2.5		
82WA120	<20.0	50.8	<0.5		
82WA122	<20.0	<20.0	1.3		
82WA124	<20.0	102	<0.5		
82WA129	<20.0	51.2	0.5		
82WA130	<20.0	47.3	<0.5		
82WA131	<20.0	125	2.4		
82WA145	<20.0	78.3	<0.5		
82WA149	<20.0	148	1.1		
82WA151	<20.0	113	<0.5		
82WA152	22.8	153	<0.5	-148.1	
82WA155	<20.0	160	0.7		
82WA157	<20.0	188	0.5		
82WA160	<20.0	152	<0.5		
82WA161	<20.0	154	0.9		
82WA163	<20.0	153	<0.5		
82WA164	<20.0	113	3.6		

Table A-46. Results of analyses for lead in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	<20.0	26.5	<0.5		
82WA101	<20.0	26.8	<0.5		
82WA102	<20.0	56.6	<0.5		
82WA103	<20.0	46.8	<0.5		
82WA105	<20.0	<20.0	<0.5		
82WA108	<20.0	<20.0	<0.5		
82WA111	<20.0	<20.0	<0.5		
82WA114	<20.0	30.6	11.2		
82WA117	<20.0	<20.0	1.2		
82WA121	<20.0	53.4	<0.5		
82WA123	<20.0	<20.0	<0.5		
82WA125	23.9	242	<0.5	-164.0	
82WA126	<20.0	21.6	<0.5		
82WA127	<20.0	264	0.8		
82WA128	<20.0	266	0.5		

Table A-47. Results of analyses for lead in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA141	<20.0	45.1	<0.5		
82WA142	<20.0	49.7	0.6		
82WA143	<20.0	128	2.7		
82WA144	<20.0	71.5	<0.5		
82WA146	<20.0	119	<0.5		
82WA147	<20.0	73.5	<0.5		
82WA148	<20.0	71.5	<0.5		
82WA150	<20.0	150	<0.5		
82WA153	<20.0	93.2	<0.5		
82WA154	<20.0	54.2	<0.5		
82WA156	21.1	184	<0.5	-158.8	
82WA158	<20.0	176	<0.5		
82WA159	<20.0	98.0	<0.5		
82WA162	<20.0	197	<0.5		
82WA166	<20.0	37.5	<0.5		
82WA170	<20.0	35.6	0.5		

Table A-48. Results of analyses for lead in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})			ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	DCP	GFAAS		
82WA118	479	215	74.4	76.1	146.2
82WA119	635	183	37.7	110.5	177.6
82WA132	<200	239	34.9		
82WA165	<200	155	<0.5		
82WA167	<200	190	3.9		
82WA168	<200	194	<0.5		
82WA169	234	148	32.2	45.0	151.6

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-49. Results of analyses for magnesium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Undiluted ICP (mg L^{-1})	Charge balance (Δ%)	Undiluted DCP (mg L^{-1})	Charge balance (Δ%)	1/10 diluted DCP (mg L^{-1})	Charge balance (Δ%)	1/100 diluted DCP (mg L^{-1})	Charge balance (Δ%)	1/1000 diluted DCP (mg L^{-1})	Charge balance (Δ%)	Ball and Nordstrom (1985) (mg L^{-1})	WATEQ4F (mg L^{-1})	WATEQ4F Charge balance (Δ%)	WATEQ4F (Δ%)
82WA104	13.3	[1]**0.21**	13.4	0.42	13.3	0.21	16.6	6.80	-	-	13	13.4	0.42	-0.7
82WA106	12.7	-0.96	12.4	-1.62	12.8	**-0.75**	15.6	5.13	-	-	12	12.4	-1.62	2.4
82WA107	14.0	**-0.54**	12.7	-3.30	12.7	-3.30	15.6	2.76	-	-	13	12.7	-3.30	9.7
82WA109	14.1	4.42	12.9	2.21	12.8	**2.03**	15.6	7.10	-	-	13	12.9	2.21	8.9
82WA110	24.9	**-0.018**	22.6	-1.91	22.3	-2.16	28.3	2.71	-	-	22	22.3	-2.16	11.0
82WA112	25.0	-3.89	23.5	-4.98	22.6	-5.64	29.3	**-0.83**	-	-	23	22.6	-5.64	10.1
82WA113	25.5	3.01	>24	-	22.8	**1.37**	29.7	5.51	-	-	23	[2]29.7	5.51	-15.2 (11.2)
82WA115	27.0	6.05	>24	-	23.3	**4.03**	30.5	7.91	-	-	23	[2]30.5	7.91	-12.2 (14.7)
82WA116	30.4	4.76	>24	-	26.5	**2.90**	33.7	6.31	-	-	26	[2]33.7	6.31	-10.3 (13.7)
82WA120	15.8	-6.36	13.8	-7.59	13.9	-7.53	19.4	**-4.17**	-	-	14	13.8	-7.59	13.5
82WA122	22.0	2.66	20.2	1.29	19.6	**0.83**	25.7	5.43	-	-	20	20.2	1.29	8.5
82WA124	56.8	2.95	>24	-	49.3	**-0.23**	59.2	3.95	-	-	49	[2]59.2	3.95	-4.1 (14.1)
82WA129	19.3	**-8.18**	18.2	-9.09	16.8	-10.25	19.1	-8.34	-	-	18	18.2	-9.09	5.9
82WA130	24.7	-9.07	23.7	-9.81	21.7	-11.29	28.5	**-6.33**	-	-	22	21.7	-11.29	12.9
82WA131	29.3	**0.66**	>24	-	24.7	-1.52	32.4	2.10	-	-	25	[2]32.4	2.10	-10.0 (17.0)
82WA145	15.5	**-0.25**	14.6	-2.14	14.9	-1.50	-	-	-	-	15	14.6	-2.14	6.0
82WA149	41.4	5.31	>24	-	35.2	**2.07**	38.0	3.55	27.1	-2.33	35	35.2	2.07	16.2
82WA151	40.8	1.23	>24	-	35.0	-1.75	38.6	**0.11**	25.3	-6.95	35	35.0	-1.75	15.3
82WA152	66.8	**-0.086**	>24	-	56.2	-2.94	61.3	-1.56	62.2	-1.32	56	56.2	-2.94	17.2
82WA155	23.5	4.14	21.7	2.27	21.5	**2.06**	27.3	7.99	-	-	22	21.5	2.06	8.9
82WA157	108	2.73	>24	-	96.5	**0.073**	105	2.05	122	5.88	96	96.5	0.073	11.2
82WA160	66.7	5.32	>24	-	55.8	**2.50**	65.3	4.96	62.2	4.17	56	55.8	2.50	17.8
82WA161	76.3	10.73	>24	-	65.4	**8.31**	75.7	10.60	76.2	10.71	65	65.4	8.31	15.4
82WA163	56.1	**-2.50**	>24	-	47.5	-4.80	55.3	-2.71	46.4	-5.10	47	47.5	-4.80	16.6
82WA164	51.5	**-1.51**	>24	-	45.5	-3.04	49.2	-2.09	41.1	-4.18	46	45.5	-3.04	12.4

[1]**Bold** in indicates best charge balance.

[2]A DCP Mg value alternative to the value published in Ball and Nordstrom (1985) was selected for WATEQ4F calculations to obtain the listed charge balance. The percent difference using the Ball and Nordstrom (1985) value appears in parentheses at the right.

Table A-50. Results of analyses for magnesium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

	Concentration (mg L^{-1})						WATEQ4F	
Sample Number	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP	1/1000 diluted DCP	Ball and Nordstrom (1985)	(mg L^{-1})	Charge balance (Δ%)
82WA100	1.45	1.63	1.89	<2	-	1.6	1.63	-11.7
82WA101	1.29	1.63	1.85	<2	-	1.6	1.63	-23.3
82WA102	1.60	1.79	2.06	<2	-	1.8	1.79	-11.2
82WA103	1.72	2.01	2.29	<2	-	2.0	2.01	-15.5
82WA105	15.5	15.4	15.2	18.8	-	15	15.4	0.6
82WA108	5.92	5.64	6.20	6.12	-	5.6	5.64	4.8
82WA111	21.6	21.2	21.3	25.4	<20	21	21.3	1.4
82WA114	7.47	7.01	7.32	8.26	-	7.0	7.01	6.4
82WA117	3.20	3.21	3.48	2.83	-	3.2	3.21	-0.3
82WA121	25.7	>24	24.5	30.6	<20	24	[1]30.6	-17.4 (4.8)
82WA123	6.30	6.05	6.04	6.83	-	6.1	6.05	4.0
82WA125	106	>24	106	115	63	110	[1]115	-8.1 (0.0)
82WA126	14.1	13.6	12.8	15.9	-	14	13.6	3.6
82WA127	100	>24	91.4	103	44	91	[1]103	-3.0 (9.0)
82WA128	112	>24	104	114	63	100	[1]114	-1.8 (7.4)

[1]A DCP Mg value alternative to the value published in Ball and Nordstrom (1985) was selected for WATEQ4F calculations to obtain the listed charge balance. The percent difference using the Ball and Nordstrom (1985) value appears in parentheses at the right.

Table A-51. Results of analyses for magnesium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

	Concentration (mg L^{-1})						WATEQ4F	
Sample Number	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP	1/1000 diluted DCP	Ball and Nordstrom (1985)	(mg L^{-1})	Charge balance (Δ%)
82WA141	3.89	3.80	4.36	-	-	3.8	3.80	2.3
82WA142	2.98	3.06	3.54	-	-	3.1	3.06	-2.6
82WA143	16.0	14.9	14.5	-	-	15	14.9	7.1
82WA144	16.5	15.8	15.6	-	-	16	15.8	4.3
82WA146	15.4	14.2	14.3	-	-	14	14.2	8.1
82WA147	6.41	5.97	6.56	-	-	6.0	5.97	7.1
82WA148	16.4	15.2	15.9	20.2	-	15	15.2	7.6
82WA150	21.1	19.7	19.1	25.4	-	20	19.7	6.9
82WA153	5.95	5.76	6.40	-	-	5.8	5.76	3.2
82WA154	4.98	4.77	5.44	-	-	4.8	4.77	4.3
82WA156	98.3	>24	95.4	101	120	95	95.4	3.0
82WA158	103	>24	104	110	124	100	104	-1.0
82WA159	12.1	11.7	11.5	-	-	12	11.7	3.4
82WA162	72.1	>24	70.1	79.2	79.7	70	70.1	2.8
82WA166	7.46	7.35	8.07	10.7	-	7.4	7.35	1.5
82WA170	4.77	4.44	5.07	-	-	4.4	4.44	7.2

Table A-52. Results of analyses for magnesium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})						WATEQ4F	
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP	1/1000 diluted DCP	Ball and Nordstrom (1985)	(mg L^{-1})	Charge balance (Δ%)
82WA118	50.7	>24	41.2	56.8	<20	[2]56	56.8	-11.3
82WA119	94.9	>24	75.0	99.1	29.0	75	[3]99.1	-4.3 (23.4)
82WA132	85.2	>24	74.7	86.9	25.0	75	[3]86.9	-2.0 (13.1)
82WA165	43.8	>24	39.8	42.6	32.3	40	39.8	9.6
82WA167	89.0	>24	82.8	87.0	93.7	83	82.8	7.2
82WA168	89.8	>24	83.9	88.9	103	84	83.9	6.8
82WA169	44.7	>24	38.6	39.6	35.8	39	38.6	14.6

[1]Samples in this set were diluted 1/10 for ICP analysis.
[2]The report of Ball and Nordstrom (1985) is apparently in error. The published value should be 57 mg L^{-1}.
[3]A DCP Mg value alternative to the value published in Ball and Nordstrom (1985) was selected for WATEQ4F calculations to obtain the listed charge balance. The percent difference using the Ball and Nordstrom (1985) value appears in parentheses at the right.

Table A-53. Results of analyses for manganese in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) ICP	Ball and Nordstrom (1985) DCP	Alternative DCP[1]	GFAAS	ICP-Ball and Nordstrom (1985) DCP (Δ%)	ICP-Alternative DCP (Δ%)	ICP-GFAAS (Δ%)
82WA104	0.927	0.986	1.02		-6.2	-9.6	
82WA106	0.925	0.996	1.02		-7.4	-9.8	
82WA107	1.05	1.02	1.09		2.9	-3.7	
82WA109	1.27	1.24	1.26		2.4	0.8	
82WA110	3.14	2.94	3.31		6.6	-5.3	
82WA112	3.14	2.97	3.40		5.6	-8.0	
82WA113	3.93	3.75	3.94		4.7	-0.3	
82WA115	4.47	4.15	4.45		7.4	0.4	
82WA116	5.27	5.23	4.98		0.8	5.7	
82WA120	2.84	2.63	2.58		7.7	9.6	
82WA122	3.91	3.79	4.07		3.1	-4.0	
82WA124	8.80	8.69	-		1.3		
82WA129	3.94	3.79	3.32		3.9	17.1	
82WA130	4.37	4.25	4.40		2.8	-0.7	
82WA131	5.19	4.91	4.84		5.5	7.0	
82WA145	0.905	0.951	-		-5.0		
82WA149	5.54	5.41	6.21		2.4	-11.4	
82WA151	5.58	5.47	6.38		2.0	-13.4	
82WA152	11.7	11.9	10.2		-1.7	13.7	
82WA155	3.40	3.08	3.15		9.9	7.6	
82WA157	19.4	19.6	20.4		-1.0	-5.0	
82WA160	12.2	13.1	10.8		-7.1	12.2	
82WA161	14.9	15.4	14.2		-3.3	4.8	
82WA163	12.0	13.2	11.1		-9.5	7.8	
82WA164	11.5	12.4	11.1		-7.5	3.5	

[1]In all cases values in the Alternative DCP column are for the next more dilute analysis.

Table A-54. Results of analyses for manganese in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) ICP	Ball and Nordstrom (1985) DCP	Alternative DCP[1]	GFAAS	ICP-Ball and Nordstrom (1985) DCP (Δ%)	ICP-Alternative DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	<0.010	<0.010		0.0061			
82WA101	<0.010	<0.010		0.0044			
82WA102	<0.010	0.018		0.016			
82WA103	<0.010	0.036		0.031			
82WA105	<0.010	0.012		0.012			
82WA108	<0.010	0.025		0.022			
82WA111	1.27	1.25	1.29		1.6	-1.6	
82WA114	<0.010	0.024		0.025			
82WA117	<0.010	0.018		0.019			
82WA121	2.16	2.10	2.24		2.8	-3.6	
82WA123	<0.010	<0.010		0.0055			
82WA125	23.1	22.8	30.3		1.3	-27.0	
82WA126	1.20	1.16	1.22		3.4	-1.7	
82WA127	17.7	16.9	20.5		4.6	-14.7	
82WA128	5.22	5.14	5.20		1.5	0.4	

[1]In all cases values in the Alternative DCP column are for the next more dilute analysis.

Table A-55. Results of analyses for manganese in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Ball and Nordstrom (1985) DCP (Δ%)	ICP-Alternative DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	Ball and Nordstrom (1985) DCP	Alternative DCP[1]	GFAAS			
82WA141	0.067	0.070		0.067	-4.4		0.0
82WA142	<0.010	<0.010		0.0060			
82WA143	0.980	0.866			12.4		
82WA144	<0.010	<0.010		0.0076			
82WA146	1.09	0.981			10.5		
82WA147	<0.010	<0.010		0.0052			
82WA148	1.62	1.51	1.46		7.0	10.4	
82WA150	0.976	0.923			5.6		
82WA153	<0.010	<0.010		0.0018			
82WA154	<0.010	<0.010		0.0001			
82WA156	20.6	21.8	23.0		-5.7	-11.0	
82WA158	2.02	1.91	1.77		5.6	13.2	
82WA159	0.022	0.012		0.011	58.8		66.7
82WA162	10.6	12.1			-13.2		
82WA166	0.776	0.773			0.4		
82WA170	0.011	<0.010		0.0085			25.6

[1]In all cases values in the Alternative DCP column are for the next more dilute analysis.

Table A-56. Results of analyses for manganese in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) ICP	Ball and Nordstrom (1985) DCP	Alternative DCP[2]	GFAAS	ICP-Ball and Nordstrom (1985) DCP (Δ%)	ICP-Alternative DCP (Δ%)	ICP-GFAAS (Δ%)
82WA118	10.2	10.7	-4.8	13.8	-30.0		
82WA119	9.09	9.55	-4.9	10.7	-16.3		
82WA132	15.7	15.1	3.9	19.9	-23.6		
82WA165	10.5	11.7	-10.8	-			
82WA167	23.0	22.1	4.0	23.3	-1.3		
82WA168	22.7	22.5	0.9	23.1	-1.7		
82WA169	7.81	8.14	-4.1	-			

[1]Samples in this set were diluted 1/10 for ICP analysis.
[2]In all cases values in the Alternative DCP column are for the next more dilute analysis.

Table A-57. Results of analyses for molybdenum in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	ICP-DCP (Δ%)
82WA104	163	9.51	178.0
82WA106	156	12.7	169.9
82WA107	<3.0	83.7	
82WA109	<3.0	7.27	
82WA110	<3.0	44.2	
82WA112	<3.0	36.3	
82WA113	<3.0	44.1	
82WA115	<3.0	45.2	
82WA116	<3.0	52.4	
82WA120	<3.0	35.0	
82WA122	<3.0	31.8	
82WA124	<3.0	71.3	
82WA129	<3.0	47.5	
82WA130	<3.0	43.6	
82WA131	<3.0	54.6	
82WA145	163	32.1	134.2
82WA149	<3.0	71.0	
82WA151	<3.0	64.6	
82WA152	<3.0	86.8	
82WA155	<3.0	56.5	
82WA157	<3.0	104	
82WA160	<3.0	86.3	
82WA161	<3.0	89.0	
82WA163	<3.0	91.9	
82WA164	<3.0	77.5	

Table A-58. Results of analyses for molybdenum in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	ICP-DCP (Δ%)
82WA100	<3.0	15.0	
82WA101	<3.0	15.6	
82WA102	<3.0	19.2	
82WA103	<3.0	17.7	
82WA105	<3.0	12.4	
82WA108	55.7	10.2	138.1
82WA111	87.8	<3.00	
82WA114	<3.0	15.3	
82WA117	<3.0	11.1	
82WA121	<3.0	48.1	
82WA123	<3.0	7.37	
82WA125	<3.0	115	
82WA126	<3.0	17.4	
82WA127	<3.0	114	
82WA128	<3.0	123	

Table A-59. Results of analyses for molybdenum in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	ICP-DCP (Δ%)
82WA141	<3.0	19.1	
82WA142	<3.0	19.9	
82WA143	<3.0	37.0	
82WA144	<3.0	27.0	
82WA146	<3.0	34.9	
82WA147	<3.0	23.0	
82WA148	<3.0	29.7	
82WA150	<3.0	57.2	
82WA153	<3.0	26.5	
82WA154	<3.0	20.9	
82WA156	<3.0	112	
82WA158	123	106	14.8
82WA159	104	33.7	102.1
82WA162	97.5	104	-6.5
82WA166	118	17.1	149.4
82WA170	<3.0	15.1	

Table A-60. Results of analyses for molybdenum in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	ICP-DCP (Δ%)
82WA118	<30.0	24.4	
82WA119	<30.0	65.7	
82WA132	<30.0	88.7	
82WA165	1890	88.1	182.2
82WA167	<30.0	108	
82WA168	<30.0	107	
82WA169	<30.0	72.9	

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-61. Results of analyses for nickel in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA104	164	179		-8.7	
82WA106	166	192	187	-14.5	-11.9
82WA107	195	195	190	0.0	2.6
82WA109	244	232	247	5.0	-1.2
82WA110	608	515		16.6	
82WA112	634	565		11.5	
82WA113	875	864		1.3	
82WA115	1050	907		14.6	
82WA116	1210	1070		12.3	
82WA120	188	191	153	-1.6	20.5
82WA122	672	616		8.7	
82WA124	348	329	323	5.6	7.5
82WA129	734	665		9.9	
82WA130	665	579		13.8	
82WA131	1270	1070		17.1	
82WA145	90.2	99.7	118	-10.0	-26.7
82WA149	684	575		17.3	
82WA151	682	590		14.5	
82WA152	1570	1470		6.6	
82WA155	96.4	100	110	-3.7	-13.2
82WA157	588	545		7.6	
82WA160	1670	1550		7.5	
82WA161	2060	1880		9.1	
82WA163	1830	1720		6.2	
82WA164	2030	1900		6.6	

Table A-62. Results of analyses for nickel in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	<4.0	7.4	0.95		
82WA101	<4.0	6.9	<0.15		
82WA102	<4.0	12.5	2.30		
82WA103	<4.0	12.6	3.75		
82WA105	<4.0	<4.0	0.48		
82WA108	9.7	17.5	14.6	-57.6	-40.6
82WA111	41.1	30.8	41.8	28.7	-1.7
82WA114	4.8	<4.0	2.41		65.4
82WA117	<4.0	5.2	0.79		
82WA121	76.5	76.9	77.8	-0.5	-1.7
82WA123	<4.0	<4.0	<0.15		
82WA125	693	774		-11.0	
82WA126	37.2	36.6	37.8	1.6	-1.6
82WA127	527	499		5.5	
82WA128	134	135	151	-0.7	-11.9

Table A-63. Results of analyses for nickel in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})			ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	DCP	GFAAS		
82WA141	<4.0	12.2	6.04		
82WA142	<4.0	6.6	0.32		
82WA143	92.9	87.9	96.4	5.5	-3.7
82WA144	4.6	2.8	0.16	46.9	186.4
82WA146	124	113	131	9.3	-5.5
82WA147	<4.0	11.3	0.32		
82WA148	211	185	184	13.1	13.7
82WA150	24.8	31.4	20.4	-23.5	19.5
82WA153	<4.0	10.2	<0.15		
82WA154	4.6	<4.0	<0.15		
82WA156	636	654		-2.8	
82WA158	49.3	40.0	42.0	20.8	16.0
82WA159	<4.0	6.8		1.26	
82WA162	415	405		2.4	
82WA166	170	161	139	5.4	20.1
82WA170	<4.0	<4.0	<0.15		

Table A-64. Results of analyses for nickel in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA118	11900	11700		1.7	
82WA119	13000	12600		3.1	
82WA132	9240	8720		5.8	
82WA165	1930	1750		9.8	
82WA167	4080	3790		7.4	
82WA168	4090	3720		9.5	
82WA169	9730	10300		-5.7	

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-65. Results of analyses for silica in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA104	44.6	38.3	[1]**46.6**		15.2	-4.4	
82WA106	41.9	38.5	**45.4**		8.5	-8.0	
82WA107	42.7	38.8	**45.6**		9.6	-6.6	
82WA109	40.0	**35.7**	42.6		11.4	-6.3	
82WA110	43.4	38.1	**46.5**		13.0	-6.9	
82WA112	41.5	**35.2**	36.4		16.4	13.1	
82WA113	47.8	44.1	**50.0**		8.1	-4.5	
82WA115	47.6	44.8	**49.5**		6.1	-3.9	
82WA116	49.3	42.3	**48.7**		15.3	1.2	
82WA120	74.1	>51	**69.8**	64.9		6.0	13.2
82WA122	42.3	37.4	**43.7**		12.3	-3.3	
82WA124	45.3	39.3	**45.9**		14.2	-1.3	
82WA129	44.9	38.5	**44.7**		15.3	0.4	
82WA130	44.6	39.3	**44.7**		12.6	-0.2	
82WA131	49.7	41.2	**48.7**		18.7	2.0	
82WA145	40.4	**33.6**	37.9		18.4	6.4	
82WA149	40.0	**33.0**	36.9		19.2	8.1	
82WA151	38.3	**31.9**	34.8		18.2	9.6	
82WA152	55.0	48.1	**47.2**		13.4	15.3	
82WA155	40.6	**34.4**	37.5		16.5	7.9	
82WA157	55.4	48.5	**49.3**		13.3	11.7	
82WA160	55.4	48.1	**48.5**		14.1	13.3	
82WA161	58.1	49.4	**50.6**		16.2	13.8	
82WA163	51.0	42.5	**45.6**		18.2	11.2	
82WA164	54.1	46.5	**47.7**		15.1	12.6	

[1]**Bold** means value was selected for publication in Ball and Nordstrom (1985) and for WATEQ4F computations.

Table A-66. Results of analyses for silica in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA100	15.8	[1]**12.9**	18.4		20.2	-15.2	
82WA101	14.6	**13.1**	18.1		10.8	-21.4	
82WA102	15.6	**13.2**	18.5		16.7	-17.0	
82WA103	16.1	**14.4**	19.6		11.1	-19.6	
82WA105	56.6	50.8	**55.6**	48.1	10.8	1.8	16.2
82WA108	40.3	**35.3**	42.6		13.2	-5.5	
82WA111	26.8	**22.7**	25.6		16.6	4.6	
82WA114	38.7	36.2	**43.2**		6.7	-11.0	
82WA117	42.7	**39.3**	42.6		8.3	0.2	
82WA121	29.0	**24.9**	31.7		15.2	-8.9	
82WA123	30.6	**26.1**	30.8		15.9	-0.7	
82WA125	43.8	33.2	**45.7**		27.5	-4.2	
82WA126	28.1	**22.8**	28.5		20.8	-1.4	
82WA127	56.4	45.7	**54.7**	45.1	21.0	3.1	22.3
82WA128	21.9	**16.3**	24.4		29.3	-10.8	

[1]**Bold** means value was selected for publication in Ball and Nordstrom (1985) and for WATEQ4F computations.

Table A-67. Results of analyses for silica in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA141	25.8	[1]**22.1**	20.8		15.4	21.5	
82WA142	23.7	**21.0**	19.7		12.1	18.4	
82WA143	45.6	**34.9**	36.2		26.6	23.0	
82WA144	63.7	49.1	**53.6**		25.9	17.2	
82WA146	41.5	**32.0**	35.7		25.9	15.0	
82WA147	41.8	**32.9**	34.4		23.8	19.4	
82WA148	39.4	**32.3**	36.4		19.8	7.9	
82WA150	28.7	**24.6**	23.2		15.4	21.2	
82WA153	29.1	**24.3**	26.0		18.0	11.3	
82WA154	27.2	**22.3**	23.4		19.8	15.0	
82WA156	40.6	**33.5**	35.7		19.2	12.8	
82WA158	20.8	**17.4**	17.5		17.8	17.2	
82WA159	44.8	**35.5**	39.0		23.2	13.8	
82WA162	29.0	**22.8**	25.0		23.9	14.8	
82WA166	45.5	38.6	**43.4**		16.4	4.7	
82WA170	50.6	**41.8**	40.8		19.0	21.4	

[1]**Bold** means value was selected for publication in Ball and Nordstrom (1985) and for WATEQ4F computations.

Table A-68. Results of analyses for silica in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP	ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
82WA118	113	>51	[2]**109**	120		3.6	-6.0
82WA119	122	>51	**109**	130		11.3	-6.3
82WA132	93.4	>51	**92.0**	98		1.5	-4.8
82WA165	55.0	43.2	**46.2**		24.0	17.4	
82WA167	65.2	>51	**54.3**	45.0		18.2	16.7
82WA168	59.9	48.7	**50.8**		20.6	16.4	
82WA169	116	>51	**98.6**	103		16.2	11.9

[1]Samples in this set were diluted 1/10 for ICP analysis.

[2]**Bold** means value was selected for publication in Ball and Nordstrom (1985) and for WATEQ4F computations.

Table A-69. Results of analyses for sodium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA104	10.5	14.1	10.7	29.3	1.9
82WA106	9.92	12.1		19.8	
82WA107	9.54	8.05		-16.9	
82WA109	8.98	8.26	8.60	-8.4	-4.3
82WA110	11.8	12.5		5.8	
82WA112	10.9	13.3		19.8	
82WA113	12.7	15.7		21.1	
82WA115	12.8	10.7		-17.9	
82WA116	11.9	11.3	11.5	-5.2	-3.4
82WA120	3.98	5.10	3.26	24.7	-19.9
82WA122	11.0	11.5		4.4	
82WA124	13.5	16.4		19.4	
82WA129	8.70	10.4		17.8	
82WA130	11.1	12.1		8.6	
82WA131	11.3	10.2		-10.2	
82WA145	10.3	12.6		20.1	
82WA149	13.7	15.2		10.4	
82WA151	13.9	14.6		4.9	
82WA152	18.9	20.1		6.2	
82WA155	11.0	10.5	10.1	-4.7	-8.5
82WA157	23.3	18.2	19.8	-24.6	-16.2
82WA160	20.3	21.6		6.2	
82WA161	20.6	17.0	17.0	-19.1	-19.1
82WA163	15.9	18.3		14.0	
82WA164	16.4	21.6		27.4	

Table A-70. Results of analyses for sodium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA100	2.87	2.89		0.7	
82WA101	2.87	2.57	2.65	-11.0	-8.0
82WA102	2.92	2.99		2.4	
82WA103	3.32	3.14		-5.6	
82WA105	15.0	14.5	16.3	-3.4	8.3
82WA108	7.09	6.63		-6.7	
82WA111	10.7	15.3		35.4	
82WA114	10.2	8.37	9.60	-19.7	-6.1
82WA117	7.26	6.53	6.39	-10.6	-12.7
82WA121	14.0	16.8		18.2	
82WA123	10.4	9.39	10.5	-10.2	1.0
82WA125	21.7	30.0	18.7	32.1	-14.9
82WA126	9.69	12.2		22.9	
82WA127	24.1	35.1		37.2	
82WA128	26.1	30.0	22.0	13.9	-17.0

Table A-71. Results of analyses for sodium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA141	9.51	7.03	7.88	-30.0	-18.7
82WA142	8.96	6.61		-30.2	
82WA143	11.6	10.5	11.7	-10.0	0.9
82WA144	14.9	13.9	16.7	-6.9	11.4
82WA146	9.70	9.37	9.81	-3.5	1.1
82WA147	7.41	5.76	6.81	-25.1	-8.4
82WA148	9.93	8.32		-17.6	
82WA150	13.2	10.7		-20.9	
82WA153	10.1	8.28	9.89	-19.8	-2.1
82WA154	9.29	7.76		-17.9	
82WA156	22.3	20.5	18.6	-8.4	-18.1
82WA158	25.3	39.8		44.5	
82WA159	12.7	14.8	14.1	15.3	10.4
82WA162	22.4	34.1	19.7	41.4	-12.8
82WA166	9.27	9.66		4.1	
82WA170	9.57	7.54		-23.7	

Table A-72. Results of analyses for sodium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA118	29.4	35.2	19.4	18.0	-41.0
82WA119	38.6	55.0	24.3	35.0	-45.5
82WA132	29.2	42.2	21.9	36.4	-28.6
82WA165	14.8	33.6	14.4	77.7	-2.7
82WA167	25.0	37.4		39.7	
82WA168	24.3	41.2		51.6	
82WA169	25.4	32.4	20.7	24.2	-20.4

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-73. Results of analyses for potassium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA104	4.16	2.60	3.81	-46.2	-8.8
82WA106	4.07	2.60		-44.1	
82WA107	3.99	3.27		-19.8	
82WA109	3.59	2.80	3.21	-24.7	-11.2
82WA110	4.57	3.48		-27.1	
82WA112	4.31	2.96		-37.1	
82WA113	5.15	4.04		-24.2	
82WA115	5.60	4.69		-17.7	
82WA116	5.23	4.68	4.72	-11.1	-10.3
82WA120	1.94	1.29	1.62	-40.2	-18.0
82WA122	4.92	4.20		-15.8	
82WA124	12.1	13.5		10.9	
82WA129	4.68	4.36		-7.1	
82WA130	5.10	4.23		-18.6	
82WA131	5.18	5.55		6.9	
82WA145	4.55	2.97		-42.0	
82WA149	5.00	4.97		-0.6	
82WA151	5.18	4.79		-7.8	
82WA152	8.38	7.80		-7.2	
82WA155	7.70	7.37	6.83	-4.4	-12.0
82WA157	9.48	9.74	8.50	2.7	-10.9
82WA160	8.71	8.24		-5.5	
82WA161	9.58	10.9	8.59	12.9	-10.9
82WA163	9.99	10.4		4.0	
82WA164	11.6	10.8		-7.1	

Table A-74. Results of analyses for potassium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA100	0.689	0.317		-74.0	
82WA101	0.681	0.400	0.80	-52.0	16.1
82WA102	0.705	<0.300			
82WA103	0.893	0.521		-52.6	
82WA105	5.31	4.84	5.17	-9.3	-2.7
82WA108	2.76	2.23	2.29	-21.2	-18.6
82WA111	3.89	3.15		-21.0	
82WA114	3.24	2.98	2.67	-8.4	-19.3
82WA117	2.51	2.36	2.08	-6.2	-18.7
82WA121	2.74	2.17		-23.2	
82WA123	1.14	1.21	2.32	6.0	68.2
82WA125	22.2	24.7	22.6	10.7	1.8
82WA126	3.58	3.25		-9.7	
82WA127	8.37	9.49		12.5	
82WA128	7.52	8.71	7.43	14.7	-1.2

Table A-75. Results of analyses for potassium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA141	1.97	1.48	1.49	-28.4	-27.7
82WA142	1.73	0.885		-64.6	
82WA143	4.90	4.58	4.20	-6.8	-15.4
82WA144	5.58	5.56	5.03	-0.4	-10.4
82WA146	4.31	4.06	3.81	-6.0	-12.3
82WA147	2.66	2.24	2.21	-17.1	-18.5
82WA148	3.85	3.54		-8.4	
82WA150	4.24	4.07		-4.1	
82WA153	0.885	0.896	0.83	1.2	-6.4
82WA154	0.665	1.01		41.2	
82WA156	27.6	27.5	23.8	-0.4	-14.8
82WA158	8.34	8.58		2.8	
82WA159	3.74	2.94	3.43	-24.0	-8.6
82WA162	4.20	3.53	3.89	-17.3	-7.7
82WA166	3.91	3.04		-25.0	
82WA170	3.99	3.34	3.37	-17.7	-16.8

Table A-76. Results of analyses for potassium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) DCP	ICP	Flame AAS	ICP-DCP (Δ%)	ICP-flame AAS (Δ%)
82WA118	16.9	24.8	13.8	37.9	-20.2
82WA119	33.4	36.4	23.2	8.6	-36.0
82WA132	15.1	20.0	12.9	27.9	-15.7
82WA165	10.2	14.0	10.2	31.4	0.0
82WA167	20.1	27.1		29.7	
82WA168	20.4	27.1		28.2	
82WA169	16.1	20.5	14.1	24.0	-13.2

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-77. Results of analyses for strontium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1}) Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP	ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
82WA104	491	[1]**389**	440		23.2	11.0	
82WA106	457	**383**	419		17.6	8.7	
82WA107	407	**385**	412		5.6	-1.2	
82WA109	440	**411**	435		6.8	1.1	
82WA110	699	664	**717**		5.1	-2.5	
82WA112	698	647	**693**		7.6	0.7	
82WA113	766	722	**776**		5.9	-1.3	
82WA115	712	724	**756**		-1.7	-6.0	
82WA116	771	714	**788**		7.7	-2.2	
82WA120	111	**112**	116		-0.9	-4.4	
82WA122	575	512	**564**		11.6	1.9	
82WA124	825	788	**855**	616	4.6	-3.6	29.0
82WA129	430	**369**	419		15.3	2.6	
82WA130	636	564	**613**		12.0	3.7	
82WA131	740	663	**757**		11.0	-2.3	
82WA145	452	**383**	429		16.5	5.2	
82WA149	1010	889	**997**	674	12.7	1.3	39.9
82WA151	963	866	**960**	674	10.6	0.3	35.3
82WA152	1400	>1200	**1320**	1200		5.9	15.4
82WA155	384	**393**	418		-2.3	-8.5	
82WA157	913	927	**988**	730	-1.5	-7.9	22.3
82WA160	1360	>1200	**1320**	1190		3.0	13.3
82WA161	1450	>1200	**1430**	1280		1.4	12.5
82WA163	1190	1070	**1150**	950	10.6	3.4	22.4
82WA164	928	852	**895**	617	8.5	3.6	40.3

[1]**Bold** indicates value selected for publication in Ball and Nordstrom (1985).

Table A-78. Results of analyses for strontium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA100	83.9	[1]**83.9**	87.4		0.0	-4.1	
82WA101	81.9	**84.7**	85.7		-3.4	-4.5	
82WA102	88.9	**88.1**	89.0		0.9	-0.1	
82WA103	93.0	**98.1**	103		-5.3	-10.2	
82WA105	319	**299**	330		6.5	-3.4	
82WA108	237	**225**	236		5.2	0.4	
82WA111	584	551	**631**		5.8	-7.7	
82WA114	387	**371**	415		4.2	-7.0	
82WA117	211	**207**	207		1.9	1.9	
82WA121	1010	1010	**1020**	833	0.0	-1.0	19.2
82WA123	353	**337**	349		4.6	1.1	
82WA125	491	468	**570**		4.8	-14.9	
82WA126	362	**338**	360		6.9	0.6	
82WA127	961	900	**1010**	755	6.6	-5.0	24.0
82WA128	1790	>1200	**1850**	1930		-3.3	-7.5

[1]**Bold** indicates value selected for publication in Ball and Nordstrom (1985).

Table A-79. Results of analyses for strontium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA141	189	[1]**209**	182		-10.1	3.8	
82WA142	169	**190**	160		-11.7	5.5	
82WA143	409	**406**	407		0.7	0.5	
82WA144	331	**327**	350		1.2	-5.6	
82WA146	398	**377**	421		5.4	-5.6	
82WA147	240	**245**	244		-2.1	-1.7	
82WA148	457	**455**	499		0.4	-8.8	
82WA150	601	628	**621**	516	-4.4	-3.3	15.2
82WA153	323	**328**	344		-1.5	-6.3	
82WA154	285	**291**	299		-2.1	-4.8	
82WA156	437	495	**560**		-12.4	-24.7	
82WA158	2180	>1200	**2100**	2180		3.7	0.0
82WA159	635	561	**632**		12.4	0.5	
82WA162	2370	>1200	**2300**	2640		3.0	-10.8
82WA166	280	**283**	305		-1.1	-8.5	
82WA170	238	**254**	235		-6.5	1.3	

[1]**Bold** indicates value selected for publication in Ball and Nordstrom (1985).

Table A-80. Results of analyses for strontium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (mg L^{-1})				ICP-Undiluted DCP (Δ%)	ICP-1/10 diluted DCP (Δ%)	ICP-1/100 diluted DCP (Δ%)
	Undiluted ICP	Undiluted DCP	1/10 diluted DCP	1/100 diluted DCP			
82WA118	2990	>1200	[2]**2690**	3430		10.6	-13.7
82WA119	3860	>1200	**3350**	4490		14.1	-15.1
82WA132	3000	>1200	**2740**	3320		9.1	-10.1
82WA165	912	780	**868**	561	15.6	4.9	47.7
82WA167	1640	>1200	**1580**	1480		3.7	10.3
82WA168	1550	>1200	**1490**	1400		3.9	10.2
82WA169	2600	>1200	**2340**	2580		10.5	0.8

[1]Samples in Table A-80 were diluted 1/10 for ICP analysis.
[2]**Bold** indicates value selected for publication in Ball and Nordstrom (1985).

Table A-81. Results of analyses for vanadium in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})			ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	DCP	GFAAS		
82WA104	<5.0	<5.0	<1.0		
82WA106	<5.0	<5.0	<1.0		
82WA107	<5.0	<5.0	<1.0		
82WA109	<5.0	<5.0	<1.0		
82WA110	<5.0	<5.0	<1.0		
82WA112	<5.0	<5.0	1.0		
82WA113	<5.0	5.3	1.9		
82WA115	<5.0	16.5	12.6		
82WA116	<5.0	29.1	29.5		
82WA120	<5.0	<5.0	2.2		
82WA122	<5.0	<5.0	1.0		
82WA124	<5.0	<5.0	1.0		
82WA129	<5.0	<5.0	1.3		
82WA130	<5.0	<5.0	1.6		
82WA131	24.2	66.8	67.7	-93.6	-94.7
82WA145	<5.0	6.5	<1.0		
82WA149	<5.0	17.6	<1.0		
82WA151	<5.0	11.5	1.5		
82WA152	<5.0	16.8	11.9		
82WA155	<5.0	17.1	<1.0		
82WA157	<5.0	14.2	<1.0		
82WA160	23.4	53.7	59.9	-78.6	-87.6
82WA161	23.6	45.8	51.2	-64.0	-73.8
82WA163	12.6	39.6	32.8	-103.4	-89.0
82WA164	61.4	85.8	99.6	-33.2	-47.5

Table A-82. Results of analyses for vanadium in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	DCP	GFAAS	ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	18.3	7.4	1.0	84.9	179.3
82WA101	<5.0	7.7	1.3		
82WA102	<5.0	16.6	1.1		
82WA103	<5.0	12.4	<1.0		
82WA105	13.0	<5.0	6.7		64.0
82WA108	18.3	<5.0	3.8		131.2
82WA111	<5.0	<5.0	<1.0		
82WA114	<5.0	<5.0	1.6		
82WA117	5.3	5.2	3.4	2.5	43.3
82WA121	<5.0	<5.0	1.6		
82WA123	8.3	<5.0	3.4		83.6
82WA125	28.4	47.8	26.8	-50.9	5.8
82WA126	6.4	<5.0	1.3		132.6
82WA127	<5.0	30.8	<1.0		
82WA128	<5.0	39.2	<1.0		

Table A-83. Results of analyses for vanadium in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})			ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	DCP	GFAAS		
82WA141	15.9	7.6	1.1	71.0	174.1
82WA142	<5.0	8.3	<1.0		
82WA143	<5.0	18.9	1.5		
82WA144	13.4	12.6	6.8	6.2	65.3
82WA146	5.7	14.3	<1.0	-86.4	
82WA147	<5.0	15.2	2.6		
82WA148	7.4	<5.0	<1.0		
82WA150	<5.0	18.0	<1.0		
82WA153	5.8	18.1	2.6	-102.4	76.8
82WA154	<5.0	8.6	1.5		
82WA156	18.7	33.6	25.6	-57.0	-31.2
82WA158	31.8	12.2	<1.0	89.1	
82WA159	17.3	11.1	<1.0	43.7	
82WA162	22.6	21.2	<1.0	6.4	
82WA166	10.3	<5.0	<1.0		
82WA170	22.0	5.5	<1.0	120.5	

Table A-84. Results of analyses for vanadium in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1})			ICP-DCP (Δ%)	ICP-GFAAS (Δ%)
	ICP	DCP	GFAAS		
82WA118	1030	862	1230	17.8	-17.7
82WA119	1570	1630	1900	-3.8	-19.0
82WA132	897	740	967	19.2	-7.5
82WA165	161	40.0	25.3	120.4	145.7
82WA167	257	177	234	36.9	9.4
82WA168	219	177	230	21.2	-4.9
82WA169	1010	1010	1100	0.0	-8.5

[1]Samples in this set were diluted 1/10 for ICP analysis.

Table A-85. Results of analyses for zinc in samples with pH from 2.50 to 5.88 [except sample 82WA145 with pH=7.78] (analytical set 1).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA104	<2.0	41.5	15.8	33.1			
82WA106	<2.0	33.5	18.0	33.5			
82WA107	21.1	31.7	18.2	32.7	-40.2	14.8	-43.1
82WA109	29.6	40.8	35.0	42.9	-31.8	-16.7	-36.7
82WA110	219	149	145		38.0	40.7	
82WA112	111	112	103		-0.9	7.5	
82WA113	144	130	133		10.2	7.9	
82WA115	177	145	148		19.9	17.8	
82WA116	204	187	184		8.7	10.3	
82WA120	317	274	276		14.6	13.8	
82WA122	167	154	143		8.1	15.5	
82WA124	489	420	415		15.2	16.4	
82WA129	142	132	371		7.3	-89.3	
82WA130	145	124	170		15.6	-15.9	
82WA131	228	188	198		19.2	14.1	
82WA145	<2.0	<2.0	<6.0	1.68			
82WA149	131	128	128		2.3	2.3	
82WA151	122	125	129		-2.4	-5.6	
82WA152	314	308	298		1.9	5.2	
82WA155	111	107	86.9		3.7	24.4	
82WA157	716	656	541		8.7	27.8	
82WA160	349	329	318		5.9	9.3	
82WA161	411	386	359		6.3	13.5	
82WA163	319	322	319		-0.9	0.0	
82WA164	389	389	371		0.0	4.7	

Table A-86. Results of analyses for zinc in samples with pH from 6.85 to 8.85 [except samples 82WA125 and 82WA127 with pH=3.19 and 3.65, respectively] (analytical set 2).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA100	<2.0	15.8	7.2	0.46			
82WA101	<2.0	17.7	<6.0	0.73			
82WA102	<2.0	18.8	<6.0	1.01			
82WA103	<2.0	18.4	<6.0	0.84			
82WA105	<2.0	<2.0	<6.0	0.17			
82WA108	532	521	477		2.1	10.9	
82WA111	<2.0	<2.0	<6.0	[1]16.0			
82WA114	<2.0	<2.0	<6.0	1.26			
82WA117	<2.0	7.1	<6.0	0.13			
82WA121	<2.0	11.2	21.7	18.2			
82WA123	<2.0	6.3	<6.0	0.06			
82WA125	976	763	808		24.5	18.8	
82WA126	<2.0	<2.0	<6.0	6.41			
82WA127	708	576	466		20.6	41.2	
82WA128	109	41.4	49.3	38.5	89.9	75.4	95.6

[1]This sample believed to have been contaminated.

Table A-87. Results of analyses for zinc in samples with pH from 5.08 to 8.25 [except sample 82WA156 with pH=3.35] (analytical set 3).

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA141	<2.0	16.0	<6.0	1.01			
82WA142	<2.0	13.3	10.0	1.38			
82WA143	<2.0	<2.0	<6.0	3.24			
82WA144	<2.0	<2.0	<6.0	0.63			
82WA146	<2.0	<2.0	<6.0	1.85			
82WA147	<2.0	6.8	<6.0	0.10			
82WA148	50.1	48.4	16.2	38.8	3.5	102.3	25.4
82WA150	<2.0	<2.0	<6.0	1.50			
82WA153	<2.0	11.0	<6.0	0.84			
82WA154	<2.0	<2.0	<6.0	0.27			
82WA156	854	785	809		8.4	5.4	
82WA158	9.5	<2.0	8.4	9.42		12.5	1.1
82WA159	<2.0	<2.0	<6.0	0.27			
82WA162	48.5	48.7	58.9	51.0	-0.4	-19.4	-5.0
82WA166	37.8	45.8	21.1	34.6	-19.1	56.7	8.8
82WA170	11.5	12.3	<6.0	10.4	-6.7		10.0

Table A-88. Results of analyses for zinc in samples with pH from 1.80 to 3.78 (analytical set 4)[1].

[see page 64 for abbreviations and acronyms]

Sample Number	Concentration (µg L^{-1}) ICP	Cassette 1 DCP	Cassette 2 DCP	GFAAS	ICP-Cassette 1 DCP (Δ%)	ICP-Cassette 2 DCP (Δ%)	ICP-GFAAS (Δ%)
82WA118	1750	1490	1290		16.0	30.3	
82WA119	2760	2580	2520		6.7	9.1	
82WA132	1530	1310	1260		15.5	19.4	
82WA165	310	346	339		-11.0	-8.9	
82WA167	675	585	764		14.3	-12.4	
82WA168	723	589	700		20.4	3.2	
82WA169	1470	1040	1050		34.3	33.3	

[1]Samples in this set were diluted 1/10 for ICP analysis.