



Water Chemistry Data for Selected Springs, Geysers, and Streams in Yellowstone National Park, Wyoming, Beginning 2009 – Methods and Quality Assurance and Quality Control

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Both photographs are of Cistern Spring, Norris Geyser Basin, Yellowstone National Park. The photograph on the left is taken on 9/11/2009 and the photograph on the right is taken on 8/7/2013 about 1 week after Steamboat Geyser erupted causing Cistern Spring to completely drain.

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Contents

Methods	1
<i>Collection and Preservation of Water Samples</i>	1
<i>Field and Laboratory Measurements</i>	4
Field Measurements	4
Laboratory Methods	7
Major Cation and Trace Metal Determinations	11
Anion and Alkalinity Determinations	12
Arsenic Redox Determinations	13
Iron Redox Determinations	15
Ammonium Determinations	15
Mercury Determinations	16
Dissolved Organic Carbon	16
Water Isotope Determinations	16
Acidity Determinations	17
Revised pH Measurements	19
Quality Assurance and Quality Control	22
References Cited	36

Figures

Figure 1. Percent difference between field and lab electrical conductivity using (A) the ISO-7888 temperature compensation factor (ISO-7888, 1985) and (B) the McCleskey (2013) temperature compensation factor	6
Figure 2. Flow-chart for the analytical technique used for the final selection of element-specific data	12

Figure 3.	As(T) concentrations determined by HGAAS in the FA-HCl split plotted against As(T) concentrations determined by ICP-OES in the FA-HNO ₃ split.	14
Figure 4.	The percent differences in the measured As concentrations plotted against H ₂ S concentrations.....	15
Figure 5.	Flow chart illustrating the process for refining the acidity pH value.....	19
Figure 6.	Flow chart showing the pH selection process. (C.I., charge imbalance)	21
Figure 7.	Frequency distribution of charge imbalance for samples having major cation and anion determinations.....	23
Figure 8.	Electrical conductivity imbalance compared with charge imbalance.	23
Figure 9.	Cation and trace metals concentrations determined by ICP-MS and ICP-OES plotted on a linear (A) and log ₁₀ (B) scale.....	26
Figure 10.	Total dissolved iron determined by ICP-OES and FerroZine for all data (A) and for iron concentrations less than 5 mg/L (B).	27

Tables

Table 1.	Sample split and preservative, constituents, and sample treatment.....	3
Table 2.	Analytical techniques, detection limits, equipment used, and analytical method references.....	8
Table 3.	Analytical Measured concentrations in standard reference water samples.....	28

Methods

Collection and Preservation of Water Samples

Water samples from hot springs, geysers, and pools were collected as close to the discharge source as possible. For streams, tributaries, and overflow drainage channels, water samples were collected as close to the center of flow as possible and in areas that appeared to be well mixed. Extreme care was taken to safely collect water samples from the geothermal sites, to protect fragile hot-spring mineral formations, and to minimize changes in temperature, pH, and water chemistry during sampling. Samples were collected from the middle of large springs, pools, and geysers by positioning the sample tubing intake using an insulated stainless-steel container as a flotation device attached to the end of an extendable aluminum pole. At more easily accessible sites, the tubing intake was positioned in the source or channel by hand. A Teflon block attached to the end of the sampling tubing was used as a weight to keep the sample tubing in place.

Samples were collected and filtered on site by one of three techniques. The first technique, used for most samples, consisted of pumping water directly from the source with a battery-operated peristaltic pump fitted with silicone tubing through a pre-cleaned 142-millimeter (mm) diameter all-plastic filter holder (Kennedy and others, 1976) containing a 0.1-micrometer (μm) pore size mixed-cellulose-ester filter membrane. The second technique, which was used for samples collected from Upper Geyser Basin in 2009, consisted of filling a 1-L bottle with source water and within an hour filtering the sample by filling a 60-milliliter (mL) syringe with sample water, rinsing three times, and immediately forcing the water through a 25-mm disposable filter having a mixed-cellulose-ester membrane with a pore size of 0.2 μm . These two techniques were used by USGS scientists and have sample numbers with coding yyWA### (where yy is the last 2 digits of the year and ### is a 3 digit

number). High-frequency samples collected by collaborators (sample numbers with coding Y10G####) were filtered through disposable 0.45- μm capsule filters (Geotech Environmental Equipment, Inc.).

As many as 12 sample bottles were filled at each site. Sequential aliquots were filtered into separate containers for the determination of inorganic constituents, redox species (iron, arsenic, and sulfur), stable hydrogen and oxygen isotopes of water, and dissolved organic carbon (DOC). Container preparation, storage, and stabilization methods for filtered samples are summarized in table 1. With the exception of intermediate sulfur redox species and silica aliquots, the sample bottles were rinsed with filtered water, the samples were then collected, and then stabilizing reagents, if needed, were added. Stabilizing reagents for intermediate sulfur species were put into the sample bottles before the samples were collected, and the silica aliquot was diluted on site with deionized water; therefore, these bottles were not pre-rinsed.

Dissolved sulfide in each sample was preserved with an equal volume of sulfide anti-oxidant buffer (SAOB, 0.2M disodium EDTA, 2M sodium hydroxide, 0.19M ascorbic acid; Thermo Fisher Orion). To prevent over-estimation of thiosulfate (S_2O_3) and polythionate concentrations by dissolved sulfide, S(-II) oxidation was minimized by adding zinc acetate ($\text{Zn}(\text{COOCH}_3)_2$) to the sample bottles before the samples were collected. This technique precipitates S(-II) as zinc sulfide (ZnS). The ZnS in the samples was further stabilized by adding NaOH. Polythionate was converted to thiocyanate (SCN) by adding potassium cyanide (KCN) to that sample split (Moses and others, 1984). For the analysis of dissolved SiO_2 in thermal waters, 0.5 mL of sample was diluted on site to 25 mL (by volume: 2009-2012 and by mass beginning in 2013) with deionized water to minimize precipitation of SiO_2 as the sample cooled in the field.

Samples for the determination of DOC were filtered and collected in a glass bottle that had been baked at 600°C. At least 1 liter (L) of sample water was passed through the all-plastic plate-filter

assembly before a DOC sample was collected. With the exception of the cation, water isotope, and silica dilution samples, all sample aliquots were chilled as soon as practical after sample collection.

Table 1. Sample split and preservative, constituents, and sample treatment.

[DOC, dissolved organic carbon; H₂SO₄, sulfuric acid; HNO₃, nitric acid; K₂Cr₂O₇, potassium dichromate; v/v, volume per volume; °C degrees Celsius]

Constituent(s) to be determined	Storage container and preparation	Stabilization treatment in addition to filtration and refrigeration
Major anions (Br, Cl, F, and SO ₄), alkalinity as HCO ₃ , acidity, density, and nitrate (NO ₃)	Clear polyethylene bottles (250-mL), soaked in deionized water and rinsed 3 times with deionized water	None
Major cations (Ca, Mg, Na, K) and trace metals (As, Sb, Ba, Be, Bi, B, Cd, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Pb, Li, Lu, Mn, Mo, Nd, Ni, Pr, Re, Rb, Sm, Se, Sr, Te, Tb, Tl, Th, Tm, Sn, W, U, V, Yb, Y, Zn, and Zr)	Clear polyethylene bottles (125-mL), soaked in 5% HCl and rinsed 3 times with deionized water	1% (v/v) concentrated redistilled HNO ₃ added; samples were not chilled
Iron, arsenic, and antimony redox species (Fe(T), Fe(II), As(T), As(III), Sb(T), and Sb(III))	Opaque polyethylene bottles (125-mL), soaked in 5% HCl and rinsed 3 times with deionized water	1% (v/v) redistilled 6 M HCl added
Arsenic redox species (As(T) and As(III))	Opaque polyethylene bottles (60-mL), soaked in 5% HCl and rinsed 3 times with deionized water	None
Ammonium (NH ₄)	Clear polyethylene bottles (30-mL), soaked in 5% HCl and rinsed 3 times with deionized water	1% (v/v) 4 M H ₂ SO ₄ added
Total mercury (Hg(T))	Borosilicate glass bottles (125-mL), soaked with 5% HNO ₃ and rinsed 3 times with deionized water	4% (v/v) Hg preservative (concentrated redistilled HNO ₃ with 1 g/L K ₂ Cr ₂ O ₇) added
Silica (SiO ₂)	Clear polyethylene bottles (30-mL), soaked in 5% HCl and rinsed 3 times with deionized water	0.5 mL sample diluted to 25 mL with distilled water on-site; samples were not chilled
Thiosulfate (S ₂ O ₃)	Clear polyethylene bottles (30-mL) rinsed 3 times with deionized water	1.7% (v/v) 0.6 M Zn(COOCH ₃) ₂ and 1% (v/v) 1 M NaOH added
Polythionate (S _n O ₆)	Clear polyethylene bottles (30-mL) rinsed 3 times with deionized water	1.7% (v/v) 0.6 M Zn(COOCH ₃) ₂ , 1% (v/v) 1 M NaOH, and 1.7% (v/v) 1 M KCN
Dissolved organic carbon (DOC)	Amber glass bottles (60-mL) baked at 600°C	None
Water Isotopes (δD and δ ¹⁸ O)	Borosilicate glass bottles (60-mL)	None; samples were not chilled
Sulfide (H ₂ S)	Clear polyethylene bottles (30-mL)	15 mL sulfide anti-oxidant buffer followed by 15 mL sample

Field and Laboratory Measurements

Field Measurements

Measurements of temperature, pH, EMF (used to determine Eh), electrical conductivity, and dissolved oxygen (DO, selected samples) were performed on site. Measurements of EMF and pH were made on unfiltered sample water pumped from the source through an acrylic plastic flow-through cell or directly in the spring, if safe. The flow-through cell contained a combination redox electrode, a combination pH electrode, a thermistor, and test tubes containing buffer solutions for pH calibration. All components were thermally equilibrated with the sample water before obtaining measurements. Where practical, electrical conductivity and source temperature were measured by immersing the combined conductance/temperature probe directly into the source as close to the sampling point as possible. Otherwise, the probe was immersed in the flow-through cell. Because sample temperatures usually were greater than the upper limit (45°C) of the DO probe, DO was determined using the azide modification of the Winkler titration on selected samples (APHA, American Public Health Association, 1971).

Because field measurement of pH in geothermal waters is challenging and accurate pH measurements are critical for interpreting analytical results (Ball and others, 2006), special care was taken when measuring this parameter. At each site, the flow-through cell, temperature probe, electrode, and calibration buffers were thermally equilibrated prior to calibration and measurement. The system was calibrated using at least two bracketing standard buffers (chosen from among 1.68, 4.01, 7.00, or 10.00) using their pH values at the sample temperature (Midgley and Torrance, 1991). After calibration, the pH electrode was placed in the sample water in the flow-through cell and monitored until no changes in temperature ($\pm 0.1^\circ\text{C}$) or pH (± 0.01 standard unit) were detected for at least 30 seconds. Following sample measurement, the electrode was immersed in the standard buffer of pH closest to that of the sample and allowed to equilibrate. The entire calibration and measurement process was repeated

as many times as necessary until the measured value for the buffer differed by no more than 0.05 standard units from its certified pH at the measured temperature.

Electrical conductivity measurements are typically referenced to 25°C using standard temperature compensation factors (α). However, typical electrical conductivity compensation for acid geothermal waters can result in large errors (>50%) because the hydrogen ion transport number (which is not accounted for with the commonly used α 's) can be substantial and the temperature is often much greater than 25°C. Figure 1 shows the percent difference between field and lab conductivity measurements using the standard ISO-7888 temperature compensation factor (ISO-7888, 1985) that is utilized by many conductivity meters and the McCleskey (2013) temperature compensation factor. The method for electrical conductivity temperature compensation by McCleskey (2013) is more reliable for calculating the electrical conductivity at 25°C for geothermal waters.

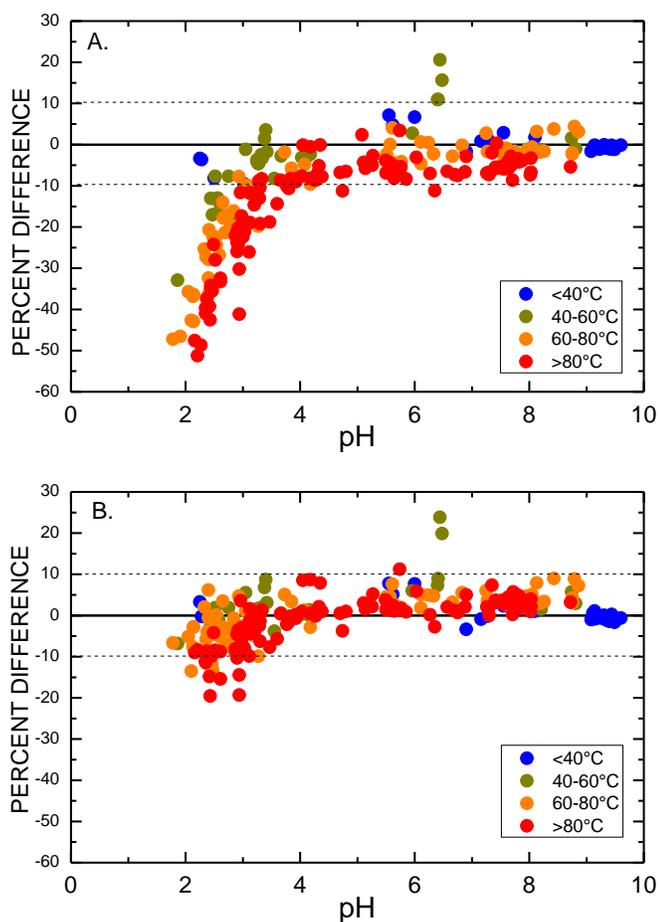


Figure 1. Percent difference between field and lab electrical conductivity using (A) the ISO-7888 temperature compensation factor (ISO-7888, 1985) and (B) the McCleskey (2013) temperature compensation factor. The dashed lines are $\pm 10\%$ for reference.

A mobile laboratory truck containing an ion chromatograph, ultraviolet-visible spectrophotometer, autotitrator, and reagent-grade water purification system was set up so that unstable intermediate sulfur oxyanion species could be determined as soon as possible after sample collection. Iron redox species also were determined in the mobile laboratory. The autotitrator was used each

evening to perform alkalinity and acidity titrations before oxidation and hydrolysis reactions occurred, and to determine H₂S concentrations in samples preserved on site. Sulfide concentrations were determined within 24 hours by ion-specific electrode. Our results to date indicate that stabilizing the sulfide in geothermal water by immediately combining the hot sample with an alkaline solution containing SAOB offers the best option for obtaining accurate estimates of sulfide concentrations (Ball and others, 2010).

Laboratory Methods

All laboratory measurements were made at the U.S. Geological Survey National Research Program laboratory in Boulder, Colorado. All reagents were of equal or higher purity than the reagent-grade standards of the American Chemical Society. Deionized water and redistilled or trace-metal-grade acids were used in all preparations. Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. Table 2 lists the analytical techniques, detection limits, equipment used, analytical method, and references for all constituents. Except for inductively coupled plasma–mass spectrometry analyses and mercury determinations, detection limits were equal to three times the standard deviation of several dozen measurements of the constituent in a blank solution analyzed as a sample. The detection limits for inductively coupled plasma–mass spectrometry and cold vapor atomic fluorescence spectrometry were determined using the method presented by Skogerboe and Grant (1970). Details on the instrumentation, techniques, general conditions, and variants from standard procedures are discussed in following sections.

Table 2. Analytical techniques, detection limits, equipment used, and analytical method references.

[cm, centimeter; CRDS, cavity ring-down spectroscopy; CVAFS, cold vapor atomic fluorescence spectrometry; °C, degrees Celsius; HCl, hydrochloric acid; HGAAS, hydride generation atomic absorption spectrometry; IC, ion chromatography; ICP-OES, inductively coupled plasma-mass spectrometry; ICP-OES, inductively coupled plasma-optical emission spectrometry; ISE, ion-selective electrode; KCl, potassium chloride; KI, potassium iodide; M, molar; mg/L, micrograms per liter; mg/L, milligrams per liter; mM, millimolar; mN, millinormal; MS, mass spectrometry; N, normal; NaHCO₃, sodium bicarbonate; Na₂CO₃, sodium carbonate; ng/L, nanograms per liter; nm, nanometer; SLAP, standard light Antarctic precipitation; TISAB, total ionic strength adjustment buffer; TOC, total organic carbon; VSMOW, Vienna standard mean ocean water; ≤, less than or equal to; %, percent] (Barnard and Nordstrom, 1982; Moses and others, 1984)

Constituent	Analytical Technique	Typical Detection Limit	Units	Equipment Used	Comments or Reference(s)
Field Measurements					
Temperature	Electronic sensor	0.1	°C	Orion Research model 1230 multi-parameter meter with temperature sensor built into conductivity electrode	Temperatures were reported to the nearest 0.1 °C
pH	Potentiometry	0.02	pH units	Orion 3-star meter with Orion Ross combination electrode	Two- or three-buffer calibration at sample temperature using 1.68, 4.01, 7.00, and 10.00 pH buffers
Electrical Conductivity (EC)	Conductometry	0.5	µS/cm	Orion Research model 1230 multi-parameter meter with conductivity electrode	Temperature correction to 25°C using the temperature compensation method by McCleskey (2013), cell constant determined with 0.010 N KCl
Eh	Potentiometry	0.001	V	Orion Research model 96-78-00 combination redox electrode	Electrode checked using ZoBell's solution (ZoBell, 1946; Nordstrom, 1977)
Dissolved oxygen (DO)	Titration	0.1	mg/L	Burette and Erlenmeyer flask	Winkler Titration using manganous sulfate, alkaline iodide-azide, sulfamic acid, starch indicator, phenyl arsine oxide (APHA, 1971)
Laboratory Measurements					
Calcium (Ca)	ICP-OES	0.04	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 317.933 nm, view: radial
Magnesium (Mg)	ICP-OES	0.003	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 285.211 nm, view: radial
	ICP-MS	0.0001	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 24.3
Sodium (Na)	ICP-OES	0.08	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 589.592 nm, view: radial
Potassium (K)	ICP-OES	0.06	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 766.495 nm view: axial
Alkalinity (as HCO ₃)	Titration	1	mg/L	Orion Research model 960/940 autotitrator, potentiometric detection, end-point determined by the first derivative technique	(Barringer and Johnsson, 1996; Fishman and Friedman, 1989)
Chloride (Cl)	IC	0.05	mg/L	Dionex model 100 or 600 ion chromatograph with AG18A guard and AS18A separator columns and Anion Self-Regenerating Suppressor-II	23 mM NaOH eluent
Fluoride (F)	ISE	0.01	mg/L	Orion Research model 96-09 combination F electrode	Sample mixed 1:1 with Orion Research 940911 TISAB III (Barnard and Nordstrom, 1980);
	IC	0.1	mg/L	Dionex model 100 or 600 ion chromatograph with AG18A guard and AS18A separator columns and Anion Self-Regenerating Suppressor-II	23 mM NaOH eluent
Bromide (Br)	IC	0.05	mg/L	Dionex model 100 or 600 ion chromatograph with AG18A guard and AS18A separator columns and Anion Self-Regenerating Suppressor-II	23 mM NaOH eluent
Sulfate (SO ₄)	IC	0.1	mg/L	Dionex model 100 or 600 ion chromatograph with AG18A guard and AS18A separator columns and Anion Self-Regenerating Suppressor-II	23 mM NaOH eluent
Thiosulfate (S ₂ O ₃)	IC	0.1	mg/L	Dionex model 100 ion chromatograph with two AG4A guard and an Anion Self-Regenerating Suppressor-II	0.028 M NaHCO ₃ + 0.022 M Na ₂ CO ₃ eluent (Moses and others, 1984)
Polythionate (S _n O ₆)	IC	0.3	mg/L	Dionex model 100 ion chromatograph with two AG4A guard and an Anion Self-Regenerating Suppressor-II	0.028 M NaHCO ₃ + 0.022 M Na ₂ CO ₃ eluent (Moses and others, 1984)

Table 2. Analytical techniques, detection limits, equipment used, and analytical method references—Continued.

Constituent	Analytical Technique	Typical Detection Limit	Units	Equipment Used	Comments or Reference(s)
Laboratory Measurements					
Hydrogen sulfide (H ₂ S)	ISE	0.001	mg/L	Orion Research model 960/940 autotitrator, Accumet model 13-620-551 Silver/Sulfide combination electrode	Sample mixed 1:1 on-site with Orion Research 941609 Sulfide Anti-Oxidant Buffer (SAOB) and analyzed within 24 hours of collection (APHA, 1998)
Silica (SiO ₂)	ICP-OES	0.04	mg/L	Perkin Elmer Optima 7300DV	Sample diluted 25X in field, Wavelength: 251.611 nm, view: axial
Nitrate (NO ₃)	IC	0.05	mg/L	Dionex model 100 or 600 ion chromatograph with AG18A guard and AS18A separator columns and Anion Self-Regenerating Suppressor-II	23 mM NaOH eluent
Ammonium (NH ₄)	IC	0.1	mg/L	Dionex model DX-300 ion chromatograph with CS12A IonPac column	22 mM H ₂ SO ₄ eluent (Smith and others, 2006)
Dissolved organic carbon (DOC)	TOC	0.1	mg/L	Oceanography International Model 700 TOC Analyzer	Wet oxidation method (Aiken, 1992)
Aluminum (Al)	ICP-OES	0.006	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 396.155 nm, view: axial
	ICP-MS	0.00004	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 27; correction: CN
Antimony (Sb)	ICP-MS	0.00003	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 121
Arsenic - total dissolved (As(T))	ICP-OES	0.03	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 188.980 nm, view: axial
	HGAAS	0.0001	mg/L	Perkin-Elmer AAnalyst 300 atomic absorption spectrometer with a FIAS-100 flow injection analysis system, quartz cell, and furnace	Pre-reduction of As(V) using KI + ascorbic acid + HCl (McCleskey and others, 2003)
Arsenite (As(III))	HGAAS	0.001	mg/L	Perkin-Elmer AAnalyst 300 atomic absorption spectrometer with a FIAS-100 flow injection analysis system, quartz cell, and furnace	
Barium (Ba)	ICP-OES	0.1	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 455.405 nm, view: radial
	ICP-MS	0.002	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 137
Beryllium (Be)	ICP-OES	0.3	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 313.107 nm, view: axial
	ICP-MS	0.001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 9
Bismuth (Bi)	ICP-MS	0.007	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 209
Boron (B)	ICP-OES	0.02	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 249.675 nm, view: axial
Cerium (Ce)	ICP-MS	0.0002	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 140
Cesium (Cs)	ICP-MS	0.000001	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 133
Copper (Cu)	ICP-OES	0.003	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 324.75 nm, view: axial
	ICP-MS	0.005	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 65; correction: SO ₂
Cadmium (Cd)	ICP-MS	0.0009	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 111; correction: MoO
Chromium (Cr)	ICP-MS	0.03	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 52; correction: HClO, ArC
Cobalt (Co)	ICP-MS	0.0007	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 59; correction: CaO
Dysprosium (Dy)	ICP-MS	0.0001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 163; correction: SmO
Erbium (Er)	ICP-MS	0.0001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 167; correction: EuO
Europium (Eu)	ICP-MS	0.00006	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 151; correction: BaO
Iron - total dissolved (Fe(T))	Colorimetry	0.002	mg/L	Hewlett-Packard model 8452A diode array spectrometer with 1-cm cells	FerroZine method (Stookey, 1970; To and others, 1999)
	ICP-OES	0.002	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 238.204 nm, view: axial
Ferrous iron (Fe(II))	Colorimetry	0.002	mg/L	Hewlett-Packard model 8452A diode array spectrometer with 1- and 5-cm cells	FerroZine method (Stookey, 1970; To and others, 1999)
Gadolinium (Gd)	ICP-MS	0.0001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 158; correction: NdO, CeO
Holmium (Ho)	ICP-MS	0.00002	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 165; correction: SmO
Lanthanum (La)	ICP-MS	0.0001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 139

Table 2. Analytical techniques, detection limits, equipment used, and analytical method references—Continued.

Constituent	Analytical Technique	Typical Detection Limit	Units	Equipment Used	Comments or Reference(s)
Laboratory Measurements					
Lithium (Li)	ICP-OES	0.001	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 670.784 nm, view: axial
	ICP-MS	0.00009	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 7
Lutetium (Lu)	ICP-MS	0.00006	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 175; correction: TbO
Manganese (Mn)	ICP-OES	0.0008	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 257.609 nm, view: axial
	ICP-MS	0.000003	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 55
Mercury - total dissolved (Hg(T))	CVAFS	0.4	ng/L	PS Analytical, model Merlin	Taylor and others (1997), Roth and others (2001)
Molybdenum (Mo)	ICP-OES	3	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 202.031 nm, view: axial
	ICP-MS	0.06	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 95
Neodymium (Nd)	ICP-MS	0.0003	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 146
Nickel (Ni)	ICP-MS	0.003	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 60; correction: CaO, CaC
Lead (Pb)	ICP-MS	0.003	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: composite of 206, 207, 208
Phosphorus (P)	ICP-OES	50	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 213.617 nm, view: axial
	ICP-MS	1	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 31
Praseodymium (Pr)	ICP-MS	0.00005	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 141
Rhenium (Re)	ICP-MS	0.00008	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 187; correction: YbO
Rubidium (Rb)	ICP-OES	2	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 780.025 nm, view: axial
Samarium (Sm)	ICP-MS	0.0003	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 147
Selenium (Se)	ICP-MS	0.08	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 77; correction: ArCl
Strontium (Sr)	ICP-OES	0.001	mg/L	Perkin Elmer Optima 7300DV	Wavelength: 407.771 nm, view: radial
	ICP-MS	0.00007	mg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 86
Tin (Sn)	ICP-MS	0.08	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 118
Terbium (Tb)	ICP-MS	0.00004	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 159; correction: NdO
Tellurium (Te)	ICP-MS	0.004	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 126
Thorium (Th)	ICP-MS	0.001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 232
Thallium (Tl)	ICP-MS	0.0006	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 205
Thulium (Tm)	ICP-MS	0.00007	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 169; correction: EuO
Tungsten (W)	ICP-MS	0.1	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 182; correction: ErO
Uranium (U)	ICP-MS	0.0002	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 238
Vanadium (V)	ICP-OES	2	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 292.402 nm, view: axial
	ICP-MS	0.008	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 51; correction: ClO
Yttrium (Y)	ICP-MS	0.0001	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 89
Ytterbium (Yb)	ICP-MS	0.00009	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 174; correction: GdO
Zinc (Zn)	ICP-OES	1	µg/L	Perkin Elmer Optima 7300DV	Wavelength: 206.197 nm, view: axial
	ICP-MS	0.02	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 66; correction: Ba++
Zirconium (Zr)	ICP-MS	0.0006	µg/L	Perkin Elmer Elan DRC II	Isotopic Mass: 90
Deuterium (δD)	CRDS	0.1 ¹	‰	Los Gatos Research – Liquid Water Isotope Analyzer	Standardization against VSMOW (δD = 0 per mil)
Oxygen (δ ¹⁸ O)	CRDS	0.1 ¹	‰	Los Gatos Research – Liquid Water Isotope Analyzer	Standardization against VSMOW (δ ¹⁸ O = 0 per mil)
Acidity (total/free H ⁺)	Titration	0.4	mN	Orion Research model 960/940 autotitrator, potentiometric detection	(Barringer and Johnsson, 1996)

¹ Relative standard deviation expressed in percent

Major Cation and Trace Metal Determinations

Concentrations of dissolved major cations and selected trace metals (filtered and acidified with HNO₃) were determined using inductively coupled plasma–optical emission spectrometry (ICP–OES, PerkinElmer 7300 DV). The axial plasma viewing orientation was used for the major cations and trace metals, except for potassium. The radial plasma viewing orientation was used for potassium. A cesium chloride ionization buffer was added in-line prior to sample nebulization to suppress the ionization of potassium and lithium in the plasma. The analytical wavelengths and method detection limits for ICP–OES determinations are reported in table 2. In addition to ICP–OES, the concentrations of dissolved trace metals, including the rare-earth elements, were also determined using inductively coupled plasma–mass spectrometry (ICP–MS, PerkinElmer Elan DRC II). An internal standard was added to the sample stream for ICP–MS measurements. Element masses used in determining elemental concentrations and method detection limits for ICP–MS determinations are reported in table 2. The concentration of many trace metals were only determined by ICP-MS. However, several trace metal concentrations were determined by ICP-OES and ICP-MS and the data from the analytical technique that produced the most accurate and precise data were selected. The selection is based on potential interferences, the analyte concentration in relation to the method detection limit, and in cases where the two techniques were comparable, ICP-OES was often selected because the technique was used in previous YNP studies. The analytical technique used for the final selection of element-specific data was determined using the process illustrated in figure 2.

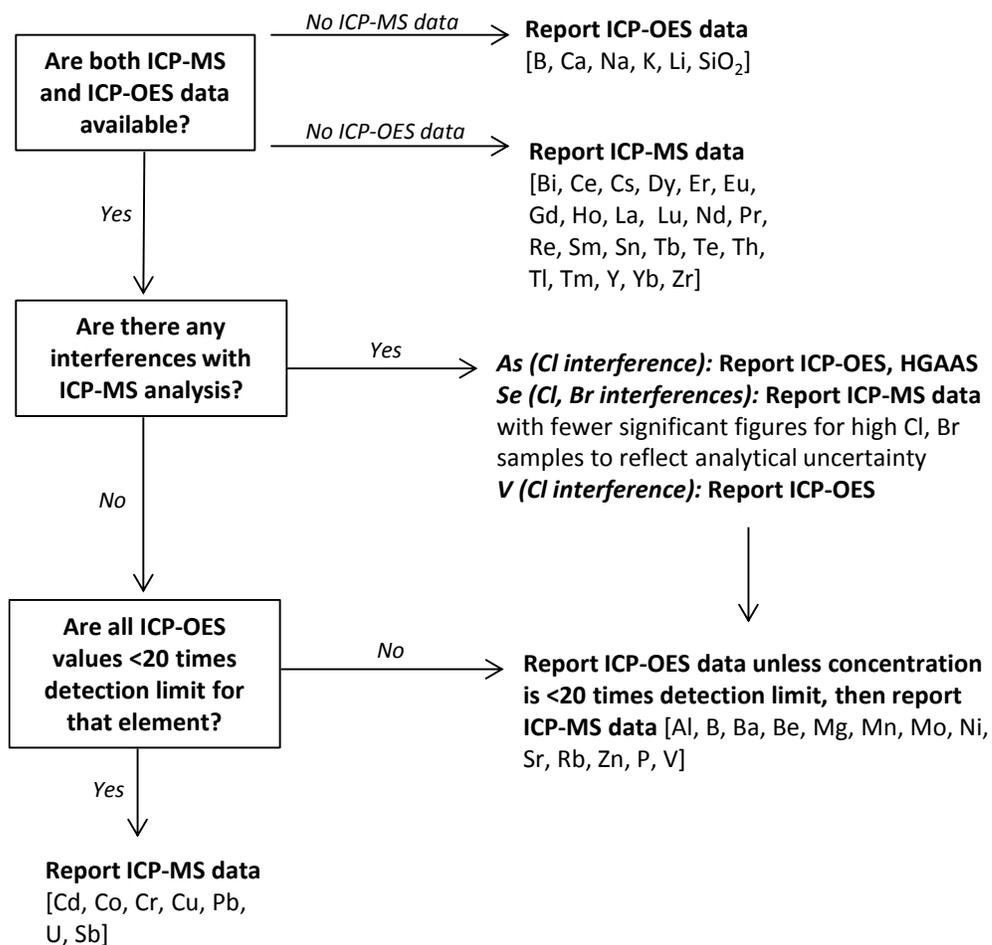


Figure 2. Flow-chart for the analytical technique used for the final selection of element-specific data.

Anion and Alkalinity Determinations

Concentrations of bromide, chloride, fluoride, nitrate, and sulfate were determined by ion chromatography (IC, Dionex DX 600) with suppressed electrical conductivity detection (Brinton and others, 1995). An IonPac AS18 Analytical Column (4 mm), AG18 Guard Column, and an Anion Self-Regenerating Suppressor (ASRS ULTRA II (4 mm)) were used. Thirty-millimolar sodium hydroxide (NaOH) eluent was pumped through the columns at 1 milliliter per minute (mL/min). Analytical errors for these constituents are typically less than 5 percent. The ion chromatography method detection limits

are reported in the accompanying Microsoft Excel spreadsheet in the "Analytical" worksheet. Samples for F determination by ISE were mixed 1:1 with a total ionic strength adjustment buffer (TISAB III) (Barnard and Nordstrom, 1980).

Alkalinity was determined by automated titration (Thermo, 940-960 autotitrator) using standardized sulfuric acid (Barringer and Johnsson, 1996; Fishman and Friedman, 1989). Fifteen milliliters of sample were titrated with 0.01 normal (equivalents per liter) sulfuric acid to the bicarbonate end-point. The analytical error in alkalinity concentrations is less than 3 percent.

Arsenic Redox Determinations

Hydride-generation atomic absorption spectrometry (HGAAS) was used to measure total dissolved arsenic (As(T)) and dissolved arsenite (As(III)) concentrations in HCl-acidified samples. A flow-injection analysis system (Perkin Elmer, FIAS 100) was used to generate arsine from As(III) with sodium borohydride mixed in a gas-liquid separator with a 10% v/v HCl carrier solution (McCleskey and others, 2003). The determination of total dissolved arsenic (As(T)) concentrations required pre-reduction of As(V) using potassium iodide (KI), ascorbic acid, and hydrochloric acid. Arsenic redox species are routinely collected by filtering (0.1 μm) the water sample into an opaque HDPE bottle and then adding 1% (v/v) 6M HCl (McCleskey and others, 2004). However, in some sulfidic waters insoluble thio-As species are known to form upon acidification with HCl (Planer-Friedrich and others, 2007). Furthermore, during the determination of As redox species by HGAAS, As-sulfur species may be formed as the sulfidic water sample mixes with the 10% HCl carrier solution. Some of these species may not be detected because they do not form arsine (Planer-Friedrich and Wallschlager, 2009). In both cases, the As(T) and As(III) concentrations may be underestimated (figure 3). The greater the H₂S concentration, the more likely As-sulfur species are to form (figure 4). Therefore, we measured total dissolved As (As(T)) in 3 different splits (FU, FA-HCl, and FA-HNO₃) to identify water samples that

form thio-As species upon acidification with HCl or during measurement by HGAAS. The As(T) determined by ICP-OES in the FA-HNO₃ sample split is considered to be the most accurate because HNO₃ is known to oxidize redox species and inhibit the formation of thio-As species. Thus, we used the As(T) measured in the FA-HNO₃ as a guide to identify the samples that likely form thio-As species upon acidification with HCl or measurement by HGAAS. In cases where the measurements of the various splits are within the analytical error ($\sim\pm 10\%$), formation of thio-As species was not significant and the As(T) concentrations and As(III) concentrations reported are from the FA-HCl split determined with HGAAS. However, in the cases where the As(T) concentration in the FA-HNO₃ split was found to be $\geq 110\%$ of the As(T) concentration in the FA-HCl, it was concluded that thio-As species had formed and that the As(T) and As(III) concentrations measured in the FA-HCl split were biased low. For these fifty samples, the reported As(T) concentration is from the FA-HNO₃ split. The As(III) concentrations are from the HCl split and reported as minimum values with a “ \geq ” symbol. The As(T) and As(III) in the remaining samples were reported for the FA-HCl split.

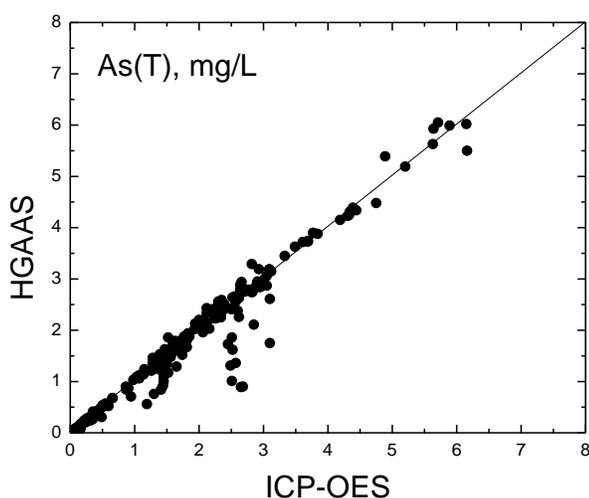


Figure 3. As(T) concentrations determined by HGAAS in the FA-HCl split plotted against As(T) concentrations determined by ICP-OES in the FA-HNO₃ split.

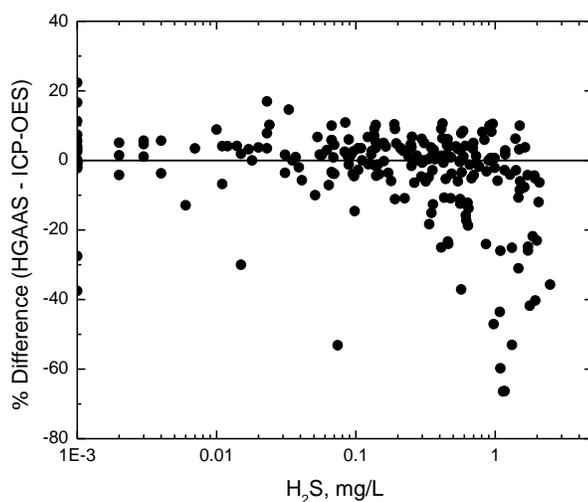


Figure 4. The percent differences in the measured As concentrations plotted against H₂S concentrations.

Iron Redox Determinations

Total dissolved iron (Fe(T)) and ferrous iron (Fe(II)) concentrations (filtered and acidified with HCl) were determined in samples preserved with HCl using a modification of the FerroZine colorimetric method (Gibbs, 1976; Stookey, 1970; To and others, 1999). All iron determinations were prepared in 25-mL volumetric flasks and then their absorbances were measured at 562 nm using a diode array spectrometer (Hewlett-Packard model 8452A). For total dissolved iron determinations, hydroxylamine hydrochloride was first added to the sample to pre-reduce any ferric iron, then the FerroZine reagent and acetate buffer were added. Ferrous iron was determined by only adding FerroZine reagent and acetate buffer.

Ammonium Determinations

Concentrations of ammonium (filtered and acidified with H₂SO₄) were determined by ion chromatography (Dionex DX 300) with suppressed electrical conductivity detection. An IonPac AS12A Analytical Column (4mm), an AG12A Guard Column, and a Cation Self-Regenerating Suppressor

(CSRS 300 (4-mm)) were used. A gradient pump was used to pump sulfuric acid (H₂SO₄) eluent through the system. The method detection limit was 0.04 milligrams per liter (mg/L).

Mercury Determinations

Total dissolved mercury (Hg) concentrations (filtered and preserved with HNO₃/K₂Cr₂O₇) for a subset of samples were determined by direct cold-vapor atomic fluorescence spectroscopy (CVAFS) using the method of Roth and others (2001). Samples are oxidized using potassium dichromate, then reduced by stannous chloride, followed by atomic fluorescence detection. The method detection limit was 0.4 nanograms per liter.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) concentrations were measured using the wet oxidation method (Aiken, 1992) with an Oceanography International Model 700 TOC Analyzer. Potassium biphthalate was used to calibrate the instrument, and sodium benzoate was used as a different organic carbon source to check the calibration. The method detection limit for DOC was 0.4 mg/L.

Water Isotope Determinations

Hydrogen and oxygen isotope ratios were determined at the USGS Laboratory in Boulder, CO using cavity ring-down spectroscopy (CRDS - Los Gatos Research – Liquid Water Isotope Analyzer). The isotopic concentration is reported in “delta notation,” which compares the isotope ratio of a sample to that of a reference standard. For the example of ¹⁸O/¹⁶O ratios, delta notation was determined with the following equation:

$$\delta^{18}\text{O}\text{‰} = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{standard}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{standard}}} \times 1000 \quad (1)$$

where ‰ is per mil, which is equivalent to parts per thousand.

Oxygen and hydrogen isotopic results are reported relative to the standard VSMOW (Vienna Standard Mean Ocean Water) and normalized (Coplen, 1994) on scales such that the oxygen and hydrogen isotopic values of SLAP (Standard Light Antarctic Precipitation) are -55.5 per mil and -428 per mil, respectively.

Acidity Determinations

Total acidity was determined by titrating samples having pH less than 4 to pH greater than 9 using an autotitrator and standardized sodium hydroxide (NaOH) solution. The NaOH titrant (0.01–0.05 N) was standardized daily by titrating a known quantity of potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$). The titrator was programmed for 50- to 100- μL constant-volume additions or constant change in millivolts (mV), typically 10 mV per addition. Equivalence points were determined using a modified Gran's function (Barringer and Johnsson, 1996; Gran, 1952):

$$F_{\text{acid}} = (v_0 + v_{\text{NaOH}}) \times 10^{-\text{pOH}} \quad (2)$$

where F_{acid} = the Gran function, v_0 = sample volume, v_{NaOH} = volume of NaOH titrant added, and $\text{pOH} = 14 - \text{pH}$.

The principal components contributing to acidity were discussed by Ball and others (2006). Free H^+ was derived from the total acidity by subtracting the hydrogen ions produced by hydrolysis of SO_4 , Fe, Al, As(V), and F, as calculated by PHREEQC (Charlton and Parkhurst, 2002; Parkhurst and Appelo, 1999) incorporating the WATEQ4F database, as follows:

$$\text{Acidity}_{\text{SO}_4} = \text{HSO}_4^- \quad (3)$$

$$\text{Acidity}_{\text{Fe}} = 3(\text{Fe}^{\text{III}}(\text{tot}) - \text{Fe}(\text{OH})_2^+) + 2\text{FeOH}^{2+} + \text{Fe}(\text{OH})_2^+ + 2\text{Fe}^{\text{II}}(\text{tot}) \quad (4)$$

$$\text{Acidity}_{\text{Al}} = 3(\text{Al}(\text{tot}) - \text{AlOH}^{2+} - \text{Al}(\text{OH})_2^+) + 2\text{AlOH}^{2+} + \text{Al}(\text{OH})_2^+ \quad (5)$$

$$\text{Acidity}_{\text{As}} = 2(\text{As}^{\text{V}}(\text{tot}) - \text{H}_2\text{AsO}_4^-) + \text{H}_2\text{AsO}_4^- \quad (6)$$

$$\text{Acidity}_{\text{F}} = \text{HF}^0 \quad (7)$$

$$\text{Acidity}_{\text{H}^+} = \text{Acidity}_{\text{Total}} - \text{Acidity}_{\text{SO}_4} - \text{Acidity}_{\text{Fe}} - \text{Acidity}_{\text{Al}} - \text{Acidity}_{\text{As}} - \text{Acidity}_{\text{F}} \quad (8)$$

Concentrations for the above equations are expressed in moles per kilogram of water. Sample pH from the acidity titration (acidity pH) was calculated by computing the product of the H^+ activity coefficient (calculated by PHREEQCi) and the free H^+ molality (equation 8) and computing the negative common logarithm of the resulting activity. This pH value was refined by repeating the PHREEQCi calculation and varying the input pH until the pH calculated from the PHREEQCi speciation was equal to the input pH. A flow-chart illustrating the process for refining the acidity pH is shown in figure 5.

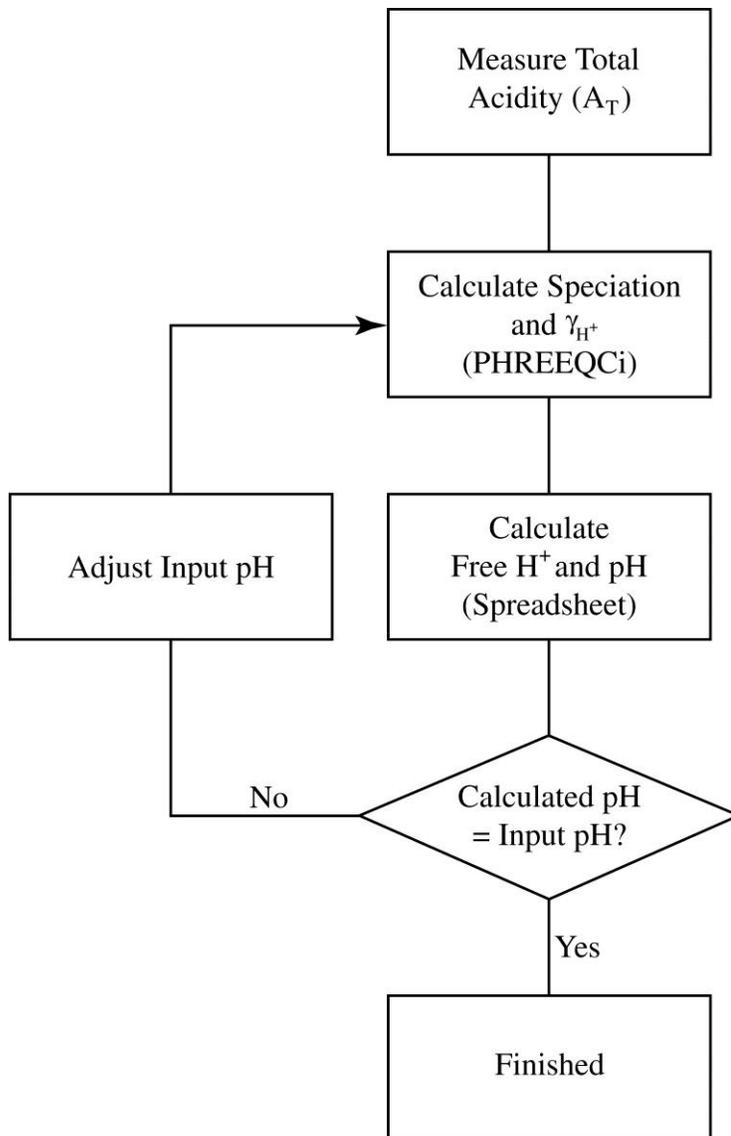


Figure 5. Flow chart illustrating the process for refining the acidity pH value.

Revised pH Measurements

Accurate measurement of pH is of primary importance for interpreting aqueous chemical speciation. The free hydrogen ion (H^+) is usually the major cation in samples with pH less than 2.5 in geothermal waters (Ball and others, 2002), is important in controlling geochemical reactions, and is

critical in calculating the charge imbalance (C.I.) for waters with pH less than 3. For the subset of 208 samples with pH less than 4, pH values determined using three different techniques were evaluated: (1) pH measured in the field; (2) pH measured in the laboratory; (3) acidity pH (calculated as discussed in the previous section). Comparison of pH values from the three sources allows evaluation of the measurements and estimation of more accurate pH values.

A flow chart showing the pH selection process is shown in figure 6. Field pH is considered to be the most accurate because pH measurements made in the laboratory may be biased from temperature changes and hydrolysis reactions, and the acidity pH calculation relies on measurements of SO₄, Fe, Al, As, and F, all of which are subject to analytical uncertainties, temperature changes, and hydrolysis reactions.

For samples having a pH less than 3.5, field pH was selected unless the sample had a speciated C.I. greater than 10 percent using field pH. For samples with pH less than 3.5 and speciated C.I. greater than 10 percent using field pH, laboratory pH was selected if the speciated C.I. was less than 10 percent. For samples with pH less than 3.5 and speciated C.I. greater than 10 percent using both field and laboratory pH, acidity pH was selected if the speciated C.I. was less than 10 percent. For samples with pH less than 3.5 and having field, laboratory, and acidity pH values that all produced speciated C.I.s greater than 10 percent, the pH that produced the lowest speciated C.I. was selected from among field, laboratory, and acidity pH.

Using the process described above and illustrated in figure 6 for the subset of 190 samples with a field pH less than 3.5, field pH was selected for 140 samples, laboratory pH was selected for 43 samples, and acidity pH was selected for 7 samples. Values of the selected pH are found in the table of chemical data along with the speciated C.I. calculated using the selected pH and field temperature.

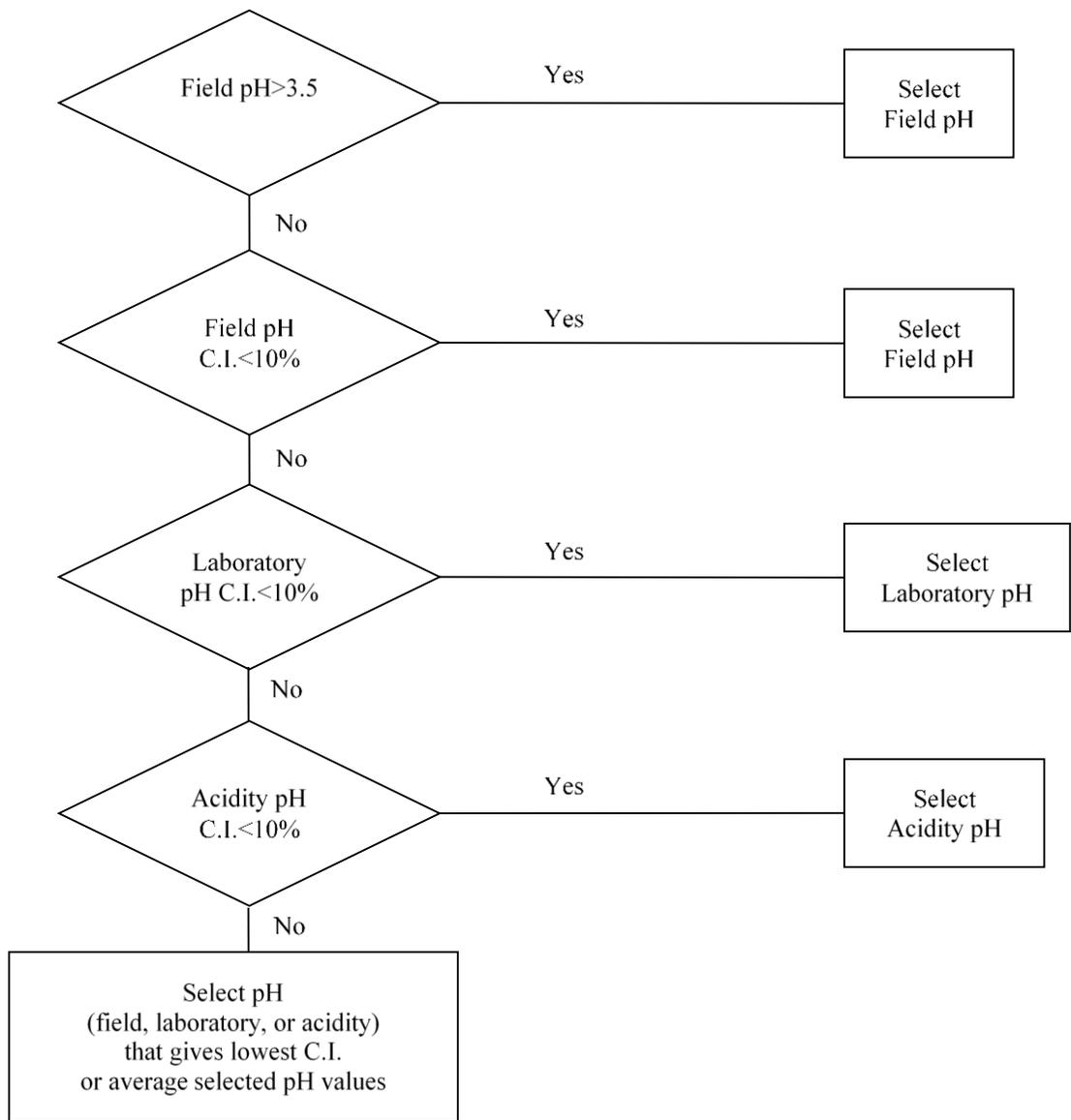


Figure 6. Flow chart showing the pH selection process. (C.I., charge imbalance)

Quality Assurance and Quality Control

Several techniques were used to assure the quality of the ionic analytical data. These techniques included calculation of charge imbalance, electrical conductivity balance, analysis of blanks, analyses by alternate methods, analysis of U.S. Geological Survey SRWS, and analysis of replicate samples.

The charge imbalance calculation is a common quality-assurance/quality-control procedure to check the accuracy of a water analysis (APHA, American Public Health Association, 1971). For samples that were analyzed for major cations and anions, the accuracy of the analyses were checked for charge imbalance using the geochemical code WATEQ4F (Ball and Nordstrom, 1991). WATEQ4F uses equation 9 to calculate charge imbalance:

$$\text{Charge imbalance (percent)} = \frac{(\text{sum cations} - \text{sum anions})}{(\text{sum cations} + \text{sum anions}) \div 2} \times 100 \quad (9)$$

where sum cations and sum anions are in milliequivalents per liter (meq/L). The charge balance calculation is discussed in more detail by Ball and others (2006). The charge imbalance, sum cations (meq/L), and sum anions (meq/L) are reported for all samples having major cation and anion determinations. A frequency plot of charge imbalance for all samples with complete analyses is shown in figure 7. The mean charge imbalance was -1.1 percent with a standard deviation of 4.8 percent. Analyses having a charge imbalance less than ± 10 percent are considered reliable for speciation calculations (Nordstrom and Munoz, 1994). Two sample analyses, out of 351, had charge imbalances greater than ± 10 percent. However, charge imbalance does not indicate whether the error is caused by a cation or an anion. Therefore, a second constraint is needed to identify the constituent most likely in error. By coupling charge imbalance and electrical conductivity imbalance, the measurement most likely in error can be identified or narrowed down to a few possibilities (McCleskey and others, 2012). A plot of electrical conductivity imbalance against charge imbalance for these samples shows that the electrical

conductivity imbalance was within ± 10 percent for all but 7 samples (figure 8).

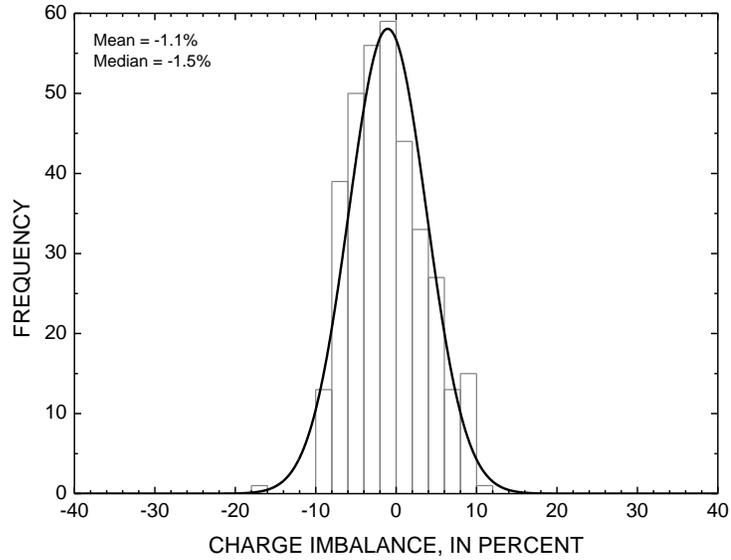


Figure 7. Frequency distribution of charge imbalance for samples having major cation and anion determinations.

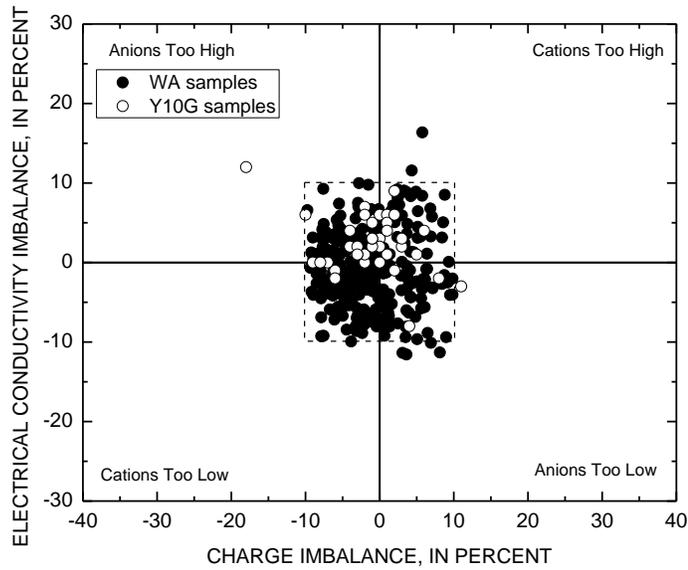


Figure 8. Electrical conductivity imbalance compared with charge imbalance.

Eight field blanks were analyzed along with the samples as unknowns. Field blanks were deionized water that was filtered and preserved in the same manner as the samples. Constituents were below detection in all these blanks, with a few exceptions. Chloride was detected in all the blanks, most likely from HCl used to wash the filter apparatus; the highest Cl concentration was 1.8 mg/L. Sulfate was detected in 3 blanks, the highest being 1.5 mg/L, most likely from small amounts of contamination within the IC columns. Trace amounts of SiO₂ (<0.4 mg/L) were detected in all samples, originating either from contaminated blank deionized water or from incompletely cleaned filters. Dissolved organic carbon was detected in all 3 blanks, the highest being 1.3 mg/L, most likely because of organic carbon in the deionized blank water. Apart from dissolved organic carbon, the constituents measured in the blanks were less than the typical error associated with the analyses and are a small fraction of the measured concentrations.

Concentrations of Al, As, B, Ba, Be, Cd, Co, Cr, Cu, F, Fe, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, Sb, Sr, U, V, W, and Zn were determined by more than one method. Comparing analytical results from alternative methods can serve as an accuracy check, although in all cases one method was preferred over the others depending on sample matrix and proximity to the method detection limit (figure 2).

Concentrations of Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, Sb, Sr, U, V, W, and Zn were determined by ICP-OES and ICP-MS (figure 9). Concentrations of Fe were determined by ICP-OES and by the FerroZine method (figure 10). The reported data were obtained using the preferred method unless there was insufficient sample volume to perform the determinations.

Comparison of analytical results for cations and trace metals from the ICP-OES and ICP-MS are in good agreement except for some low-level concentrations and high Al concentrations. Low-level concentrations of Cd, Cu, Ni, Pd, U, and Zn are likely overestimated by ICP-OES (figure 9) because the analyte concentration is near the detection limit. In the case of Cd, elevated As concentrations interfere

with the Cd determination. For the low-level concentrations of Cd, Cu, Ni, Pd, U, and Zn the concentration determined by ICP-MS was the preferred value (figure 2). Aluminum concentrations in some samples ($\text{Al} > 2 \text{ mg/L}$) determined by ICP-MS are lower than the concentrations determined by ICP-OES by more than 10%. The accuracy of both techniques is thought to be good at these concentrations, but the ICP-OES values were selected (figure 2) in part because the ICP-MS is optimized for low-level determinations and a large dilution was required to bring the Al concentration into the ICP-MS calibration range.

Concentrations of Fe by FerroZine were determined on a subsample preserved with HCl, whereas Fe concentrations determined by ICP-OES were determined on a subsample preserved with HNO_3 (figure 10). The uncertainty line was calculated based on the method with the higher detection limit. At the method detection limit the uncertainty is ± 100 percent and decreases to ± 5 percent at 20 times the detection limit (quantitation limit). With only a few exceptions, Fe concentrations determined by FerroZine and by ICP-OES are in good agreement. When available, results for Fe are reported for the sample preserved with HCl because the redox species concentrations were obtained from this split. Considering the uncertainty of the measurements and that the analyses were performed on different splits, analytical results for total dissolved Fe obtained by the alternative methods are in good agreement.

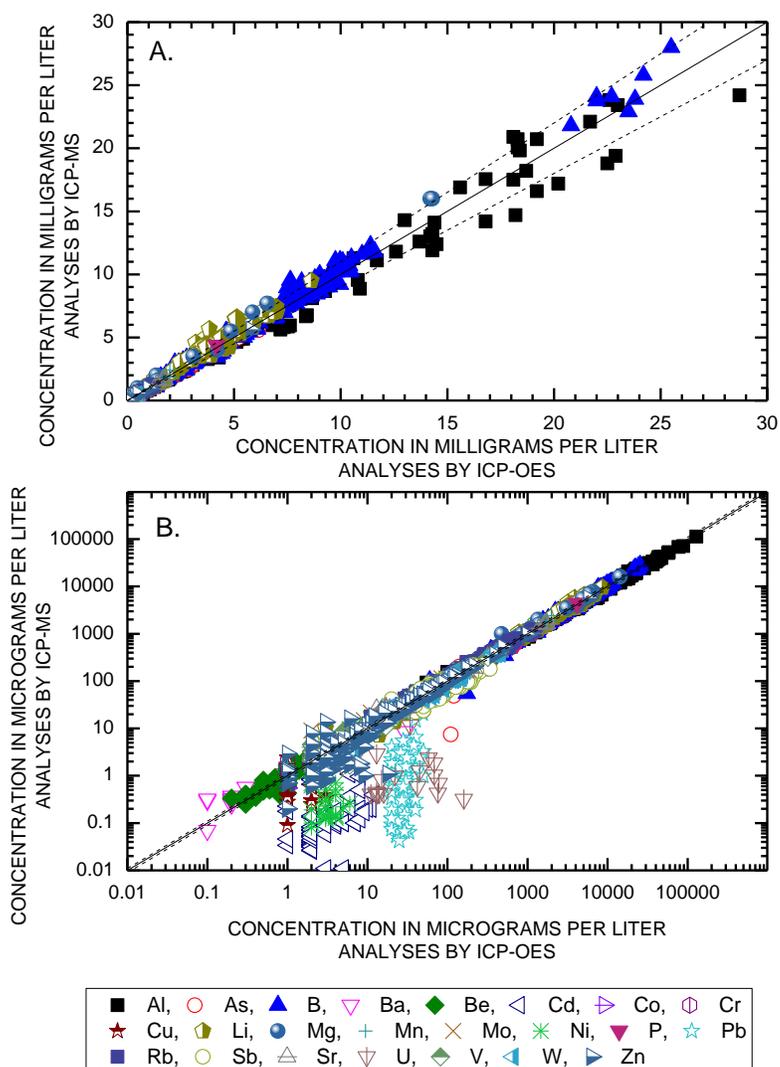


Figure 9. Cation and trace metals concentrations determined by ICP-MS and ICP-OES plotted on a linear (A) and log₁₀ (B) scale. The solid line is a one to one concentration line and the dashed lines are ±10%.

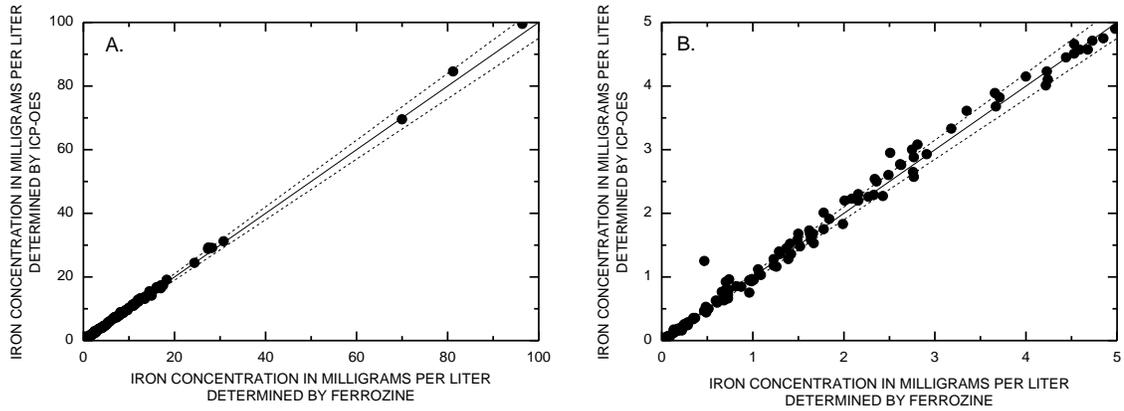


Figure 10. Total dissolved iron determined by ICP-OES and FerroZine for all data (A) and for iron concentrations less than 5 mg/L (B). The solid line is a one to one concentration line and the dashed lines are $\pm 10\%$.

Several standard reference water samples were analyzed as unknowns several times during each analytical run to check for accuracy. U.S. Geological Survey standard reference water samples (SRWS) M158, M164, M184, M186, M190, M192, M196, M198, M200, M202, M204, N103, N104, N106, N107, N108, N111, N112, T135, T173, T175, T181, T189, T195, T199, T201, T203, T205, T207, T209, Hg08, Hg21, and Hg27 (U.S. Geological Survey, 2013) were used to check the analytical methods for major and trace metals, ammonium, anions, and mercury. The SRWS PPREE and SCREE were used to check the analytical methods for rare earth elements (Verplanck and others, 2001). The National Institute of Standards and Technology (NIST) standard NIST1643d (NIST, 1999) was used to check the accuracy of trace metals determined by ICP-MS. The Environment Canada standards FP99Hg05, FP97Hg09, FP97Hg06, FP97Hg04, FP97Hg03, FP97Hg01, FP95Hg09, FP95Hg06, FP95Hg05, FP95Hg03, FP93Hg10, FP93Hg06, FP85Hg03, and FP81Hg10 were used to check the CVAFS determination of Hg (Environment Canada, 2014). For each SRWS constituent, the analytical result, the most probable value (MPV), and the percent difference are presented in table 3.

Table 3. Measured concentrations in standard reference water samples.

[CVAFS, cold vapor atomic fluorescence spectrometry; HGAAS, hydride generation atomic absorption spectrometry; IC, ion chromatography; ICP-OES, inductively coupled plasma-optical emission spectrometry; ISE, ion selective electrode; mg/L, milligrams per liter; n, number of analyses; ng/L, nanograms per liter; s, standard deviation; SRWS, standard reference water sample; %RSD, percent relative standard deviation; <, less than; ---, no data]

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Alkalinity (as CaCO ₃)	Titration	M204	mg/L	4	40.9	0.4	1.0	40.9	-0.1
Alkalinity (as CaCO ₃)	Titration	M200	mg/L	2	28.6	0.1	0.3	28.3	1.1
Alkalinity (as CaCO ₃)	Titration	M196	mg/L	13	79.8	2.2	2.8	78.9	1.1
Alkalinity (as CaCO ₃)	Titration	M192	mg/L	6	23.5	0.7	3.0	24	-2.1
Alkalinity (as CaCO ₃)	Titration	M186	mg/L	17	50.4	0.8	1.6	50.4	0.0
Alkalinity (as CaCO ₃)	Titration	M184	mg/L	8	43.2	0.7	1.6	43.5	-0.7
Alkalinity (as CaCO ₃)	Titration	M158	mg/L	1	64.1	---	---	63.6	0.8
Aluminum (Al)	ICP-OES	T209	mg/L	6	0.0192	0.0012	6.3	0.0192	0.0
Aluminum (Al)	ICP-OES	T207	mg/L	31	0.329	0.013	4.0	0.324	1.5
Aluminum (Al)	ICP-OES	T205	mg/L	25	0.0299	0.0017	5.7	0.0315	-5.1
Aluminum (Al)	ICP-OES	T203	mg/L	25	0.107	0.004	3.7	0.109	-1.8
Aluminum (Al)	ICP-OES	T201	mg/L	31	0.0787	0.0028	3.6	0.0778	1.2
Aluminum (Al)	ICP-OES	T199	mg/L	6	0.0867	0.0015	1.7	0.0916	-5.3
Aluminum (Al)	ICP-MS	T175	µg/L	72	51.3	2.5	4.9	52.0	-1.3
Aluminum (Al)	ICP-MS	T173	µg/L	72	71.8	3.3	4.6	71.0	1.1
Aluminum (Al)	ICP-MS	T135	µg/L	72	10.3	1.2	11.7	10.5	-1.9
Aluminum (Al)	ICP-MS	NBSd	µg/L	72	12.8	1.1	8.6	12.8	0.0
Ammonium (as NH ₃ -N)	IC	N103	mg/L	1	0.345	---	---	0.320	7.8
Ammonium (as NH ₃ -N)	IC	N104	mg/L	0	0.663	0.051	7.7	0.705	-6.0
Ammonium (as NH ₃ -N)	IC	N106	mg/L	1	1.04	---	---	1.10	-5.5
Ammonium (as NH ₃ -N)	IC	N107	mg/L	0	0.214	0.011	5.1	0.193	10.9
Ammonium (as NH ₃ -N)	IC	N108	mg/L	0	0.439	0.025	5.7	0.460	-4.6
Ammonium (as NH ₃ -N)	IC	N111	mg/L	0	0.253	0.013	5.1	0.280	-9.6
Ammonium (as NH ₃ -N)	IC	N112	mg/L	0	0.839	0.041	4.9	0.840	-0.1
Antimony (Sb)	ICP-OES	T209	mg/L	6	<0.01	0.0065	---	0.0003	---
Antimony (Sb)	ICP-OES	T207	mg/L	31	<0.01	0.0067	---	0.0001	---
Antimony (Sb)	ICP-OES	T205	mg/L	25	<0.01	0.0077	---	0.0018	---
Antimony (Sb)	ICP-OES	T203	mg/L	25	<0.01	0.0081	---	0.0005	---
Antimony (Sb)	ICP-OES	T201	mg/L	31	<0.01	0.0109	---	0.0158	---
Antimony (Sb)	ICP-OES	T199	mg/L	6	<0.01	0.0056	---	0.0001	---
Antimony (Sb)	ICP-MS	T175	µg/L	72	1.98	0.16	8.1	1.90	4.2
Antimony (Sb)	ICP-MS	T173	µg/L	72	5.04	0.09	1.8	5.20	-3.1
Antimony (Sb)	ICP-MS	T135	µg/L	72	76.3	0.9	1.2	76.3	0.0
Antimony (Sb)	ICP-MS	NBSd	µg/L	72	5.31	0.10	1.9	5.41	-1.8

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Arsenic (As)	HGAAS	T207	mg/L	2	0.0007	0	0.0	0.0009	-22
Arsenic (As)	HGAAS	T201	mg/L	7	0.0244	0.0011	4.5	0.0244	0.0
Arsenic (As)	HGAAS	T195	mg/L	3	0.0014	0	0.0	0.0015	-6.7
Arsenic (As)	HGAAS	AMW4	mg/L	81	0.178	0.008	4.5	0.168	6.0
Arsenic (As)	ICP-OES	T209	mg/L	6	<0.03	---	---	0.0002	---
Arsenic (As)	ICP-OES	T207	mg/L	31	<0.03	---	---	0.0009	---
Arsenic (As)	ICP-OES	T205	mg/L	25	<0.03	---	---	0.0018	---
Arsenic (As)	ICP-OES	T203	mg/L	25	<0.03	---	---	0.0016	---
Arsenic (As)	ICP-OES	T201	mg/L	31	<0.03	---	---	0.0244	---
Arsenic (As)	ICP-OES	T199	mg/L	6	<0.03	---	---	0.0002	---
Arsenic (As)	ICP-MS	T175	µg/L	72	7.40	0.14	1.9	7.38	0.3
Arsenic (As)	ICP-MS	T173	µg/L	72	2.63	0.13	4.9	2.67	-1.5
Arsenic (As)	ICP-MS	T135	µg/L	72	10.2	0.2	2.0	10.0	2.0
Arsenic (As)	ICP-MS	NBSd	µg/L	72	5.17	0.16	3.1	5.60	-7.7
Barium (Ba)	ICP-OES	T209	mg/L	6	0.0315	0.0003	1.0	0.0316	-0.3
Barium (Ba)	ICP-OES	T207	mg/L	31	0.0435	0.0012	2.8	0.0429	1.4
Barium (Ba)	ICP-OES	T205	mg/L	25	0.0224	0.0007	3.1	0.0217	3.2
Barium (Ba)	ICP-OES	T203	mg/L	25	0.0107	0.0003	2.8	0.0101	5.9
Barium (Ba)	ICP-OES	T201	mg/L	31	0.0445	0.0012	2.7	0.0447	-0.4
Barium (Ba)	ICP-OES	T199	mg/L	6	0.0069	0.0001	1.4	0.0068	1.5
Barium (Ba)	ICP-MS	T175	µg/L	72	17.9	0.5	2.8	18.0	-0.6
Barium (Ba)	ICP-MS	T173	µg/L	72	41.4	1.3	3.1	42.2	-1.9
Barium (Ba)	ICP-MS	T135	µg/L	72	68.0	1.5	2.2	67.8	0.3
Barium (Ba)	ICP-MS	NBSd	µg/L	72	50.7	1.3	2.6	50.7	0.0
Beryllium (Be)	ICP-OES	T209	mg/L	6	<0.0001	0	---	0.0001	---
Beryllium (Be)	ICP-OES	T207	mg/L	31	<0.0001	0.0001	---	0.0001	---
Beryllium (Be)	ICP-OES	T205	mg/L	25	0.0002	0.0001	50	0.0002	0.0
Beryllium (Be)	ICP-OES	T203	mg/L	25	0.0006	0.0001	17	0.0005	20
Beryllium (Be)	ICP-OES	T201	mg/L	31	0.0084	0.0003	3.6	0.0084	0.0
Beryllium (Be)	ICP-OES	T199	mg/L	6	<0.0001	0.0001	---	0.0001	---
Beryllium (Be)	ICP-MS	T175	µg/L	72	2.96	0.10	3.4	2.92	1.4
Beryllium (Be)	ICP-MS	T173	µg/L	72	2.02	0.09	4.5	2.00	1.0
Beryllium (Be)	ICP-MS	T135	µg/L	72	58.9	2.2	3.7	59.0	-0.2
Beryllium (Be)	ICP-MS	NBSd	µg/L	72	1.18	0.06	5.1	1.25	-5.6
Bismuth (Bi)	ICP-MS	NBSd	µg/L	72	1.29	0.04	3.1	1.30	-0.8
Boron (B)	ICP-OES	T209	mg/L	6	<0.08	0.0141	---	0.0353	---
Boron (B)	ICP-OES	T207	mg/L	31	<0.08	0.0143	---	0.0135	---
Boron (B)	ICP-OES	T205	mg/L	25	<0.08	0.0141	---	0.0075	---
Boron (B)	ICP-OES	T203	mg/L	25	<0.08	0.0153	---	0.0046	---
Boron (B)	ICP-OES	T201	mg/L	31	<0.08	0.0221	---	0.0469	---
Boron (B)	ICP-OES	T199	mg/L	6	<0.08	0.0134	---	0.0167	---
Boron (B)	ICP-OES	M202	mg/L	6	<0.08	0.015	---	0.0102	---
Boron (B)	ICP-OES	M198	mg/L	25	<0.08	0.0166	---	0.0522	---
Boron (B)	ICP-MS	T175	µg/L	72	48.2	2.9	6.0	48.3	-0.2
Boron (B)	ICP-MS	T173	µg/L	72	158	6	3.8	158	0.0
Boron (B)	ICP-MS	T135	µg/L	72	9.51	2.13	22.4	13.1	-27.4
Boron (B)	ICP-MS	NBSd	µg/L	72	12.8	2.4	18.8	14.5	-11.7

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Bromide (Br)	IC	M200	mg/L	27	0.62	0.157	25	0.659	-5.9
Bromide (Br)	IC	M198	mg/L	16	0.138	0.037	27	0.1	38
Bromide (Br)	IC	M196	mg/L	8	0.195	0.059	30	0.165	18
Bromide (Br)	IC	M192	mg/L	12	0.172	0.036	21	0.191	-9.9
Bromide (Br)	IC	M190	mg/L	12	0.241	0.03	12	0.28	-14
Bromide (Br)	IC	M186	mg/L	27	1.4	0.09	6.4	1.42	-1.4
Bromide (Br)	IC	DX	mg/L	26	99.7	4.6	4.6	100	-0.3
Cadium (Cd)	ICP-OES	T209	mg/L	6	<0.001	0.0001	---	0	---
Cadium (Cd)	ICP-OES	T207	mg/L	31	<0.001	0.0007	---	0.0006	---
Cadium (Cd)	ICP-OES	T205	mg/L	25	0.001	0.0007	70	0.0012	-17
Cadium (Cd)	ICP-OES	T203	mg/L	25	<0.001	0.0006	---	0.0009	---
Cadium (Cd)	ICP-OES	T201	mg/L	31	0.0155	0.0009	5.8	0.0157	-1.3
Cadium (Cd)	ICP-OES	T199	mg/L	6	0.0015	0.0002	13	0.0015	0.0
Cadium (Cd)	ICP-MS	T175	µg/L	72	8.39	0.13	1.5	8.20	2.3
Cadium (Cd)	ICP-MS	T173	µg/L	72	1.26	0.03	2.4	1.26	0.0
Cadium (Cd)	ICP-MS	T135	µg/L	72	50.4	0.7	1.4	50.5	-0.2
Cadium (Cd)	ICP-MS	NBSd	µg/L	72	0.601	0.025	4.2	0.647	-7.1
Calcium (Ca)	ICP-OES	T209	mg/L	6	18	0.2	1.1	18	0.0
Calcium (Ca)	ICP-OES	T207	mg/L	31	23.3	0.6	2.6	23.4	-0.4
Calcium (Ca)	ICP-OES	T205	mg/L	25	8.2	0.24	2.9	8.28	-1.0
Calcium (Ca)	ICP-OES	T203	mg/L	25	11.1	0.3	2.7	11.1	0.0
Calcium (Ca)	ICP-OES	T201	mg/L	31	53.2	1.5	2.8	53.1	0.2
Calcium (Ca)	ICP-OES	T199	mg/L	6	3.96	0.1	2.5	3.8	4.2
Calcium (Ca)	ICP-OES	M202	mg/L	6	5.59	0.1	1.8	5.56	0.5
Calcium (Ca)	ICP-OES	M198	mg/L	25	10.5	0.4	3.8	10.4	1.0
Cerium (Ce)	ICP-MS	SCREE	µg/L	48	0.241	0.009	3.7	0.246	-2.0
Cerium (Ce)	ICP-MS	PPREE	µg/L	48	1.69	0.06	3.6	1.63	3.7
Chloride (Cl)	IC	M200	mg/L	27	17.5	0.2	1.1	17.9	-2.2
Chloride (Cl)	IC	M198	mg/L	20	14.5	0.2	1.4	14.6	-0.7
Chloride (Cl)	IC	M196	mg/L	7	33	0.3	0.9	32.7	0.9
Chloride (Cl)	IC	M192	mg/L	21	13.4	0.7	5.2	12.9	3.9
Chloride (Cl)	IC	M190	mg/L	14	29.2	1.3	4.5	29.1	0.3
Chloride (Cl)	IC	M186	mg/L	27	24.3	1.7	7.0	23.6	3.0
Chloride (Cl)	IC	M184	mg/L	5	7.57	0.15	2.0	7.8	-2.9
Chloride (Cl)	IC	DX	mg/L	26	28.6	9.2	32	30	-4.7
Chromium (Cr)	ICP-OES	T209	mg/L	6	<0.0006	0.0002	---	0.0001	---
Chromium (Cr)	ICP-OES	T207	mg/L	31	0.0014	0.0007	50	0.0004	250
Chromium (Cr)	ICP-OES	T205	mg/L	25	0.0016	0.0007	44	0.0011	45
Chromium (Cr)	ICP-OES	T203	mg/L	25	0.0014	0.0006	43	0.0009	56
Chromium (Cr)	ICP-OES	T201	mg/L	31	0.0355	0.0017	4.8	0.0337	5.3
Chromium (Cr)	ICP-OES	T199	mg/L	6	0.0015	0.0002	13	0.0013	15
Chromium (Cr)	ICP-MS	T175	µg/L	72	2.03	0.07	3.4	1.93	5.2
Chromium (Cr)	ICP-MS	T173	µg/L	72	5.01	0.16	3.2	4.88	2.7
Chromium (Cr)	ICP-MS	T135	µg/L	72	79.1	1.9	2.4	79.0	0.1
Chromium (Cr)	ICP-MS	NBSd	µg/L	72	1.88	0.09	4.8	1.85	1.6

Table 3. Measured concentrations in standard reference water samples–Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Cobalt (Co)	ICP-OES	T209	mg/L	6	<0.002	0.0006	---	0.0001	---
Cobalt (Co)	ICP-OES	T207	mg/L	31	<0.002	0.0015	---	0.001	---
Cobalt (Co)	ICP-OES	T205	mg/L	25	<0.002	0.0015	---	0.0009	---
Cobalt (Co)	ICP-OES	T203	mg/L	25	<0.002	0.0014	---	0.0006	---
Cobalt (Co)	ICP-OES	T201	mg/L	31	0.018	0.0015	8.3	0.0174	3.4
Cobalt (Co)	ICP-OES	T199	mg/L	6	<0.002	0.0007	---	0.0001	---
Cobalt (Co)	ICP-MS	T175	µg/L	72	7.46	0.20	2.7	7.44	0.3
Cobalt (Co)	ICP-MS	T173	µg/L	72	1.26	0.04	3.2	1.26	0.0
Cobalt (Co)	ICP-MS	T135	µg/L	72	40.0	1.0	2.5	40.0	0.0
Cobalt (Co)	ICP-MS	NBSd	µg/L	72	2.43	0.06	2.5	2.5	-2.8
Copper (Cu)	ICP-OES	T209	mg/L	6	0.0015	0.0002	13	0.0016	-6.3
Copper (Cu)	ICP-OES	T207	mg/L	31	0.0085	0.0005	5.9	0.0084	1.2
Copper (Cu)	ICP-OES	T205	mg/L	25	0.0015	0.0007	47	0.0014	7.1
Copper (Cu)	ICP-OES	T203	mg/L	25	0.0015	0.0006	40	0.0016	-6.3
Copper (Cu)	ICP-OES	T201	mg/L	31	0.0208	0.0007	3.4	0.0208	0.0
Copper (Cu)	ICP-OES	T199	mg/L	6	0.0018	0.0003	17	0.002	-10
Copper (Cu)	ICP-MS	T175	µg/L	72	1.97	0.09	4.6	1.85	6.5
Copper (Cu)	ICP-MS	T173	µg/L	72	7.64	0.23	3.0	7.50	1.9
Copper (Cu)	ICP-MS	T135	µg/L	72	62.0	1.3	2.1	62.0	0.0
Copper (Cu)	ICP-MS	NBSd	µg/L	72	2.21	0.09	4.1	2.05	7.8
Dysprosium (Dy)	ICP-MS	SCREE	µg/L	48	0.080	0.003	3.8	0.0814	-1.7
Dysprosium (Dy)	ICP-MS	PPREE	µg/L	48	0.228	0.010	4.4	0.220	3.6
Erbium (Er)	ICP-MS	SCREE	µg/L	48	0.043	0.002	4.7	0.0437	-1.6
Erbium (Er)	ICP-MS	PPREE	µg/L	48	0.122	0.005	4.1	0.120	1.7
Europium (Eu)	ICP-MS	SCREE	µg/L	48	0.0142	0.0007	4.9	0.0148	-4.1
Europium (Eu)	ICP-MS	PPREE	µg/L	48	0.061	0.002	3.3	0.060	1.7
Fluoride (F)	IC	M200	mg/L	27	0.251	0.037	15	0.25	0.4
Fluoride (F)	IC	M198	mg/L	20	0.214	0.03	14	0.2	7.0
Fluoride (F)	IC	M196	mg/L	8	0.859	0.05	5.8	0.84	2.3
Fluoride (F)	IC	M192	mg/L	12	0.151	0.011	7.3	0.128	18
Fluoride (F)	IC	M190	mg/L	12	0.506	0.073	14	0.49	3.3
Fluoride (F)	IC	M186	mg/L	27	0.877	0.076	8.7	0.96	-8.6
Fluoride (F)	IC	M184	mg/L	5	1.69	0.08	4.7	1.75	-3.4
Fluoride (F)	IC	M164	mg/L	3	0.651	0.032	4.9	0.604	7.8
Fluoride (F)	IC	DX	mg/L	27	19.3	0.5	2.6	20	-3.5
Fluoride (F)	ISE	M200	mg/L	9	0.25	0.004	1.6	0.25	0.0
Fluoride (F)	ISE	M198	mg/L	4	0.202	0.002	1.0	0.2	1.0
Fluoride (F)	ISE	M196	mg/L	8	0.842	0.021	2.5	0.84	0.2
Fluoride (F)	ISE	M186	mg/L	4	0.971	0.005	0.5	0.96	1.1
Fluoride (F)	ISE	M184	mg/L	5	1.81	0.04	2.2	1.75	3.4
Gadolinium (Gd)	ICP-MS	SCREE	µg/L	48	0.083	0.004	4.8	0.0829	0.1
Gadolinium (Gd)	ICP-MS	PPREE	µg/L	48	0.243	0.007	2.9	0.240	1.3
Holmium (Ho)	ICP-MS	SCREE	µg/L	48	0.0162	0.0006	3.7	0.0162	0.0
Holmium (Ho)	ICP-MS	PPREE	µg/L	48	0.046	0.002	4.3	0.0443	3.8

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Iron (Fe)	FerroZine	T207	mg/L	4	0.448	0.016	3.6	0.432	3.7
Iron (Fe)	FerroZine	T201	mg/L	13	1.83	0.05	2.7	1.81	1.1
Iron (Fe)	FerroZine	T199	mg/L	9	0.173	0.004	2.3	0.171	1.2
Iron (Fe)	FerroZine	T195	mg/L	4	0.421	0.007	1.7	0.43	-2.1
Iron (Fe)	FerroZine	T189	mg/L	1	0.033	---	---	0.0325	1.5
Iron (Fe)	FerroZine	T181	mg/L	2	0.116	0.001	0.9	0.119	-2.5
Iron (Fe)	FerroZine	T173	mg/L	1	0.0217	---	---	0.0214	1.2
Iron (Fe)	ICP-OES	T209	mg/L	6	0.155	0.002	1.3	0.158	-1.9
Iron (Fe)	ICP-OES	T207	mg/L	31	0.432	0.013	3.0	0.432	0.0
Iron (Fe)	ICP-OES	T205	mg/L	25	0.0688	0.0039	5.7	0.0669	2.8
Iron (Fe)	ICP-OES	T203	mg/L	25	0.0523	0.0022	4.2	0.0521	0.4
Iron (Fe)	ICP-OES	T201	mg/L	31	1.78	0.05	2.8	1.81	-1.7
Iron (Fe)	ICP-OES	T199	mg/L	6	0.165	0.002	1.2	0.171	-3.5
Lanthanum (La)	ICP-MS	SCREE	µg/L	48	0.098	0.003	3.1	0.099	-1.0
Lanthanum (La)	ICP-MS	PPREE	µg/L	48	0.827	0.026	3.1	0.804	2.9
Lead (Pb)	ICP-OES	T209	mg/L	6	<0.02	0.0064	---	0.0004	---
Lead (Pb)	ICP-OES	T207	mg/L	31	<0.02	0.0082	---	0.0048	---
Lead (Pb)	ICP-OES	T205	mg/L	25	<0.02	0.0107	---	0.0014	---
Lead (Pb)	ICP-OES	T203	mg/L	25	<0.02	0.0092	---	0.011	---
Lead (Pb)	ICP-OES	T201	mg/L	31	0.0733	0.0225	31	0.0739	-0.8
Lead (Pb)	ICP-OES	T199	mg/L	6	<0.02	0.0073	---	0.0014	---
Lead (Pb)	ICP-MS	T175	µg/L	72	3.10	0.05	1.6	3.00	3.3
Lead (Pb)	ICP-MS	T173	µg/L	72	4.70	0.08	1.7	4.59	2.4
Lead (Pb)	ICP-MS	T135	µg/L	72	103	1	1.0	103	0.0
Lead (Pb)	ICP-MS	NBSd	µg/L	72	1.94	0.04	2.1	1.82	6.6
Lithium (Li)	ICP-OES	T209	mg/L	6	0.0033	0	0.0	0.0032	3.1
Lithium (Li)	ICP-OES	T207	mg/L	31	0.0213	0.0011	5.2	0.0222	-4.1
Lithium (Li)	ICP-OES	T205	mg/L	25	0.0017	0.0004	24	0.0017	0.0
Lithium (Li)	ICP-OES	T203	mg/L	25	0.006	0.0005	8.3	0.0063	-4.8
Lithium (Li)	ICP-OES	T201	mg/L	31	0.0303	0.0012	4.0	0.0279	8.6
Lithium (Li)	ICP-OES	T199	mg/L	6	0.0011	0	0.0	0.0012	-8.3
Lithium (Li)	ICP-MS	T175	µg/L	72	3.11	0.28	9.0	3.20	-2.8
Lithium (Li)	ICP-MS	T173	µg/L	72	17.4	0.9	5.2	17.1	1.8
Lithium (Li)	ICP-MS	T135	µg/L	72	73.2	3.7	5.1	73.7	-0.7
Lithium (Li)	ICP-MS	NBSd	µg/L	72	1.60	0.24	15.0	1.65	-3.0
Lutetium (Lu)	ICP-MS	SCREE	µg/L	48	0.0044	0.0003	6.8	0.00453	-2.9
Lutetium (Lu)	ICP-MS	PPREE	µg/L	48	0.0115	0.0007	6.1	0.0111	3.6
Magnesium (Mg)	ICP-OES	T209	mg/L	6	4.89	0.05	1.0	4.91	-0.4
Magnesium (Mg)	ICP-OES	T207	mg/L	31	6.13	0.18	2.9	6.19	-1.0
Magnesium (Mg)	ICP-OES	T205	mg/L	25	2.23	0.07	3.1	2.32	-3.9
Magnesium (Mg)	ICP-OES	T203	mg/L	25	1.22	0.04	3.3	1.25	-2.4
Magnesium (Mg)	ICP-OES	T201	mg/L	31	22.3	1.1	4.9	23.8	-6.3
Magnesium (Mg)	ICP-OES	T199	mg/L	6	6.17	0.06	1.0	6.2	-0.5
Magnesium (Mg)	ICP-OES	M202	mg/L	6	1.51	0.03	2.0	1.52	-0.7
Magnesium (Mg)	ICP-OES	M198	mg/L	25	4.73	0.19	4.0	4.8	-1.5
Manganese (Mn)	ICP-OES	T209	mg/L	6	0.0108	0.0001	0.9	0.011	-1.8
Manganese (Mn)	ICP-OES	T207	mg/L	31	0.238	0.007	2.9	0.237	0.4
Manganese (Mn)	ICP-OES	T205	mg/L	25	0.0094	0.0004	4.3	0.0093	1.1
Manganese (Mn)	ICP-OES	T203	mg/L	25	0.128	0.004	3.1	0.127	0.8
Manganese (Mn)	ICP-OES	T201	mg/L	31	1.74	0.05	2.9	1.8	-3.3
Manganese (Mn)	ICP-OES	T199	mg/L	6	0.0139	0.0001	0.7	0.0141	-1.4

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Manganese (Mn)	ICP-MS	T175	µg/L	72	57.5	2.0	3.5	49.4	16.4
Manganese (Mn)	ICP-MS	T173	µg/L	72	498	12	2.4	495	0.6
Manganese (Mn)	ICP-MS	T135	µg/L	72	417	10	2.4	423	-1.4
Manganese (Mn)	ICP-MS	NBSd	µg/L	72	4.46	0.26	5.8	3.77	18.3
Mercury (Hg)	CVAFS	Hg8	ng/L	23	2840	90	3.2	2850	-0.4
Mercury (Hg)	CVAFS	Hg21	ng/L	19	2990	110	3.7	3030	-1.3
Mercury (Hg)	CVAFS	Hg27	ng/L	22	1500	60	4.0	1630	-8.0
Mercury (Hg)	CVAFS	FP99Hg05	ng/L	33	149	5	3.4	149	0.0
Mercury (Hg)	CVAFS	FP97Hg09	ng/L	9	487	25	5.1	496	-1.8
Mercury (Hg)	CVAFS	FP97Hg06	ng/L	15	196	6	3.1	200	-2.0
Mercury (Hg)	CVAFS	FP97Hg04	ng/L	32	302	5	1.7	300	0.7
Mercury (Hg)	CVAFS	FP97Hg03	ng/L	25	91.0	5	5.5	90.0	1.1
Mercury (Hg)	CVAFS	FP97Hg01	ng/L	19	323	8	2.5	320	0.9
Mercury (Hg)	CVAFS	FP95Hg09	ng/L	18	362	13	3.6	366	-1.1
Mercury (Hg)	CVAFS	FP95Hg06	ng/L	15	48.0	4	8.3	47.8	0.4
Mercury (Hg)	CVAFS	FP95Hg05	ng/L	29	329	5	1.5	323	1.9
Mercury (Hg)	CVAFS	FP95Hg03	ng/L	10	160	4	2.5	157	1.9
Mercury (Hg)	CVAFS	FP93Hg10	ng/L	5	167	4	2.4	164	1.8
Mercury (Hg)	CVAFS	FP93Hg06	ng/L	15	331	3	0.9	322	2.8
Mercury (Hg)	CVAFS	FP85Hg03	ng/L	18	43.0	2	4.7	41.0	4.9
Mercury (Hg)	CVAFS	FP81Hg10	ng/L	30	477	5	1.0	480	-0.6
Molybdenum (Mo)	ICP-OES	T209	mg/L	6	<0.003	0.0012	---	0.0006	---
Molybdenum (Mo)	ICP-OES	T207	mg/L	31	0.0036	0.0018	50	0.0046	-22
Molybdenum (Mo)	ICP-OES	T205	mg/L	25	<0.003	0.0021	---	0.001	---
Molybdenum (Mo)	ICP-OES	T203	mg/L	25	0.0035	0.0016	46	0.0041	-15
Molybdenum (Mo)	ICP-OES	T201	mg/L	31	0.0278	0.002	7.2	0.0305	-8.9
Molybdenum (Mo)	ICP-OES	T199	mg/L	6	<0.003	0.0009	---	0.0003	---
Molybdenum (Mo)	ICP-MS	T175	µg/L	72	1.78	0.32	18.0	1.79	-0.6
Molybdenum (Mo)	ICP-MS	T173	µg/L	72	6.95	0.16	2.3	7.22	-3.7
Molybdenum (Mo)	ICP-MS	T135	µg/L	72	63.1	0.8	1.3	63.0	0.2
Molybdenum (Mo)	ICP-MS	NBSd	µg/L	72	11.0	0.3	2.7	11.3	-2.7
Neodymium (Nd)	ICP-MS	SCREE	µg/L	48	0.221	0.007	3.2	0.222	-0.5
Neodymium (Nd)	ICP-MS	PPREE	µg/L	48	0.961	0.028	2.9	0.934	2.9
Nickel (Ni)	ICP-OES	T209	mg/L	6	<0.002	0.0004	---	0.0005	---
Nickel (Ni)	ICP-OES	T207	mg/L	31	<0.002	0.0014	---	0.0017	---
Nickel (Ni)	ICP-OES	T205	mg/L	25	<0.002	0.0014	---	0.0012	---
Nickel (Ni)	ICP-OES	T203	mg/L	25	<0.002	0.0013	---	0.0004	---
Nickel (Ni)	ICP-OES	T201	mg/L	31	0.0661	0.0024	3.6	0.064	3.3
Nickel (Ni)	ICP-OES	T199	mg/L	6	<0.002	0.0006	---	0.0004	---
Nickel (Ni)	ICP-MS	T175	µg/L	72	3.31	0.08	2.4	3.18	4.1
Nickel (Ni)	ICP-MS	T173	µg/L	72	5.34	0.17	3.2	5.38	-0.7
Nickel (Ni)	ICP-MS	T135	µg/L	72	65.6	1.7	2.6	65.6	0.0
Nickel (Ni)	ICP-MS	NBSd	µg/L	72	5.82	0.17	2.9	5.81	0.2
Nitrate (NO ₃)	IC	N108	mg/L	4	3.27	0.07	2.1	3.24	0.9
Nitrate (NO ₃)	IC	DX	mg/L	27	100	2	2.0	100	0.0
Phosphorus (P)	ICP-OES	M202	mg/L	6	<0.03	0.0072	---	0.023	---

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Potassium (K)	ICP-OES	T209	mg/L	6	2.64	0.07	2.7	2.66	-0.8
Potassium (K)	ICP-OES	T207	mg/L	31	2.18	0.05	2.3	2.19	-0.5
Potassium (K)	ICP-OES	T205	mg/L	25	0.777	0.03	3.9	0.795	-2.3
Potassium (K)	ICP-OES	T203	mg/L	25	1.24	0.04	3.2	1.22	1.6
Potassium (K)	ICP-OES	T201	mg/L	31	5.32	0.2	3.8	5.24	1.5
Potassium (K)	ICP-OES	T199	mg/L	6	1.83	0.04	2.2	1.87	-2.1
Potassium (K)	ICP-OES	M202	mg/L	6	1.27	0.03	2.4	1.31	-3.1
Potassium (K)	ICP-OES	M198	mg/L	25	1.5	0.05	3.3	1.49	0.7
Potassium (K)	ICP-MS	T175	µg/L	72	3.81	0.12	3.1	3.83	-0.5
Potassium (K)	ICP-MS	T173	µg/L	72	3.96	0.16	4.0	3.85	2.9
Potassium (K)	ICP-MS	T135	µg/L	72	0.923	0.031	3.4	0.960	-3.9
Potassium (K)	ICP-MS	NBSd	µg/L	72	0.219	0.014	6.4	0.236	-7.2
Praseodymium (Pr)	ICP-MS	SCREE	µg/L	48	0.043	0.001	2.3	0.0431	-0.2
Praseodymium (Pr)	ICP-MS	PPREE	µg/L	48	0.221	0.007	3.2	0.212	4.2
Selenium (Se)	ICP-OES	T209	mg/L	6	<0.04	0.0164	---	0.0008	---
Selenium (Se)	ICP-OES	T207	mg/L	31	<0.04	0.0177	---	0.0008	---
Selenium (Se)	ICP-OES	T205	mg/L	25	<0.04	0.0255	---	0.0004	---
Selenium (Se)	ICP-OES	T203	mg/L	25	<0.04	0.0219	---	0.0004	---
Selenium (Se)	ICP-OES	T201	mg/L	31	<0.04	0.0237	---	0.009	---
Selenium (Se)	ICP-OES	T199	mg/L	6	<0.04	0.0195	---	0.0003	---
Selenium (Se)	ICP-MS	T175	µg/L	72	1.94	0.15	7.7	2.10	-7.6
Selenium (Se)	ICP-MS	T173	µg/L	72	2.02	0.28	13.9	2.47	-18.2
Selenium (Se)	ICP-MS	T135	µg/L	72	10.3	0.5	4.9	10.0	3.0
Selenium (Se)	ICP-MS	NBSd	µg/L	72	1.03	0.12	11.7	1.14	-9.6
Silica (SiO ₂)	ICP-OES	T209	mg/L	6	12.4	0.2	1.6	12.5	-0.8
Silica (SiO ₂)	ICP-OES	T207	mg/L	31	8.13	0.23	2.8	8.1	0.4
Silica (SiO ₂)	ICP-OES	T205	mg/L	25	8.65	0.25	2.9	8.78	-1.5
Silica (SiO ₂)	ICP-OES	T203	mg/L	25	4.59	0.17	3.7	4.71	-2.5
Silica (SiO ₂)	ICP-OES	T201	mg/L	31	13.2	0.4	3.0	12.9	2.3
Silica (SiO ₂)	ICP-OES	T199	mg/L	6	5.51	0.04	0.7	5.46	0.9
Silica (SiO ₂)	ICP-OES	M202	mg/L	6	6.21	0.09	1.4	6.2	0.2
Silica (SiO ₂)	ICP-OES	M198	mg/L	25	7.93	0.38	4.8	7.56	4.9
Samarium (Sm)	ICP-MS	SCREE	µg/L	48	0.067	0.004	6.0	0.067	0.0
Samarium (Sm)	ICP-MS	PPREE	µg/L	48	0.207	0.006	2.9	0.204	1.5
Sodium (Na)	ICP-OES	T209	mg/L	6	20.4	0.4	2.0	20.3	0.5
Sodium (Na)	ICP-OES	T207	mg/L	31	21.6	0.7	3.2	21.5	0.5
Sodium (Na)	ICP-OES	T205	mg/L	25	8.24	0.27	3.3	8.45	-2.5
Sodium (Na)	ICP-OES	T203	mg/L	25	10.8	0.4	3.7	10.8	0.0
Sodium (Na)	ICP-OES	T201	mg/L	30	47.8	1.3	2.7	47.6	0.4
Sodium (Na)	ICP-OES	T199	mg/L	6	7.68	0.15	2.0	7.72	-0.5
Sodium (Na)	ICP-OES	M202	mg/L	6	7.31	0.16	2.2	7.41	-1.3
Sodium (Na)	ICP-OES	M198	mg/L	25	9.33	0.39	4.2	9.38	-0.5
Strontium (Sr)	ICP-OES	T209	mg/L	6	0.104	0.001	1.0	0.104	0.0
Strontium (Sr)	ICP-OES	T207	mg/L	31	0.167	0.005	3.0	0.161	3.7
Strontium (Sr)	ICP-OES	T205	mg/L	25	0.0609	0.0018	3.0	0.0589	3.4
Strontium (Sr)	ICP-OES	T203	mg/L	25	0.0478	0.0015	3.1	0.0455	5.1
Strontium (Sr)	ICP-OES	T201	mg/L	31	0.404	0.014	3.5	0.396	2.0
Strontium (Sr)	ICP-OES	T199	mg/L	6	0.0208	0.0003	1.4	0.0207	0.5
Strontium (Sr)	ICP-OES	M202	mg/L	6	0.0377	0.0004	1.1	0.0374	0.8
Strontium (Sr)	ICP-OES	M198	mg/L	25	0.0546	0.0019	3.5	0.0524	4.2

Table 3. Measured concentrations in standard reference water samples—Continued.

Analyte	Analytical Method	SRWS	Units	n	mean	s	%RSD	MPV	Percent Difference
Strontium (Sr)	ICP-MS	T175	µg/L	72	63.1	1.2	1.9	63.6	-0.8
Strontium (Sr)	ICP-MS	T173	µg/L	72	279	4	1.4	279	0.0
Strontium (Sr)	ICP-MS	T135	µg/L	72	46.9	1.0	2.1	46.0	2.0
Strontium (Sr)	ICP-MS	NBSd	µg/L	72	29.1	0.8	2.7	29.5	-1.4
Sulfate (SO ₄)	IC	M200	mg/L	27	11.3	0.3	2.7	11.6	-2.6
Sulfate (SO ₄)	IC	M198	mg/L	20	9.81	0.6	6.1	10	-1.9
Sulfate (SO ₄)	IC	M196	mg/L	8	33.4	0.3	0.9	33.2	0.6
Sulfate (SO ₄)	IC	M192	mg/L	15	4.41	0.13	2.9	4.54	-2.9
Sulfate (SO ₄)	IC	M190	mg/L	15	7.17	0.22	3.1	7.42	-3.4
Sulfate (SO ₄)	IC	M186	mg/L	27	14.5	0.4	2.8	14.6	-0.7
Sulfate (SO ₄)	IC	M184	mg/L	5	19.2	0.3	1.6	19.9	-3.5
Sulfur (S)	ICP-OES	M202	mg/L	6	1.6	0.06	3.8	1.45	10
Sulfur (S)	ICP-OES	M198	mg/L	25	3.69	0.18	4.9	3.33	11
Terbium (Tb)	ICP-MS	SCREE	µg/L	48	0.0133	0.0006	4.5	0.0134	-0.7
Terbium (Tb)	ICP-MS	PPREE	µg/L	48	0.038	0.002	5.3	0.0367	3.5
Tellurium (Te)	ICP-MS	NBSd	µg/L	72	0.095	0.013	13.7	0.100	-5.0
Thallium (Tl)	ICP-MS	T175	µg/L	72	1.99	0.04	2.0	1.97	1.0
Thallium (Tl)	ICP-MS	T173	µg/L	72	5.94	0.10	1.7	5.94	0.0
Thallium (Tl)	ICP-MS	NBSd	µg/L	72	0.761	0.018	2.4	0.728	4.5
Thulium (Tm)	ICP-MS	SCREE	µg/L	48	0.0057	0.0004	7.0	0.00585	-2.6
Thulium (Tm)	ICP-MS	PPREE	µg/L	48	0.0153	0.0008	5.2	0.0148	3.4
Uranium (U)	ICP-MS	T175	µg/L	72	1.48	0.03	2.0	1.48	0.0
Uranium (U)	ICP-MS	T173	µg/L	72	1.92	0.04	2.1	1.92	0.0
Vanadium (V)	ICP-OES	T209	mg/L	6	<0.006	0.0005	---	0.0002	---
Vanadium (V)	ICP-OES	T207	mg/L	6	<0.006	0.001	---	0.0009	---
Vanadium (V)	ICP-OES	T201	mg/L	6	0.0287	0.0008	2.8	0.0284	1.1
Vanadium (V)	ICP-OES	T199	mg/L	6	<0.006	0.0012	---	0.0005	---
Vanadium (V)	ICP-MS	T175	µg/L	72	2.90	0.07	2.4	2.94	-1.4
Vanadium (V)	ICP-MS	T173	µg/L	72	4.33	0.12	2.8	4.31	0.5
Vanadium (V)	ICP-MS	T135	µg/L	72	52.8	1.2	2.3	52.8	0.0
Vanadium (V)	ICP-MS	NBSd	µg/L	72	3.33	0.09	2.7	3.51	-5.1
Yttrium (Y)	ICP-MS	SCREE	µg/L	48	0.457	0.013	2.8	0.472	-3.2
Yttrium (Y)	ICP-MS	PPREE	µg/L	48	1.38	0.05	3.6	1.35	2.2
Ytterbium (Yb)	ICP-MS	SCREE	µg/L	48	0.034	0.002	5.9	0.034	0.0
Ytterbium (Yb)	ICP-MS	PPREE	µg/L	48	0.085	0.003	3.5	0.0818	3.9
Zinc (Zn)	ICP-OES	T209	mg/L	6	0.0108	0.0002	1.9	0.0094	15
Zinc (Zn)	ICP-OES	T207	mg/L	31	0.207	0.006	2.9	0.2	3.5
Zinc (Zn)	ICP-OES	T205	mg/L	25	0.0108	0.0009	8.3	0.0094	15
Zinc (Zn)	ICP-OES	T203	mg/L	25	0.0386	0.0013	3.4	0.036	7.2
Zinc (Zn)	ICP-OES	T201	mg/L	31	1.12	0.03	2.7	1.11	0.9
Zinc (Zn)	ICP-OES	T199	mg/L	6	0.0065	0.0002	3.1	0.0062	4.8
Zinc (Zn)	ICP-MS	T175	µg/L	72	75.6	1.9	2.5	71.6	5.6
Zinc (Zn)	ICP-MS	T173	µg/L	72	346	8	2.3	348	-0.6
Zinc (Zn)	ICP-MS	T135	µg/L	72	49.4	1.5	3.0	48.2	2.5
Zinc (Zn)	ICP-MS	NBSd	µg/L	72	7.08	0.38	5.4	7.25	-2.3

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