



Multi-Elemental Analysis of Aqueous Geochemical Samples by Quadrupole Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

By Ruth E. Wolf and Monique Adams

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
Volume		
ounce, fluid (fl. oz)	0.02957	liter (L)
pint (pt)	0.4732	liter (L)
quart (qt)	0.9464	liter (L)
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
cubic inch (in ³)	16.39	cubic centimeter (cm ³)
cubic inch (in ³)	0.01639	liter (L)
Flow rate		
foot per second (ft/s)	0.3048	meter per second (m/s)
foot per minute (ft/min)	0.3048	meter per minute (m/min)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Pressure		
atmosphere, standard (atm)	101.3	kilopascal (kPa)
bar	100	kilopascal (kPa)
Density		
pound per cubic foot (lb/ft ³)	0.01602	gram per cubic centimeter (g/cm ³)
Energy		
kilowatthour (kWh)	3,600,000	joule (J)

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Multi-Elemental Analysis of Aqueous Geochemical Samples by Quadrupole Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

By Ruth E. Wolf and Monique Adams

Principle

Typically, quadrupole inductively coupled plasma-mass spectrometry (ICP-MS) is used to determine as many as 57 major, minor, and trace elements in aqueous geochemical samples, including natural surface water and groundwater, acid mine drainage water, and extracts or leachates from geological samples. The sample solution is aspirated into the inductively coupled plasma (ICP) which is an electrodeless discharge of ionized argon gas at a temperature of approximately 6,000 degrees Celsius. The elements in the sample solution are subsequently volatilized, atomized, and ionized by the ICP. The ions generated are then focused and introduced into a quadrupole mass filter which only allows one mass to reach the detector at a given moment in time. As the settings of the mass analyzer change, subsequent masses are allowed to impact the detector. Although the typical quadrupole ICP-MS system is a sequential scanning instrument (determining each mass separately), the scan speed of modern instruments is on the order of several thousand masses per second. Consequently, typical total sample analysis times of 2–3 minutes are readily achievable for up to 57 elements.

For the protocol described, the ICP-MS is calibrated using a blank and a minimum of four standards prepared from commercially available multi-element standard solutions in conjunction with two standards for phosphorus and sulfur. At the discretion of the analyst, additional elements may be determined after suitable method modifications and performance data are established. Calibration curves are verified using a minimum of one standard prepared from a second commercial source and two reference water samples or certified reference materials obtained from a commercial source in a ready to analyze state. Samples to be analyzed for “dissolved” constituents must be filtered and acid-preserved in 1–2 percent nitric acid (HNO₃) at sample collection or as soon as possible after collection prior to analyses (no digestion is required). Samples to be analyzed for “total” elements require a digestion before analysis such as U.S. Environmental Protection Agency (EPA) Method 3015A—Microwave Assisted Acid Digestion for Aqueous Samples and Extracts (U.S. Environmental Protection Agency, 2007a). This method may also be used to analyze digested biological samples including insects, plants, and biological tissue.

Interferences and Other Sources of Analytical Bias

ICP-MS interferences come from spectroscopic and nonspectroscopic (or matrix) sources (Jarvis, 1992). Spectroscopic interferences include direct isobaric overlaps, where an isotope of one element exists at the same nominal mass as an isotope of another element, for example chromium and iron both have naturally occurring isotopes at mass 54 (⁵⁴Cr and ⁵⁴Fe). Polyatomic isobaric interferences may occur because of the formation of ions from plasma and sample matrix species; for example, ⁴⁰Ar from the plasma and ³⁵Cl from samples containing chloride or hydrochloric acid form ⁴⁰Ar³⁵Cl⁺ at mass 75, interfering with the determination of arsenic at ⁷⁵As⁺. Double-charged

interferences can occur when an element forms a double-charged species in the plasma and can interfere with elements at lower masses; for example, in high barium matrices, $^{138}\text{Ba}^{2+}$ formation in the plasma results in a signal at a mass-to-charge ratio of 69, interfering with the determination of gallium at ^{69}Ga . Refractory oxides can result from incomplete atomization of the sample matrix or recombination of the species in the plasma. Plasma tuning parameters such as radio frequency (RF) power and cooling, auxiliary, and sample argon flows are generally established during the instrument tuning process to minimize oxide formation; however, for some applications, such as the determination of rare earth elements (REEs), oxide formation is a serious source of interference and analytical bias. Commonly, the isotopes measured for each element to be determined are selected to minimize isobaric overlap from other elements and molecular species that may be present in the sample matrix or formed in the argon plasma. For some isotopes, isobaric overlap corrections are computed based on relative isotopic abundances of the elements involved, and oxide or double-charged ion intensities. For the REEs, empirical oxide correction equations are used that must be re-evaluated on a routine basis when instrument tuning parameters are changed. Instrumentation with Dynamic Reaction Cell (DRC) technology (Perkin Elmer, Inc., Shelton, Conn.) also has the capability to use different reaction gases in the DRC cell between the ICP ion source and the analyzer quadrupole to break apart and remove molecular interferences or to shift the analyte ion away from a nonremovable interference by selective gas phase reaction chemistry (Tanner and others, 2002).

Nonspectroscopic interferences include effects that cause suppression or enhancement of the analytical signal or physical effects caused by high total dissolved solids. Nonspectroscopic effects are commonly referred to as matrix effects, because they can vary with each sample matrix type. Matrix effects are often unpredictable and not well understood. Known matrix effects include viscosity differences between different types and (or) concentrations of acids that result in changes in sample uptake, nebulization, and vaporization rates (Olesik and Bates, 1995). Specific examples include signal enhancements observed in matrices containing organic solvents, signal suppression of low mass elements in solutions containing significant levels of high mass elements, signal enhancements of certain elements in high carbon-containing solutions, and suppression of some elements in the presence of easily ionizable elements such as Na, K, and Cs (Allain and others, 1991; Jarvis, 1992; Kralj and Veber, 2003). High levels of total dissolved solids can lead to partial clogging of the sample interface cones between the atmospheric ICP discharge and the high vacuum of the mass analyzer and result in significant levels of signal drift over time. Although matrix interferences can be minimized by careful matching of sample and calibration matrices, the use of internal standards is generally required to compensate for matrix effects and long-term instrumental drift (Lichte and others, 1987; Jarvis, 1992; Horlick and Montaser, 1998). When internal standards are used, the ratio of the analyte intensity to the internal standard intensity is calculated and used in all subsequent calibration calculations.

Most aqueous samples are not digested prior to analysis, but usually they will have been filtered. Samples that have been filtered and acid preserved (FA) generally do not require additional filtering unless particulate matter has precipitated during storage and transport. Raw, acidified (RA) samples that have not been filtered at collection may contain particulate material because some elements will precipitate over time. At the analyst's discretion, these samples may be filtered (using 0.45 μm disposable syringe filters) or decanted prior to analysis to prevent particulate matter from clogging the sample introduction system (for example, the sample probe or nebulizer). Samples with conductivities greater than 1,500 $\mu\text{S}/\text{cm}$ or total dissolved solids (TDS) levels of greater than 0.1 percent are generally diluted by the analyst in order to prevent clogging of the sample introduction system and minimize matrix interferences. The analyst should notify the sample submitter if this or any other procedures were necessary to analyze the samples.

Scope

ICP-MS has been applied to the determination of 57 elements in various aqueous matrices, including natural waters, acid mine drainage waters, and extract and leachate samples. Analytes for which EPA has demonstrated the acceptability of ICP-MS determinations for waters and waste extracts (U.S. Environmental Protection Agency, 2007b) are included in this work. In addition to the 23 EPA target analyte list (TAL) elements, 34 elements are included in this protocol per the provisions of Method 6020A, including the REEs. The elements analyzed, masses utilized, and interference correction equations utilized are shown in table 1.

Some major elements are determined using extended dynamic range (EDR) mode in order to limit the need to dilute samples. In EDR mode, the quadrupole inside the DRC is utilized in direct current (dc) voltage-only mode without a reaction cell gas to attenuate the ion beam passed through to the analyzer quadrupole (Tanner and Baranov, 1999; Abou-Shakar, F., 2005), resulting in higher linear ranges. In order to implement EDR mode, the elements expected to be at high concentrations in the samples are analyzed with the DRC parameter RPa at two or three nonzero values in addition to the normal mode value of RPa=0 while the RF-controlling parameter, RPq, is held at the normal mode value of RPq=0.25. The values of RPq and RPa control the mass bandpass in the DRC. RPq is the low mass cutoff and controls the RF applied to the quadrupole rods in the DRC. RPa is analogous to a high mass cutoff and controls the dc voltage applied to the quadrupole rods in the DRC (Tanner and others, 2002). The elements in EDR mode can be determined at various RPa attenuation values within the same analytical run, eliminating the need to dilute most samples. Table 2 shows some examples of the levels of signal attenuation that can be obtained using the EDR mode.

Apparatus

- Quadrupole Inductively Coupled Plasma-Mass Spectrometer equipped with Dynamic Reaction Cell (PerkinElmer ELAN DRC-e, ELAN DRCII, NexION 300D, or NexION 350D are the models currently used, PerkinElmer Life and Analytical Sciences, Shelton, Conn.)
- Random access autosampler compatible with ICP-MS instrumentation listed above
- Peltier-cooled quartz spray chamber (Model PC-3, Elemental Scientific, Inc., Omaha, Nebr.) or quartz cyclonic spray chamber (PerkinElmer Life and Analytical Sciences, Shelton, Conn.)
- Glass or quartz concentric nebulizer, 0.5–1.0 milliliter per minute (mL/min) uptake rate, A- or C-type (Meinhard Inc., Golden, Colo.)
- 13 x 100 millimeter (mm) disposable, polypropylene test tubes with caps (VWR International, Radnor, Pa., vials part number 60818–860 and caps part number 60828–738)
- Adjustable mechanical or electronic pipettes, typical volume ranges needed are from 5 to 120 microliters (μL), from 50 to 1,000 μL , and from 100 to 5,000 μL
- 15 and 50 milliliter (mL) BD Falcon polypropylene tubes (BD Biosciences, San Jose, Calif.)
- Peristaltic pump tubing, polyvinyl chloride (PVC) type (Meinhard Inc., Golden, Colo.):
 - Internal standard: Orange-orange (0.89 mm inner diameter [i.d.])
 - Sample: Orange-orange (0.89 mm i.d.)
 - Drain: Purple-purple (2.06 mm i.d.)
- Autosampler peristaltic pump tubing, Santoprene type: Red-red (1.14 mm i.d.), 3-stop
- Plastic mixing tee (1/16-in. i.d.) (Cole-Parmer, EW-30506-15)

Table 1. Elements determined in aqueous samples by Inductively Coupled Plasma-Mass Spectrometry and determination parameters.

[cps, counts per second; MCA, multichannel analyzer; ms, milliseconds; EDR, extended dynamic range; IEC, interelement correction]

Internal standard	Analyte	Mass	Scan mode	MCA channels	Dwell time	Integration time	Mode	Equations	Equation type
	Li	6.015	Peak Hopping	1	50.0 ms	750 ms	Normal		
6 Li	Li	7.016	Peak Hopping	1	50.0 ms	750 ms	Normal		
6 Li	Be	9.012	Peak Hopping	1	50.0 ms	750 ms	Normal		
103 Rh	Na	22.99	Peak Hopping	1	50.0 ms	750 ms	Normal		
103 Rh	Na-1	22.99	Peak Hopping	1	50.0 ms	750 ms	EDR - Rpa=0.014		
103 Rh	Na-2	22.99	Peak Hopping	1	50.0 ms	750 ms	EDR - Rpa=0.016		
103 Rh	Mg	24.986	Peak Hopping	1	50.0 ms	750 ms	Normal		
103 Rh	Al	26.982	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Al-1	26.982	Peak Hopping	1	50.0 ms	750 ms	EDR - Rpa=0.012		
103 Rh	Si	28.977	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	P	30.994	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	S	33.968	Peak Hopping	1	50.0 ms	750 ms	Normal		
103 Rh	K	38.964	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ca	42.959	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ca	43.956	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Sc	44.956	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ti	48.948	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	V	50.944	Peak Hopping	1	20.0 ms	300 ms	Normal	$-3.127*(ClO53-(0.113*Cr52))$	Isobaric
103 Rh	Cr	51.941	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Cr	52.941	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Fe	53.94	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.028226 * Cr 52$	Isobaric
103 Rh	Mn	54.938	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Fe	56.935	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.049304*Ca43$	Empirical-IEC

Table 1. Elements determined in aqueous samples by Inductively Coupled Plasma-Mass Spectrometry and determination parameters.—Continued
[cps, counts per second; MCA, multichannel analyzer; ms, milliseconds; EDR, extended dynamic range; IEC, interelement correction]

Internal standard	Analyte	Mass	Scan mode	MCA channels	Dwell time	Integration time	Mode	Equations	Equation type
103 Rh	Ni	57.935	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.0428*Fe54-0.0037*Ca43$	Empirical-IEC
103 Rh	Co	58.933	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.001231*Ca43$	Empirical-IEC
103 Rh	Ni	59.933	Peak Hopping	1	50.0 ms	750 ms	Normal	$-0.0025*Ca43$	Empirical-IEC
103 Rh	Cu	64.928	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Zn	65.926	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.0026*Ti49$	Isobaric
103 Rh	Ga	70.925	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ge	73.922	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.116645 * Se 77$	Isobaric
103 Rh	As	74.922	Peak Hopping	1	100.0 ms	1500 ms	Normal		
103 Rh	As-1	74.922	Peak Hopping	1	100.0 ms	1500 ms	Normal	$-3.127*(ArCl77-0.825*Se82)$	Isobaric
103 Rh	Se	76.92	Peak Hopping	1	100.0 ms	1500 ms	Normal		
103 Rh	Se	81.917	Peak Hopping	1	100.0 ms	1500 ms	Normal	$-1.007833 * Kr 83$	Isobaric
103 Rh	Rb	84.912	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Sr	87.906	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Y	88.905	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Zr	89.904	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Nb	92.906	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Mo	97.906	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.110588 * Ru 101$	Isobaric
	Rh	102.905	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ag	108.905	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.006819*Nb93$	Isobaric
103 Rh	Cd	113.904	Peak Hopping	1	20.0 ms	300 ms	Normal	$-0.027250 * Sn 118$	Isobaric
103 Rh	Sb	120.904	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Cs	132.905	Peak Hopping	1	20.0 ms	300 ms	Normal		
103 Rh	Ba	134.906	Peak Hopping	1	20.0 ms	300 ms	Normal		
193 Ir	La	138.906	Peak Hopping	1	20.0 ms	300 ms	Normal		

Table 1. Elements determined in aqueous samples by Inductively Coupled Plasma-Mass Spectrometry and determination parameters.—Continued
[cps, counts per second; MCA, multichannel analyzer; ms, milliseconds; EDR, extended dynamic range; IEC, interelement correction]

Internal standard	Analyte	Mass	Scan mode	MCA channels	Dwell time	Integration time	Mode	Equations	Equation type
193 Ir	Ce	139.905	Peak Hopping	1	20.0 ms	300 ms	Normal		
193 Ir	Pr	140.907	Peak Hopping	1	10.0 ms	150 ms	Normal		
193 Ir	Nd	145.913	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.00034*Ba135	Empirical-IEC
193 Ir	Sm	148.917	Peak Hopping	1	10.0 ms	150 ms	Normal		
193 Ir	Eu	150.92	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.001238*Ba135	Empirical-IEC
193 Ir	Tb	158.925	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.011207*Nd146	Empirical-IEC
193 Ir	Gd	159.927	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.079197*Dy164-0.0197*Nd146-0.000596*Sm149	Empirical-IEC
193 Ir	Dy	163.929	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.046589*Er166-0.00542*Nd146-0.00359*Sm149	Empirical-IEC
193 Ir	Ho	164.93	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.004782*Sm149	Empirical-IEC
193 Ir	Er	165.93	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.005547*Nd146 -0.002507*Sm149	Empirical-IEC
193 Ir	Tm	168.934	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.000804*Eu151	Empirical-IEC
193 Ir	Yb	171.937	Peak Hopping	1	10.0 ms	150 ms	Normal	-0.008746*Gd160	Empirical-IEC
193 Ir	Lu	174.941	Peak Hopping	1	10.0 ms	150 ms	Normal		
193 Ir	Ta	180.948	Peak Hopping	1	20.0 ms	300 ms	Normal	-0.005965*Ho165	Empirical-IEC
193 Ir	W	183.951	Peak Hopping	1	20.0 ms	300 ms	Normal	-0.004947*Er166	Empirical-IEC
	Ir	192.963	Peak Hopping	1	20.0 ms	300 ms	Normal		
193 Ir	Tl	204.975	Peak Hopping	1	50.0 ms	750 ms	Normal		
193 Ir	Pb	207.977	Peak Hopping	1	20.0 ms	300 ms	Normal	+1*Pb206+1*Pb207	Isobaric
193 Ir	Bi	208.98	Peak Hopping	1	20.0 ms	300 ms	Normal		
193 Ir	Th	232.038	Peak Hopping	1	20.0 ms	300 ms	Normal		
193 Ir	U	238.05	Peak Hopping	1	20.0 ms	300 ms	Normal		

Table 2. Attenuation levels achieved using Extended Dynamic Range mode.

[cps, counts per second; mg/L, milligrams per liter; µg/L, micrograms per liter; %, percent]

Rpa	Na cps (5 mg/L standard)	Attenuation factor
0.000	35153179	0
0.014	4127026	88.3%
0.016	128618	99.6%
Rpa	Al cps (50 µg/L standard)	Attenuation factor
0.000	330886	0
0.012	178419	46.1%

Reagents

- Deionized (DI) water, ASTM Type I, 18 megaohm (MΩ) (Milli-Q, EMD Millipore, Billerica, Mass.)
- Nitric acid (HNO₃), concentrated (70 percent), sub-boiling distilled (Reagent grade HNO₃, VWR International, Radnor, Pa., purified using Milestone DuoPur, Milestone, Shelton, Conn.) or ULTREX grade or equivalent
- Two percent HNO₃ (vol/vol)—Dilute 40 mL concentrated HNO₃ to 2,000 mL with DI water

Internal Standards

Prepare 2 L of a solution containing 500 µg/L ⁶Li, 20 µg/L Rh, and 20 µg/L Ir by serial dilution of commercial 1,000 mg/L aqueous standards (High Purity Standards, Charleston, S.C.), using 2 percent HNO₃. This solution is mixed in a 1:1 ratio with the sample to be analyzed using two channels of the instrument peristaltic pump equipped with a plastic mixing tee and two lines of the orange-orange (0.89 mm i.d.) tubing. The concentrations of the internal standard solution may be adjusted, if necessary, to give target signal intensities between 200,000 and 600,000 counts per second (cps) for each internal standard element.

Calibration Standards

All calibration standards, continuous calibration verification (CCV) standards, and independent calibration verification (ICV) standards are prepared by serial dilution of commercially available multi-element ICP-MS stock solutions and custom blended matrix stock solutions. The sources, elements, and concentrations of the commercially available stock solutions are given in table 3. The elements and concentrations of the Water Matrix Stock solution are given in table 4. The water matrix stock can either be prepared from single element ICP-grade 10,000 mg/L or 1,000 mg/L commercially available standards or custom ordered prepared at the concentrations listed in table 4. Two separate sources of the Water Matrix Stock solution are required, one for preparation of the calibration standards and the second for the preparation of the independent calibration verification solution(s). Currently used sources of these custom-prepared standards include High Purity Standards (Charleston, S.C.) and Inorganic Ventures, Inc., (Christiansburg, Va.). The water matrix stock solution is added to the trace element stock solutions to provide an increasing concentration of common water matrix elements, reducing possible matrix effects from easily ionizable elements on trace element signal intensities (Horlick and Montaser, 1998; Wolf and others, 2001). Other 1,000 mg/L stock standards used for calibration standard preparation are available commercially (High Purity Standards, Charleston, S.C.). The preparation of

Table 3. Sources, elements, and concentrations of commercially available stock solutions.

[mg/L, milligram per liter]

Name	Calibration stock A	Calibration stock B	ICV stock 1A Inorganic	ICV stock 1B	ICV stock 2A	ICV stock 2B	ICV stock 2C
Source	High Purity	High Purity	Ventures	Inorganic Ventures	PerkinElmer	PerkinElmer	PerkinElmer
Part number	ICP-MS-68A	ICP-MS-68B	IV-ICPMS-71A	IV-ICPMS-71B	N9300233	N9300232	N9300235
Concentration	10 mg/L	10 mg/L	10 mg/L	10 mg/L	10 mg/L	10 mg/L	10 mg/L
Elements	Al	Ag	Ag	Ge	Ag	Ce	B
	As	Ge	Al	Hf	Al	Dy	Ge
	B	Hf	As	Mo	As	Er	Mo
	Ba	Mo	B	Nb	Ba	Eu	Nb
	Be	Nb	Ba	Sb	Be	Gd	P
	Bi	Sb	Be	Si	Bi	Ho	Re
	Ca	Si	Ca	Sn	Ca	La	S
	Cd	Sn	Cd	Ta	Cd	Lu	Si
	Ce	Ta	Ce	Te	Co	Nd	Ta
	Co	Te	Co	Ti	Cr	Pr	Ti
	Cr	Ti	Cr	W	Cs	Sc	W
	Cs	W	Cs	Zr	Cu	Sm	Zr
	Cu	Zr	Cu		Fe	Tb	
	Dy		Dy		Ga	Th	
	Er		Er		In	Tm	
	Eu		Eu		K	Y	
	Fe		Fe		Li	Yb	
	Ga		Ga		Mg		
	Gd		Gd		Mn		
	Ho		Ho		Na		
	In		K		Ni		
	K		La		Pb		
	La		Lu		Rb		
	Li		Mg		Se		
	Lu		Mn		Sr		
	Mg		Na		Tl		
	Mn		Nd		U		
	Na		Ni		V		
	Nd		P		Zn		
	Ni		Pb				
	P		Pr				
	Pb		Rb				
	Pr		S				
	Rb		Se				
	Re		Sm				
	Sc		Sr				
	Se		Th				
	Sm		Tl				
	Sr		Tm				
	Tb		U				
	Th		V				
	Tl		Yb				
	Tm		Zn				
	U						
	V						
	Y						
	Yb						
	Zn						

the calibration standards and final concentrations are given in table 5. Note that because of the high sodium matrix in the commercially available phosphate and sulfate 1,000 mg/L stock standards, 25 mg/L of Ca is added to the final prepared phosphate and sulfate calibration standards to eliminate signal enhancement effects caused by Easily Ionizable Element (EIE) effects. Standards are generally prepared to final volume by weight using the following procedure: (1) tare an empty 50 mL centrifuge tube on the balance; (2) pipette the designated amount of all stock solutions into the centrifuge tube; (3) add 2 percent HNO₃ (vol/vol) up to the final desired weight using a wash bottle containing 2 percent HNO₃ prepared with sub-boiling distilled HNO₃ [Note: for 2 percent (vol/vol) HNO₃, the density is 1.0 g per 1.0 mL. If higher acid concentrations are used, density corrections may be necessary to prepare final volumes by weight. The density of the acid concentration being used can be measured by determining the weight of 1.00 mL of the acid pipetted into a tared vessel].

Table 4. Elements and concentrations of Water Matrix Stock solution.

[mg/L, milligram per liter]

Element	Concentration (mg/L)
Na	250
Ca	250
Mg	50
K	50
Si	50

Table 5. Preparation and final concentration of calibration standards for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis.

[cal., calibration; µg/L, microgram per liter; mg/L, milligram per liter; %, percent; mL, milliliter; µL, microliter; g, gram; mg, milligram]

Cal. Standard 1	Stock solution	Volume (µL)	Final concentration (µg/L)
	Cal. Standard 2 2% HNO ₃	5 mL to 50 mL (or 50 g)	1 µg/L (all elements)
Cal. Standard 2	Stock solution	Volume (µL)	Final concentration (µg/L)
	ICP-MS-68A (High Purity)	50 µL	10 µg/L (all elements)
	ICP-MS-68B (High Purity)	50 µL	10 µg/L (all elements)
	2% HNO ₃	to 50 mL (or 50 g)	
Cal. Standard 3	Stock solution	Volume (µL)	Final concentration (µg/L)
	ICP-MS-68A (High Purity)	250 µL	50 µg/L (all elements)
	ICP-MS-68B (High Purity)	250 µL	50 µg/L (all elements)
	Water Matrix Stock	1000 µL	5 mg/L Na, Ca; 1 mg/L Mg, K, Si
	2% HNO ₃	to 50 mL (or 50 g)	
Cal. Standard 4	Stock solution	Volume (µL)	Final concentration (µg/L)
	ICP-MS-68A (High Purity)	500 µL	100 µg/L (all elements)
	ICP-MS-68B (High Purity)	500 µL	100 µg/L (all elements)
	Water Matrix Stock	5 mL	25 mg/L Na, Ca; 5 mg/L Mg, K, Si
	2% HNO ₃	to 50 mL (or 50 g)	
Cal. Standard 5	Stock solution	Volume (µL)	Final concentration (µg/L)
	ICP-MS-68A (High Purity)	500 µL	250 µg/L (all elements)
	ICP-MS-68B (High Purity)	500 µL	250 µg/L (all elements)
	Water Matrix Stock	4 mL	50 mg/L Na, Ca; 10 mg/L Mg, K, Si
	2% HNO ₃	to 20 mL (or 20 g)	
Cal. Standard 6	Stock solution	Volume (µL)	Final concentration (µg/L)
(SO ₄ and PO ₄ Low)	1,000 mg/L PO ₄	2.5 mL	125 mg/L PO ₄ /40.8 mg/L P (1)
	1,000 mg/L SO ₄	2.5 mL	125 mg/L SO ₄ /41.8 mg/L S (2)
	10,000 mg/L Ca	50 µL	25 mg/L Ca
	2% HNO ₃	to 20 mL (or 20 g)	
Cal. Standard 7	Stock solution	Volume (µL)	Final concentration (µg/L)
(SO ₄ and PO ₄ High)	1,000 mg/L PO ₄	5 mL	250 mg/L PO ₄ /81.6 mg/L P (1)
	1,000 mg/L SO ₄	5 mL	250 mg/L SO ₄ /83.6 mg/L S (2)
	10,000 mg/L Ca	50 µL	25 mg/L Ca
	2% HNO ₃	to 20 mL (or 20 g)	

Note 1: 1,000 mg/L PO₄ is equivalent to 326.4 mg/L P

Note 2: 1,000 mg/L SO₄ is equivalent to 334.4 mg/L S

Safety Precautions

All laboratory personnel are required to wear safety glasses, gloves, closed toe shoes, and lab coats when working in the laboratory. Refer to the laboratory chemical hygiene plan and material safety data sheets (MSDSs) for specific precautions, effects of overexposure, and first-aid treatment for reagents used in the preparation procedure and operation of the ICP-MS system.

Sample Preparation

Samples need to be preserved with HNO₃ to a pH ≤ 2 at sample collection or as soon as possible after sample collection. Most sampling protocols require that the samples are filtered and acidified in the field (Wanty and others, 1999; Wilde and others, 2004; U.S. Geological Survey, 2006). At the analyst's discretion, unfiltered samples collected as raw acidified (RA) may be filtered or decanted prior to analysis if visible particulates or solids are present to prevent clogging of the sample introduction system (for example, sample probe or nebulizer). Samples with conductivities greater than 1,500 $\mu\text{S}/\text{cm}$ are generally diluted by the analyst in 2 percent HNO₃ using a suitable dilution factor to bring the conductivity down to $<1,500 \mu\text{S}/\text{cm}$ in order to prevent clogging of the sample introduction system and minimize matrix interferences. The analyst should notify the sample submitter if this or any other procedures were necessary to analyze the samples. If the sample results are over the calibration curve, dilution and reanalysis of the affected samples for the over range elements is required or a high-level standard at a concentration above the highest measured sample level is analyzed with results within 5 percent of the true or prepared value.

Procedure

After a 30-minute warm-up time, the ICP-MS instrument is optimized to meet manufacturer or USGS-specific operating parameters, including Autolens and dual-detector calibration according to the instructions in the ELAN version 3.4 ICP-MS software. The instrument is then calibrated using the standard solutions listed in table 5, and the operating parameters shown in table 6. The operating parameters may vary slightly depending on the specific model ICP-MS, nebulizer, and spray chamber being used for analysis.

The ICP-MS is calibrated using a blank and the seven standards listed in table 5 at the beginning of each analytical session using a linear through zero calibration equation. The calibration blank should be prepared from the same source and at the same acid concentration used in the calibration standards. Blank subtraction is performed to negate the effect of the reagents when the blank is higher than the detection limit. The accuracy of the method is checked using a minimum of three aqueous quality control samples such as certified reference materials (CRMs) from the National Institutes for Standards and Technology (NIST, <http://www.nist.gov>) and various other reference materials suppliers or Standard Reference Samples (SRSs) available from the USGS Standard Reference Sample Project (<http://bqs.usgs.gov/srs/>).

Table 6. ELAN DRC-e operating parameters.

[RF, radio frequency; W, watts; L/min, liters per minute; mm, millimeter; rpm, rotations per minute; i.d., internal diameter; s, seconds; ms, milliseconds]

Instrument parameter	Setting or type
RF power	1350W
Cool gas (L/min)	18
Auxiliary gas (L/min)	1.5
Nebulizer gas (L/min)	0.78 – 0.82
Injector	2 mm quartz
Spray chamber	Cyclonic, quartz, Peltier-cooled (PC3, ESI, Inc., Omaha, Neb.)
Pump Speed	10 rpm
Pump Tubing	Orange-orange (0.89 mm i.d.)
Uptake Rate	1 mL/min (sample and internal standard lines together)
Integration time (ms)	10 – 100 milliseconds
Nebulizer	Meinhard Concentric, Type TR-50-C1 (Meinhard, Inc., Golden, Colo.)
Rinse time (s)	90 seconds at 10 rpm
Specific method name	HP_Waters.mth

Before running unknown samples, the calibration is verified using one or more independent calibration verification (ICV) standards that are prepared from a stock originating from a different supplier than the stock(s) used to prepare the calibration standards. The ICV solution should be prepared at a level near the mid-point of each the calibration curve for each element. To verify calibrations for all 57 elements present in the calibration solutions, three separate ICV solutions are typically used—see table 7. The measured ICV concentrations must be within ± 10 percent of the true or prepared value. If the ICV results are not within acceptable limits, then the source of the error should be identified and corrected and the instrument recalibrated and the ICV solution(s) reanalyzed. Common errors include improperly prepared calibration standards or stock solutions and inadequate mixing of the internal standard solution with the sample solutions. The results for all quality control sample (CRM or SRS) analyses should be within ± 20 percent of the certified or proposed values, including stated errors. If the results are not within ± 20 percent of the stated values, the samples are prepared again and reanalyzed by ICP-MS. If the results are still not within acceptable values, the instrument and method parameters are checked and the instrument is recalibrated using freshly prepared calibration standards and the quality control samples are reanalyzed. For every 10 unknown samples, a blank, continuous calibration verification (CCV), and a quality control sample are analyzed. The CCV solution(s) are prepared from the same stock standards used to prepare the calibration standards and may be one or more of the calibration standards reanalyzed to verify continuing calibration accuracy. The measured CCV concentrations should be within ± 10 percent of the true or prepared value. If the CCV values are not within limits, the instrument and method parameters are checked and the instrument is recalibrated using freshly prepared calibration standards and any affected quality control and unknown samples are reanalyzed. If the quality control sample is not within ± 20 percent of the accepted value, the instrument and method parameters are checked and the instrument is recalibrated using freshly prepared calibration standards, and any affected quality control and unknown samples are reanalyzed.

Table 7. Preparation and final concentration of independent calibration verification standards for Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis.

[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; %, percent; mL, milliliter; μL , microliter; g, gram; mg, milligram]

I.V. ICV-75	Stock solution	Volume (μL)	Final concentration ($\mu\text{g/L}$)
	ICV Stock 1A (IV-ICPMS-71A)	150 μL	75 $\mu\text{g/L}$ (all elements)
	ICV Stock 1B (IV-ICPMS-71B)	150 μL	75 $\mu\text{g/L}$ (all elements)
	Second Source Water Matrix Stock 2% HNO_3	2 mL to 20 mL (or 20 g)	25 mg/L Na, Ca; 5 mg/L Mg, K, Si
PE ICV-75	Stock solution	Volume (μL)	Final concentration ($\mu\text{g/L}$)
	ICV Stock 2A (N9300233)	150 μL	75 $\mu\text{g/L}$ (all elements)
	ICV Stock 2B (N9300232)	150 μL	75 $\mu\text{g/L}$ (all elements)
	ICV Stock 2C (N9300235)	150 μL	75 $\mu\text{g/L}$ (all elements)
	Second Source Water Matrix Stock 2% HNO_3	2 mL to 20 mL (or 20 g)	25 mg/L Na, Ca; 5 mg/L Mg, K, Si
P-S ICV-50	Stock solution	Volume (μL)	Final concentration ($\mu\text{g/L}$)
(SO ₄ and PO ₄ ICV)	Second Source 1000 mg/L PO ₄	3.0 mL	150 mg/L PO ₄ /49.0 mg/L P
	Second Source 1000 mg/L SO ₄	3.0 mL	150 mg/L SO ₄ /50.2 mg/L S
	10,000 mg/L Ca	50 μL	25 mg/L Ca
	2% HNO_3	to 20 mL (or 20 g)	

Method Performance—Blank Analysis and Reporting Limits

The instrument detection limits and reporting limits calculated from more than 40 blank analyses are shown in table 8. The preferred masses for reporting are selected based on background equivalent concentration (BEC), achieved detection limits, analytical performance of quality control samples, and minimal interferences at the particular mass for a particular sample matrix. For some elements, more than one mass is analyzed in order to rule out possible interferences in unusual samples. Prior to reporting, the results for Si and S are converted to SiO₂ and SO₄ using 2.139 and 2.995 conversion factors, respectively. In table 8, the method detection limit (MDL) is calculated as a value equaling three times the standard deviation (SD) of a large number ($n > 40$) of blank analyses during a 3-month period. The lower reporting limit in table 8 is established by rounding the calculated MDL to a suitable number of significant figures and raising reporting levels for ubiquitous elements based on professional judgment to prevent false positives. The instrument MDLs and reporting limits are reevaluated on an annual basis or as instrument operating parameters are changed. The upper reporting limit is generally extended to two times the highest calibration standard. For samples with results reading above the highest calibration standard, either a quality control sample at a higher level or a high-level calibration standard can be used to verify linearity above the highest calibration concentration.

Table 8. Blanks analysis, method detection limits, and reporting limits.[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; SD, standard deviation; MDL, method detection limit]

Element	Mass	Calibration units	Number of samples	Mean	Standard deviation (SD)	MDL = 3 x SD	Reporting limit ($\mu\text{g/L}$)	Upper reporting limit (1)
Li	7	$\mu\text{g/L}$	42	-0.1243	0.8166	2.450	5	500
Be	9	$\mu\text{g/L}$	42	-0.0008	0.0066	0.020	0.05	500
Na	23	mg/L	42	0.0026	0.0122	0.037	0.05	100
Na-1	23	mg/L	42	0.0025	0.0122	0.036	0.05	100
Na-2	23	mg/L	42	0.0027	0.0136	0.041	0.05	100
Mg	25	mg/L	42	0.0004	0.0030	0.009	0.01	20
Al	27	$\mu\text{g/L}$	42	0.3403	0.7442	2.233	3	500
Al-1	27	$\mu\text{g/L}$	42	0.4815	0.7503	2.251	3	500
Si (2)	29	mg/L	42	0.0419	0.0670	0.201	0.2	40
P	31	mg/L	42	0.0022	0.0032	0.009	0.01	200
S (3)	34	mg/L	42	0.5845	1.6279	4.884	5	200
K	39	mg/L	42	0.0039	0.0065	0.019	0.03	20
Ca	43	mg/L	42	0.0002	0.0234	0.070	0.2	100
Ca	44	mg/L	42	0.0024	0.0105	0.032	0.2	100
Sc	45	$\mu\text{g/L}$	42	0.0358	0.1111	0.333	0.6	500
Ti	49	$\mu\text{g/L}$	42	-0.0024	0.0473	0.142	0.5	500
V	51	$\mu\text{g/L}$	42	-0.0012	0.0237	0.071	0.5	500
Cr	52	$\mu\text{g/L}$	42	0.0060	0.0913	0.274	1	500
Cr	53	$\mu\text{g/L}$	42	0.0185	0.2494	0.748	1	500
Fe	54	$\mu\text{g/L}$	42	3.1744	6.6543	19.963	60	500
Mn	55	$\mu\text{g/L}$	42	-0.0014	0.0074	0.022	0.2	500
Fe	57	$\mu\text{g/L}$	42	-4.7339	19.6910	59.073	60	500
Ni	58	$\mu\text{g/L}$	42	-0.0374	0.0896	0.269	0.3	500
Co	59	$\mu\text{g/L}$	42	0.0001	0.0011	0.003	0.4	500
Ni	60	$\mu\text{g/L}$	42	-0.0125	0.0739	0.222	0.4	500
Cu	63	$\mu\text{g/L}$	42	-0.0030	0.0128	0.038	0.5	500
Zn	66	$\mu\text{g/L}$	42	0.0359	0.0619	0.186	1	500
Ga	71	$\mu\text{g/L}$	42	-0.0002	0.0027	0.008	0.05	500
Ge	74	$\mu\text{g/L}$	42	0.0002	0.0038	0.011	0.05	500
As-1	75	$\mu\text{g/L}$	42	-0.0229	0.0654	0.196	1	500
As	75	$\mu\text{g/L}$	42	-0.0042	0.0264	0.079	1	500
Se	77	$\mu\text{g/L}$	42	0.0800	0.2186	0.656	1	500
Se	82	$\mu\text{g/L}$	42	-0.0059	0.1515	0.455	1	500
Rb	85	$\mu\text{g/L}$	42	0.0010	0.0018	0.005	0.01	500
Sr	88	$\mu\text{g/L}$	42	0.0096	0.0191	0.057	0.5	500
Y	89	$\mu\text{g/L}$	42	0.0002	0.0008	0.002	0.01	500
Zr	90	$\mu\text{g/L}$	42	0.0021	0.0031	0.009	0.2	500
Nb	93	$\mu\text{g/L}$	42	0.0100	0.0097	0.029	0.2	500

Table 8. Blanks analysis, method detection limits, and reporting limits.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; SD, standard deviation; MDL, method detection limit]

Element	Mass	Calibration units	Number of samples	Mean	Standard deviation (SD)	MDL = 3 x SD	Reporting limit ($\mu\text{g/L}$)	Upper reporting limit (1)
Mo	98	$\mu\text{g/L}$	42	-0.0225	0.0901	0.270	2	500
Ag	109	$\mu\text{g/L}$	42	-0.0501	0.0884	0.265	1	500
Cd	114	$\mu\text{g/L}$	42	0.0003	0.0011	0.003	0.02	500
Sb	121	$\mu\text{g/L}$	42	0.0188	0.0178	0.053	0.3	500
Cs	133	$\mu\text{g/L}$	42	0.0009	0.0010	0.003	0.02	500
Ba	135	$\mu\text{g/L}$	42	0.0036	0.0127	0.038	0.2	500
La	139	$\mu\text{g/L}$	42	0.0003	0.0007	0.002	0.01	500
Ce	140	$\mu\text{g/L}$	42	0.0002	0.0008	0.002	0.01	500
Pr	141	$\mu\text{g/L}$	42	0.0004	0.0005	0.002	0.01	500
Nd	146	$\mu\text{g/L}$	42	0.0008	0.0015	0.004	0.01	500
Sm	149	$\mu\text{g/L}$	42	0.0008	0.0017	0.005	0.01	500
Eu	151	$\mu\text{g/L}$	42	0.0003	0.0008	0.002	0.005	500
Tb	159	$\mu\text{g/L}$	42	0.0003	0.0006	0.002	0.005	500
Gd	160	$\mu\text{g/L}$	42	0.0006	0.0012	0.004	0.005	500
Dy	164	$\mu\text{g/L}$	42	0.0002	0.0014	0.004	0.005	500
Ho	165	$\mu\text{g/L}$	42	0.0004	0.0006	0.002	0.005	500
Er	166	$\mu\text{g/L}$	42	-0.0002	0.0010	0.003	0.005	500
Tm	168	$\mu\text{g/L}$	42	0.0002	0.0005	0.002	0.005	500
Yb	172	$\mu\text{g/L}$	42	-0.0001	0.0013	0.004	0.01	500
Lu	175	$\mu\text{g/L}$	42	0.0002	0.0004	0.001	0.1	500
Ta	181	$\mu\text{g/L}$	42	0.0150	0.0130	0.039	0.05	500
W	184	$\mu\text{g/L}$	42	0.0320	0.0278	0.084	0.5	500
Tl	205	$\mu\text{g/L}$	42	0.0064	0.0073	0.022	0.1	500
Pb	108	$\mu\text{g/L}$	42	0.0005	0.0034	0.010	0.05	500
Bi	209	$\mu\text{g/L}$	42	0.0033	0.0045	0.013	0.2	500
Th	232	$\mu\text{g/L}$	42	0.0019	0.0019	0.006	0.2	500
U	238	$\mu\text{g/L}$	42	0.0000	0.0009	0.003	0.1	500

(1) Upper limit is based on 2 times the highest calibration standard. Samples higher than this should be verified by running a check standard higher than the highest reading sample(s).

(2) multiply by 2.139 to report as SiO_2

(3) multiply by 2.995 factor to report as SO_4

Table 9. Analysis of quality control samples.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Arsenic, As			$\mu\text{g/L}$			
T-131	trace constituents	29	56.8	1.30	56.6	100%
T-201	trace constituents	34	26.4	0.70	24.4	108%
T-207	trace constituents	13	0.98	0.08	0.87	114%
M-194	major constituents	27	< 0.3	NA	NA	NA
M-198	major constituents	33	< 0.3	NA	NA	NA
M-202	major constituents	23	< 0.3	NA	NA	NA
PPREE-1	trace constituents	10	1.5	0.30	1.5	100%
SCREE-1	trace constituents	10	< 0.3	NA	0.2	NA
Barium, Ba			$\mu\text{g/L}$			
T-131	trace constituents	29	523	47	507	103%
T-201	trace constituents	34	45.6	3.20	44.7	102%
T-207	trace constituents	13	43.6	1.67	42.9	102%
M-194	major constituents	27	41.1	8.70	NA	NA
M-198	major constituents	33	14.4	2.70	NA	NA
M-202	major constituents	23	14.8	0.40	NA	NA
PPREE-1	trace constituents	10	7.49	0.38	7.10	106%
SCREE-1	trace constituents	10	37.6	1.30	34.5	109%
Beryllium, Be			$\mu\text{g/L}$			
T-131	trace constituents	29	12.2	0.90	12.2	100%
T-201	trace constituents	34	8.29	0.74	8.35	99%
T-207	trace constituents	13	0.084	0.02	0.09	92%
M-194	major constituents	27	< 0.05	NA	NA	NA
M-198	major constituents	33	< 0.05	NA	NA	NA
M-202	major constituents	23	< 0.05	NA	NA	NA
PPREE-1	trace constituents	10	1.97	0.33	2.50	79%
SCREE-1	trace constituents	10	< 0.5	NA	0.4	NA
Bismuth, Bi			$\mu\text{g/L}$			
T-131	trace constituents	29	14.4	1.13	NA	NA
T-201	trace constituents	34	< 0.2	0.01	NA	NA
T-207	trace constituents	18	< 0.2	0.00	NA	NA
M-194	major constituents	27	< 0.2	0.02	NA	NA
M-198	major constituents	32	< 0.2	0.01	NA	NA
M-202	major constituents	22	< 0.2	0.01	NA	NA
PPREE-1	trace constituents	10	< 0.2	0.00	NA	NA
SCREE-1	trace constituents	10	< 0.2	0.00	NA	NA

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Calcium, Ca	mg/L					
T-131	trace constituents	29	31.6	1.50	30.6	103%
T-201	trace constituents	34	53.7	2.70	53.1	101%
T-207	trace constituents	18	23.5	1.10	23.4	100%
M-194	major constituents	27	23.3	5.50	24.4	95%
M-198	major constituents	32	10.2	0.61	10.4	98%
M-202	major constituents	22	5.5	0.20	5.6	98%
PPREE-1	trace constituents	10	481	56.3	NA	NA
SCREE-1	trace constituents	10	95.6	9.50	NA	NA
Cadmium, Cd	µg/L					
T-131	trace constituents	29	6.6	0.34	6.1	108%
T-201	trace constituents	34	16.7	0.57	15.7	106%
T-207	trace constituents	18	0.63	0.03	0.59	107%
M-194	major constituents	27	< 0.02	0.01	NA	NA
M-198	major constituents	32	< 0.02	0.00	NA	NA
M-202	major constituents	22	< 0.02	0.00	NA	NA
PPREE-1	trace constituents	10	0.5	0.02	NA	NA
SCREE-1	trace constituents	10	12.5	0.39	NA	NA
Cerium, Ce	µg/L					
T-131	trace constituents	29	0.01	0.01	NA	NA
T-201	trace constituents	34	2.8	0.28	NA	NA
T-207	trace constituents	18	3.8	0.14	NA	NA
M-194	major constituents	27	< 0.01	0.01	NA	NA
M-198	major constituents	32	< 0.01	0.01	NA	NA
M-202	major constituents	22	< 0.01	0.01	NA	NA
PPREE-1	trace constituents	10	181	7.20	161	112%
SCREE-1	trace constituents	10	26.3	1.20	24.6	107%
Cobalt, Co	µg/L					
T-131	trace constituents	29	26.3	0.75	24.6	107%
T-201	trace constituents	34	18.1	0.73	17.4	104%
T-207	trace constituents	18	0.95	0.03	0.98	97%
M-194	major constituents	27	< 0.02	0.00	NA	NA
M-198	major constituents	32	< 0.02	0.00	NA	NA
M-202	major constituents	22	< 0.02	0.00	NA	NA
PPREE-1	trace constituents	10	114	7.80	NA	NA
SCREE-1	trace constituents	10	35.2	1.50	NA	NA

Table 9. Analysis of quality control samples.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Chromium, Cr	$\mu\text{g/L}$					
T-131	trace constituents	29	19.5	0.61	18.6	105%
T-201	trace constituents	34	35.2	1.50	33.7	104%
T-207	trace constituents	18	< 1	0.10	NA	NA
M-194	major constituents	27	< 1	0.10	NA	NA
M-198	major constituents	32	2	0.50	NA	NA
M-202	major constituents	22	< 1	0.10	NA	NA
PPREE-1	trace constituents	10	< 1	0.20	NA	NA
SCREE-1	trace constituents	10	< 1	0.20	NA	NA
Cesium, Cs	$\mu\text{g/L}$					
T-131	trace constituents	29	4.8	0.41	NA	NA
T-201	trace constituents	34	0.22	0.01	NA	NA
T-207	trace constituents	18	0.5	0.02	NA	NA
M-194	major constituents	27	< 0.02	0.00	NA	NA
M-198	major constituents	32	< 0.02	0.00	NA	NA
M-202	major constituents	22	< 0.02	0.00	NA	NA
PPREE-1	trace constituents	10	1.4	0.05	NA	NA
SCREE-1	trace constituents	10	0.18	0.01	NA	NA
Copper, Cu	$\mu\text{g/L}$					
T-131	trace constituents	29	21.9	1.20	20.2	108%
T-201	trace constituents	34	22	1.10	20.8	106%
T-207	trace constituents	18	10.1	1.70	8.4	120%
M-194	major constituents	27	< 0.5	0.05	NA	NA
M-198	major constituents	32	< 0.5	0.04	NA	NA
M-202	major constituents	22	< 0.5	0.10	NA	NA
PPREE-1	trace constituents	10	1.4	0.07	NA	NA
SCREE-1	trace constituents	10	817	21.9	NA	NA
Iron, Fe	$\mu\text{g/L}$					
T-131	trace constituents	29	63.8	33.3	90.7	70%
T-201	trace constituents	34	1990	195	1810	110%
T-207	trace constituents	18	463	26.1	432	107%
M-194	major constituents	27	< 50	48.0	NA	NA
M-198	major constituents	32	< 50	27.6	NA	NA
M-202	major constituents	22	< 50	5.00	NA	NA
PPREE-1	trace constituents	10	88600	6370	NA	NA
SCREE-1	trace constituents	10	4850	179	NA	NA

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Gallium, Ga	µg/L					
T-131	trace constituents	29	< 0.05	NA	NA	NA
T-201	trace constituents	34	0.08	0.02	NA	NA
T-207	trace constituents	18	0.08	0.01	NA	NA
M-194	major constituents	27	< 0.05	NA	NA	NA
M-198	major constituents	32	< 0.05	NA	NA	NA
M-202	major constituents	22	< 0.05	NA	NA	NA
PPREE-1	trace constituents	10	1.5	0.10	NA	NA
SCREE-1	trace constituents	10	0.31	0.02	NA	NA
Gadolinium, Gd	µg/L					
T-131	trace constituents	29	< 0.005	NA	NA	NA
T-201	trace constituents	34	0.34	0.04	NA	NA
T-207	trace constituents	18	0.27	0.03	NA	NA
M-194	major constituents	27	< 0.005	NA	NA	NA
M-198	major constituents	32	< 0.005	NA	NA	NA
M-202	major constituents	22	< 0.005	NA	NA	NA
PPREE-1	trace constituents	10	29.7	1.90	23.8	125%
SCREE-1	trace constituents	10	10.6	0.73	8.2	129%
Germanium, Ge	µg/L					
T-131	trace constituents	29	0.1	0.00	NA	NA
T-201	trace constituents	34	< 0.05	NA	NA	NA
T-207	trace constituents	18	< 0.05	NA	NA	NA
M-194	major constituents	27	< 0.05	NA	NA	NA
M-198	major constituents	32	< 0.05	NA	NA	NA
M-202	major constituents	22	< 0.05	NA	NA	NA
PPREE-1	trace constituents	10	0.37	0.02	NA	NA
SCREE-1	trace constituents	10	0.1	0.10	0.1	100%
Holmium, Ho	µg/L					
T-131	trace constituents	29	< 0.005	NA	NA	NA
T-201	trace constituents	34	0.057	0.01	NA	NA
T-207	trace constituents	18	0.04	0.00	NA	NA
M-194	major constituents	27	< 0.005	NA	NA	NA
M-198	major constituents	32	< 0.005	NA	NA	NA
M-202	major constituents	22	< 0.005	NA	NA	NA
PPREE-1	trace constituents	10	5	0.40	4.4	114%
SCREE-1	trace constituents	10	1.9	0.19	1.6	119%

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Potassium, K	mg/L					
T-131	trace constituents	29	2.4	0.16	2.4	100%
T-201	trace constituents	34	5.2	0.32	5.2	99%
T-207	trace constituents	18	2.2	0.11	2.2	100%
M-194	major constituents	27	3.1	0.60	3.3	94%
M-198	major constituents	32	1.4	0.10	1.5	97%
M-202	major constituents	22	1.3	0.05	1.3	99%
PPREE-1	trace constituents	10	0.97	0.11	NA	NA
SCREE-1	trace constituents	10	5.6	0.45	NA	NA
Lanthanum, La	µg/L					
T-131	trace constituents	29	0.02	0.00	NA	NA
T-201	trace constituents	34	1.7	0.18	NA	NA
T-207	trace constituents	18	1.7	0.08	NA	NA
M-194	major constituents	27	< 0.01	< 0.01	NA	NA
M-198	major constituents	32	< 0.01	< 0.01	NA	NA
M-202	major constituents	22	< 0.01	< 0.01	NA	NA
PPREE-1	trace constituents	10	86.4	3.61	80.4	110%
SCREE-1	trace constituents	10	10.6	0.44	9.8	110%
Lithium, Li	µg/L					
T-131	trace constituents	29	16.4	1.67	17	100%
T-201	trace constituents	34	27.3	1.60	27.9	100%
T-207	trace constituents	18	21.5	2.47	22.2	100%
M-194	major constituents	27	2.5	0.80	NA	NA
M-198	major constituents	32	0.4	0.70	NA	NA
M-202	major constituents	22	0.3	1.20	NA	NA
PPREE-1	trace constituents	10	1.1	0.30	NA	NA
SCREE-1	trace constituents	10	9	2.61	NA	NA
Lutetium, Lu	µg/L					
T-131	trace constituents	29	< 0.1	NA	NA	NA
T-201	trace constituents	34	< 0.1	NA	NA	NA
T-207	trace constituents	18	< 0.1	NA	NA	NA
M-194	major constituents	27	< 0.1	NA	NA	NA
M-198	major constituents	32	< 0.1	NA	NA	NA
M-202	major constituents	22	< 0.1	NA	NA	NA
PPREE-1	trace constituents	10	1.3	0.05	1.1	110%
SCREE-1	trace constituents	10	0.5	0.04	0.5	110%

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Magnesium, Mg	mg/L					
T-131	trace constituents	29	8.2	0.59	8	100%
T-201	trace constituents	34	22.9	1.30	23.8	96%
T-207	trace constituents	18	6.2	0.23	6.2	99%
M-194	major constituents	27	5.8	1.30	6.2	93%
M-198	major constituents	32	4.4	0.47	4.8	92%
M-202	major constituents	22	1.5	0.07	1.5	96%
PPREE-1	trace constituents	10	36.7	1.80	NA	NA
SCREE-1	trace constituents	10	27.1	1.39	NA	NA
Manganese, Mn	µg/L					
T-131	trace constituents	29	38.4	2.85	37.8	100%
T-201	trace constituents	34	1810	135	1800	100%
T-207	trace constituents	18	237	9.19	237	100%
M-194	major constituents	27	4	0.87	NA	NA
M-198	major constituents	32	3.5	0.40	NA	NA
M-202	major constituents	22	6.8	0.20	NA	NA
PPREE-1	trace constituents	10	6240	610	NA	NA
SCREE-1	trace constituents	10	1760	118	NA	NA
Molybdenum, Mo	µg/L					
T-131	trace constituents	29	115	3.03	112	103%
T-201	trace constituents	34	29	0.98	30.5	95%
T-207	trace constituents	18	4.6	0.20	4.6	100%
M-194	major constituents	27	< 2	NA	NA	NA
M-198	major constituents	32	< 2	NA	NA	NA
M-202	major constituents	22	< 2	NA	NA	NA
PPREE-1	trace constituents	10	< 2	NA	NA	NA
SCREE-1	trace constituents	10	< 2	NA	NA	NA
Sodium, Na	mg/L					
T-131	trace constituents	29	21.9	1.11	21.4	100%
T-201	trace constituents	34	46.2	2.88	47.6	97%
T-207	trace constituents	18	21.9	2.16	21.5	100%
M-194	major constituents	27	23.5	5.00	25	94%
M-198	major constituents	32	8.9	0.56	9.4	94%
M-202	major constituents	22	7.5	0.68	7.4	100%
PPREE-1	trace constituents	10	10	1.71	NA	NA
SCREE-1	trace constituents	10	14.1	2.26	NA	NA

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Niobium, Nb			µg/L			
T-131	trace constituents	29	< 0.2	NA	NA	NA
T-201	trace constituents	34	< 0.2	NA	NA	NA
T-207	trace constituents	18	< 0.2	NA	NA	NA
M-194	major constituents	27	< 0.2	NA	NA	NA
M-198	major constituents	32	< 0.2	NA	NA	NA
M-202	major constituents	22	< 0.2	NA	NA	NA
PPREE-1	trace constituents	10	< 0.2	NA	NA	NA
SCREE-1	trace constituents	10	< 0.2	NA	NA	NA
Neodymium, Nd			µg/L			
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	34	1.3	0.13	NA	NA
T-207	trace constituents	18	1.9	0.09	NA	NA
M-194	major constituents	27	< 0.01	NA	NA	NA
M-198	major constituents	32	< 0.01	NA	NA	NA
M-202	major constituents	22	< 0.01	NA	NA	NA
PPREE-1	trace constituents	10	106	4.35	92.3	120%
SCREE-1	trace constituents	10	26.5	1.40	22.1	120%
Nickel, Ni			µg/L			
T-131	trace constituents	29	60.3	1.66	56.3	110%
T-201	trace constituents	34	66.8	2.93	64	100%
T-207	trace constituents	18	1.9	0.24	1.7	110%
M-194	major constituents	27	0.7	0.22	NA	NA
M-198	major constituents	32	< 0.4	< 0.4	NA	NA
M-202	major constituents	22	< 0.4	0.00	NA	NA
PPREE-1	trace constituents	10	20.4	0.848	NA	NA
SCREE-1	trace constituents	10	13.3	0.53	NA	NA
Phosphorus, P			mg/L			
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	34	< 0.01	NA	NA	NA
T-207	trace constituents	18	0.02	0.005	NA	NA
M-194	major constituents	27	0.3	0.08	0.3	100%
M-198	major constituents	32	0.2	0.00	0.2	100%
M-202	major constituents	22	0.02	0.01	0.02	70%
PPREE-1	trace constituents	10	0.06	0.00	NA	NA
SCREE-1	trace constituents	10	< 0.01	0.00	NA	NA

Table 9. Analysis of quality control samples.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Lead, Pb	$\mu\text{g/L}$					
T-131	trace constituents	29	19.4	1.48	18.1	107%
T-201	trace constituents	34	76.4	6.91	73.9	103%
T-207	trace constituents	18	4.96	0.22	4.8	103%
M-194	major constituents	27	< 0.05	0.06	NA	NA
M-198	major constituents	32	< 0.05	NA	NA	NA
M-202	major constituents	22	< 0.05	NA	NA	NA
PPREE-1	trace constituents	10	0.19	0.01	NA	NA
SCREE-1	trace constituents	10	13.4	0.49	NA	NA
Praseodymium, Pr	$\mu\text{g/L}$					
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	34	0.34	0.03	NA	NA
T-207	trace constituents	18	0.48	0.02	NA	NA
M-194	major constituents	27	< 0.01	NA	NA	NA
M-198	major constituents	32	< 0.01	NA	NA	NA
M-202	major constituents	22	< 0.01	NA	NA	NA
PPREE-1	trace constituents	10	22.7	0.86	21.2	110%
SCREE-1	trace constituents	10	4.7	0.25	4.3	110%
Rubidium, Rb	$\mu\text{g/L}$					
T-131	trace constituents	29	12.1	0.37	NA	NA
T-201	trace constituents	34	5.2	0.18	NA	NA
T-207	trace constituents	18	6.2	0.26	NA	NA
M-194	major constituents	27	1.4	0.22	NA	NA
M-198	major constituents	32	0.62	0.06	NA	NA
M-202	major constituents	22	0.65	0.02	NA	NA
PPREE-1	trace constituents	10	2.8	0.11	NA	NA
SCREE-1	trace constituents	10	7.1	0.21	NA	NA
Sulfate, SO_4	mg/L					
T-131	trace constituents	29	< 2	1.11	NA	NA
T-201	trace constituents	33	187.3	13.8	NA	NA
T-207	trace constituents	18	44	3.63	NA	NA
M-194	major constituents	27	15	3.95	16	94%
M-198	major constituents	32	9.6	2.11	10	96%
M-202	major constituents	22	5.1	0.88	4.4	116%
PPREE-1	trace constituents	10	1200	51.64	NA	NA
SCREE-1	trace constituents	10	440	21.08	NA	NA

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Antimony, Sb	µg/L					
T-131	trace constituents	29	56	4.05	56.2	100%
T-201	trace constituents	34	15.9	0.74	15.8	101%
T-207	trace constituents	18	< 0.3	NA	NA	NA
M-194	major constituents	27	< 0.3	NA	NA	NA
M-198	major constituents	32	< 0.3	0.142	NA	NA
M-202	major constituents	22	< 0.3	NA	NA	NA
PPREE-1	trace constituents	10	< 0.3	NA	NA	NA
SCREE-1	trace constituents	10	< 0.3	NA	NA	NA
Scandium, Sc	µg/L					
T-131	trace constituents	29	0.6	0.06	NA	NA
T-201	trace constituents	34	1.3	0.22	NA	NA
T-207	trace constituents	18	0.7	0.08	NA	NA
M-194	major constituents	27	1.2	0.29	NA	NA
M-198	major constituents	32	0.8	0.13	NA	NA
M-202	major constituents	22	< 0.6	NA	NA	NA
PPREE-1	trace constituents	10	2.3	0.14	NA	NA
SCREE-1	trace constituents	10	4.7	0.35	NA	NA
Selenium, Se	µg/L					
T-131	trace constituents	29	12.1	0.43	11.2	110%
T-201	trace constituents	34	10.5	0.50	9	120%
T-207	trace constituents	18	< 1	0.04	NA	NA
M-194	major constituents	27	< 1	0.70	NA	NA
M-198	major constituents	32	< 1	0.13	NA	NA
M-202	major constituents	22	2.3	0.55	NA	NA
PPREE-1	trace constituents	10	1.7	0.29	NA	NA
SCREE-1	trace constituents	10	2.3	0.32	NA	NA
Silicon Dioxide, SiO ₂	mg/L					
T-131	trace constituents	29	6.4	0.49	5.8	100%
T-201	trace constituents	33	13	0.93	13	100%
T-207	trace constituents	18	7.9	0.32	8.1	100%
M-194	major constituents	27	13	2.35	13	100%
M-198	major constituents	32	7.8	0.73	7.6	100%
M-202	major constituents	22	5.8	0.20	6.2	90%
PPREE-1	trace constituents	10	28	1.71	NA	NA
SCREE-1	trace constituents	10	38	1.08	NA	NA

Table 9. Analysis of quality control samples.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Samarium, Sm			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	33	0.27	0.03	NA	NA
T-207	trace constituents	18	0.34	0.02	NA	NA
M-194	major constituents	27	< 0.01	NA	NA	NA
M-198	major constituents	32	< 0.01	NA	NA	NA
M-202	major constituents	22	< 0.01	NA	NA	NA
PPREE-1	trace constituents	10	23.1	0.95	20.3	110%
SCREE-1	trace constituents	10	8	0.52	6.7	120%
Strontium, Sr			$\mu\text{g/L}$			
T-131	trace constituents	29	297	16	295	100%
T-201	trace constituents	33	397	21	396	100%
T-207	trace constituents	18	157	5.87	161	97%
M-194	major constituents	25	129	13	135	95%
M-198	major constituents	32	47.9	4.28	52.4	91%
M-202	major constituents	22	36	1.32	37.4	96%
PPREE-1	trace constituents	10	2850	128	NA	NA
SCREE-1	trace constituents	10	123	3.93	NA	NA
Tantalum, Ta			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.02	0.01	NA	NA
T-201	trace constituents	33	< 0.02	0.01	NA	NA
T-207	trace constituents	18	< 0.02	NA	NA	NA
M-194	major constituents	27	< 0.02	NA	NA	NA
M-198	major constituents	32	0.03	0.02	NA	NA
M-202	major constituents	22	< 0.02	NA	NA	NA
PPREE-1	trace constituents	10	< 0.02	NA	NA	NA
SCREE-1	trace constituents	10	< 0.02	NA	NA	NA
Terbium, Tb			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.005	NA	NA	NA
T-201	trace constituents	33	0.05	0.01	NA	NA
T-207	trace constituents	18	0.04	0.00	NA	NA
M-194	major constituents	27	< 0.005	NA	NA	NA
M-198	major constituents	32	< 0.005	NA	NA	NA
M-202	major constituents	22	< 0.005	NA	NA	NA
PPREE-1	trace constituents	10	4	0.28	3.6	110%
SCREE-1	trace constituents	10	1.5	0.12	1.3	110%

Table 9. Analysis of quality control samples.—Continued[$\mu\text{g/L}$, microgram per liter; mg/L , milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Thorium, Th			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.2	NA	NA	NA
T-201	trace constituents	33	< 0.2	NA	NA	NA
T-207	trace constituents	18	< 0.2	NA	NA	NA
M-194	major constituents	27	< 0.2	NA	NA	NA
M-198	major constituents	32	< 0.2	NA	NA	NA
M-202	major constituents	22	< 0.2	NA	NA	NA
PPREE-1	trace constituents	10	< 0.2	NA	NA	NA
SCREE-1	trace constituents	10	< 0.2	NA	NA	NA
Titanium, Ti			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.5	NA	NA	NA
T-201	trace constituents	33	3.7	0.71	NA	NA
T-207	trace constituents	18	7	0.31	NA	NA
M-194	major constituents	27	< 0.5	NA	NA	NA
M-198	major constituents	32	< 0.5	NA	NA	NA
M-202	major constituents	22	< 0.5	NA	NA	NA
PPREE-1	trace constituents	10	13.7	0.45	NA	NA
SCREE-1	trace constituents	10	5.1	0.27	NA	NA
Thallium, Tl			$\mu\text{g/L}$			
T-131	trace constituents	29	8	0.58	NA	NA
T-201	trace constituents	33	6.82	0.59	6.32	108%
T-207	trace constituents	18	0.51	0.02	0.48	106%
M-194	major constituents	27	< 0.1	NA	NA	NA
M-198	major constituents	32	< 0.1	NA	NA	NA
M-202	major constituents	22	< 0.1	NA	NA	NA
PPREE-1	trace constituents	10	< 0.1	NA	NA	NA
SCREE-1	trace constituents	10	0.73	0.03	NA	NA
Thulium, Tm			$\mu\text{g/L}$			
T-131	trace constituents	29	< 0.005	NA	NA	NA
T-201	trace constituents	33	0.02	0.00	NA	NA
T-207	trace constituents	18	0.01	0.00	NA	NA
M-194	major constituents	27	< 0.005	NA	NA	NA
M-198	major constituents	32	< 0.005	NA	NA	NA
M-202	major constituents	22	< 0.005	NA	NA	NA
PPREE-1	trace constituents	10	1.7	0.15	1.5	110%
SCREE-1	trace constituents	10	0.66	0.06	0.58	110%

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Uranium, U	µg/L					
T-131	trace constituents	29	< 0.1	NA	NA	NA
T-201	trace constituents	33	9.56	1.11	9.22	104%
T-207	trace constituents	18	1.87	0.10	1.8	104%
M-194	major constituents	27	1.65	0.47	NA	NA
M-198	major constituents	32	0.2	0.04	NA	NA
M-202	major constituents	22	0.17	0.01	NA	NA
PPREE-1	trace constituents	10	0.13	0.007	NA	NA
SCREE-1	trace constituents	10	0.28	0.02	NA	NA
Vanadium, V	µg/L					
T-131	trace constituents	29	36.8	1.18	34.2	110%
T-201	trace constituents	33	29.2	1.33	28.4	100%
T-207	trace constituents	18	0.9	0.06	NA	NA
M-194	major constituents	27	2.7	0.18	2.8	100%
M-198	major constituents	32	6.4	0.41	6.6	100%
M-202	major constituents	22	< 0.5	NA	NA	NA
PPREE-1	trace constituents	10	1.8	0.25	NA	NA
SCREE-1	trace constituents	10	< 0.5	NA	NA	NA
Tungsten, W	µg/L					
T-131	trace constituents	29	< 0.5	NA	NA	NA
T-201	trace constituents	33	< 0.5	NA	NA	NA
T-207	trace constituents	18	< 0.5	NA	NA	NA
M-194	major constituents	27	< 0.5	NA	NA	NA
M-198	major constituents	32	< 0.5	0.54	NA	NA
M-202	major constituents	22	< 0.5	NA	NA	NA
PPREE-1	trace constituents	10	< 0.5	NA	NA	NA
SCREE-1	trace constituents	10	< 0.5	NA	NA	NA
Yttrium, Y	µg/L					
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	33	2	0.07	NA	NA
T-207	trace constituents	18	1	0.05	NA	NA
M-194	major constituents	27	< 0.01	NA	NA	NA
M-198	major constituents	32	< 0.01	NA	NA	NA
M-202	major constituents	22	< 0.01	NA	NA	NA
PPREE-1	trace constituents	10	140	0.279	NA	NA
SCREE-1	trace constituents	10	45.1	1.40	NA	NA

Table 9. Analysis of quality control samples.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; NA, not applicable; n, number; %, percent; SD, standard deviation]

Quality Control Sample	Description	n	Average determined value	SD	Accepted value	% Recovery
Ytterbium, Yb			µg/L			
T-131	trace constituents	29	< 0.01	NA	NA	NA
T-201	trace constituents	33	0.1	0.01	NA	NA
T-207	trace constituents	18	0.07	0.01	NA	NA
M-194	major constituents	27	< 0.01	NA	NA	NA
M-198	major constituents	32	< 0.01	NA	NA	NA
M-202	major constituents	22	< 0.01	NA	NA	NA
PPREE-1	trace constituents	10	9.5	0.59	NA	NA
SCREE-1	trace constituents	10	4	0.26	NA	NA
Zinc, Zn			ug/L			
T-131	trace constituents	29	75	3.26	72	104%
T-201	trace constituents	33	1200	54	1110	108%
T-207	trace constituents	18	225	7.75	200	113%
M-194	major constituents	27	4.3	0.58	NA	NA
M-198	major constituents	32	< 3	NA	NA	NA
M-202	major constituents	22	< 3	0.06	NA	NA
PPREE-1	trace constituents	10	586	34	NA	NA
SCREE-1	trace constituents	10	2030	72	NA	NA
Zirconium, Zr			µg/L			
T-131	trace constituents	29	< 0.2	NA	NA	NA
T-201	trace constituents	33	< 0.2	0.08	NA	NA
T-207	trace constituents	18	< 0.2	0.06	NA	NA
M-194	major constituents	27	< 0.2	NA	NA	NA
M-198	major constituents	32	< 0.2	NA	NA	NA
M-202	major constituents	22	< 0.2	NA	NA	NA
PPREE-1	trace constituents	10	< 0.2	NA	NA	NA
SCREE-1	trace constituents	10	< 0.2	NA	NA	NA

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Appendix 1. Determination of Empirical Oxide Corrections

For the rare earth elements (REEs), elements affected by high levels of Ca in samples such as Fe, Ni, and Co, and for the correction of $^{91}\text{Zr}^{16}\text{O}$ and $^{93}\text{Nb}^{16}\text{O}$ interferences on ^{107}Ag and ^{109}Ag , respectively; empirical oxide correction equations are used that must be reevaluated on a routine basis as instrument tuning parameters are changed. Before performing oxide corrections, optimize the instrument and record the CeO/Ce ratio from the Daily Performance Report. If operating parameters result in a CeO/Ce ratio more than 50 percent different than when the corrections were previously evaluated, the oxide corrections should be redetermined. The instrumental parameters for determining oxide corrections are given in table 1–1.

Table 1–1. Elements and timing parameters for oxide interference correction determination.

[cps, counts per second; MCA, multichannel analyzer; ms, milliseconds]

Number of Sweeps: 15					
Number of Replicates: 3					
Element	Mass	Scan mode	MCA channels	Dwell time (ms)	Integration time (ms)
Ca	42.9588	Peak Hopping	1	50	750
Ca	43.9555	Peak Hopping	1	50	750
Fe	56.9354	Peak Hopping	1	50	750
Ni	57.9353	Peak Hopping	1	50	750
Co	58.9332	Peak Hopping	1	50	750
Ni	59.9332	Peak Hopping	1	50	750
Ni	60.931	Peak Hopping	1	50	750
Zr	89.9043	Peak Hopping	1	50	750
Nb	92.906	Peak Hopping	1	50	750
Mo	94.9058	Peak Hopping	1	50	750
Mo	97.9055	Peak Hopping	1	50	750
Ag	106.905	Peak Hopping	1	50	750
Ag	108.905	Peak Hopping	1	50	750
Cd	110.904	Peak Hopping	1	50	750
Cd	113.904	Peak Hopping	1	50	750
Ba	134.906	Peak Hopping	1	50	750
Ba	137.905	Peak Hopping	1	50	750
La	138.906	Peak Hopping	1	50	750
Ce	139.905	Peak Hopping	1	50	750
Pr	140.907	Peak Hopping	1	50	750
Nd	142.91	Peak Hopping	1	50	750
Nd	145.913	Peak Hopping	1	50	750
Sm	146.915	Peak Hopping	1	50	750
Sm	148.917	Peak Hopping	1	50	750
Eu	150.92	Peak Hopping	1	50	750
Eu	152.929	Peak Hopping	1	50	750

Table 1–1. Elements and timing parameters for oxide interference correction determination.

[cps, counts per second; MCA, multichannel analyzer; ms, milliseconds]

Number of Sweeps: 15					
Number of Replicates: 3					
Element	Mass	Scan mode	MCA channels	Dwell time (ms)	Integration time (ms)
Gd	157.924	Peak Hopping	1	50	750
Tb	158.925	Peak Hopping	1	50	750
Gd	159.927	Peak Hopping	1	50	750
Dy	160.927	Peak Hopping	1	50	750
Dy	163.929	Peak Hopping	1	50	750
Ho	164.93	Peak Hopping	1	50	750
Er	165.93	Peak Hopping	1	50	750
Tm	168.934	Peak Hopping	1	50	750
Yb	171.937	Peak Hopping	1	50	750
Yb	172.938	Peak Hopping	1	50	750
Lu	174.941	Peak Hopping	1	50	750
Hf	178.946	Peak Hopping	1	50	750
Hf	179.947	Peak Hopping	1	50	750
Ta	180.948	Peak Hopping	1	50	750
W	183.951	Peak Hopping	1	50	750

Procedure for Determining Oxide Corrections

1. Create a quantitative method using the isotopes and timing parameters given in table 1–1. Be sure to go into the Equations tab in the Method Editor and delete ALL correction equations. Save the method under a suitable name such as Oxide Corrections.mth. The resulting data can either be printed or sent to an electronic file.
2. Prepare single element solutions of the following elements at a concentration of 10 micrograms per liter ($\mu\text{g/L}$)—Zr, Nb, Mo, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, and W; A 50 milliliter (mL) volume of each is sufficient for several analyses.
3. Prepare a single element solution of calcium (Ca) at 10 milligram per liter (mg/L); a 50 mL volume is sufficient for several analyses.
4. Prepare 50 mL of 2 percent nitric acid (HNO_3) using double-distilled nitric acid and 18 megaohm ($\text{M}\Omega$) deionized water to be used as a blank solution.
5. Set up the autosampler to run a minimum of 5 blanks initially, followed by a single analysis of each individual element solution with two blanks in between each solution. A washout time of at least two minutes between each solution is recommended to prevent carryover effects.
6. Once the solutions are analyzed, enter the resulting intensities for the blanks and each individual element solution into the shaded areas of the oxide correction calculations spreadsheet in table 1–2. The basis for calculating the correction equations is to calculate the ratio of the apparent signal for each interfering element at the interfered with element's mass

to the net intensity of the interfering element. This correction ratio is then multiplied by the measured intensity of each interfering element measured in the sample solutions to adjust for changing concentrations of the interfering elements. Whenever possible, choose masses to measure the interfering element signals that do not contain interferences. The equations used to perform calculations are shown in table 1–2. All formulas for table 1–2 are available in a downloadable Microsoft Excel file at http://pubs.usgs.gov/of/2015/1010/pdf/ofr2015-1010_table1-2.xlsx. Collected data are entered into the appropriate blank fields and the calculations are performed automatically.

7. The spreadsheet in table 1–2 contains sections for elements where there are multiple interfering elements affecting an analyte mass. The correction equations for the first section, called First Order Corrections, for the REEs are calculated and then entered into the analytical method used to collect the data and the raw data reprocessed for the elements contained in the next set of REE correction equations, called Second Order Corrections in table 1–2. The resulting corrected raw data are then entered into the second area of the spreadsheet to generate the Second Order Corrections. The second order corrections are then entered into the analytical method in addition to any first order corrections and the data reprocessed again to generate the corrected raw data for generation of the Third Order Corrections in the third area of the spreadsheet. At each step, the analyst will review the results for the corrected raw data to ensure the corrections are resulting in signals for the interference-affected elements near the background levels observed in the blank solution analyses.
8. The corrections in the Other Oxide corrections area of the spreadsheet in table 1–2 can be generated along with the First Order Corrections, because these are not interrelated to the rare earth element oxide corrections.
9. The correction equations generated in the spreadsheet in table 1–2 must be saved, recorded, and entered into every individual method where these correction equations should be utilized. Note that the ELAN Instrument Control software offers no capability for correction equations to be automatically updated in multiple methods.

Table 1–2. Correction equations calculation worksheet with formulas used for calculations shown.

[cps, counts per second]

	A	B	C	D	E	F	G	H	I	J	K	L	M	M	O	P
1	First Order Corrections interfering element	Blank (cps)	Blank (cps)	Average blank (cps)	Hi standard (cps)	Net intensity for element	Interfered with element	Blank (cps)	Blank (cps)	Average blank (cps)	Apparent Element Intensity (cps)	Net apparent element intensity (cps)	Calculated correction	Interfering element	Correction to enter	
2	Ba135			=AVERAGE(B2:C2)		=E2-D2	Eu151			=AVERAGE(H2:I2)		=K2-J2	=L2/F2	=G2	=-1*M2	=""&A2
3	Ba135			=AVERAGE(B3:C3)		=E3-D3	Nd146			=AVERAGE(H3:I3)		=K3-J3	=L3/F3	=G3	=-1*M3	=""&A3
4	Nd146			=AVERAGE(B4:C4)		=E4-D4	Tb159			=AVERAGE(H4:I4)		=K4-J4	=L4/F4	=G4	=-1*M4	=""&A4
5	Sm149			=AVERAGE(B5:C5)		=E5-D5	Ho165			=AVERAGE(H5:I5)		=K5-J5	=L5/F5	=G5	=-1*M5	=""&A5
6	Eu151			=AVERAGE(B6:C6)		=E6-D6	Tm169			=AVERAGE(H6:I6)		=K6-J6	=L6/F6	=G6	=-1*M6	=""&A6
7	Eu151			=AVERAGE(B7:C7)		=E7-D7	Er166			=AVERAGE(H7:I7)		=K7-J7	=L7/F7	=G7	=-1*M7	=""&A7
8	Gd160			=AVERAGE(B8:C8)		=E8-D8	Yb172			=AVERAGE(H8:I8)		=K8-J8	=L8/F8	=G8	=-1*M8	=""&A8
9	Gd160			=AVERAGE(B9:C9)		=E9-D9	Yb173			=AVERAGE(H9:I9)		=K9-J9	=L9/F9	=G9	=-1*M9	=""&A9
10	Ho165			=AVERAGE(B10:C10)		=E10-D10	Ta181			=AVERAGE(H10:I10)		=K10-J10	=L10/F10	=G10	=-1*M10	=""&A10
11	Er166			=AVERAGE(B11:C11)		=E11-D11	W184			=AVERAGE(H11:I11)		=K11-J11	=L11/F11	=G11	=-1*M11	=""&A11
12	Ta181			=AVERAGE(B12:C12)		=E12-D12	Hf180			=AVERAGE(H12:I12)		=K12-J12	=L12/F12	=G12	=-1*M12	=""&A12
13	Dy164			=AVERAGE(B13:C13)		=E13-D13	Gd160			=AVERAGE(H13:I13)		=K13-J13	=L13/F13	=G13	=-1*M13	=""&A13
14	Er166			=AVERAGE(B14:C14)		=E14-D14	Dy164			=AVERAGE(H14:I14)		=K14-J14	=L14/F14	=G14	=-1*M14	=""&A14
15	Nd146			=AVERAGE(B15:C15)		=E15-D15	Er166			=AVERAGE(H15:I15)		=K15-J15	=L15/F15	=G15	=-1*M15	=""&A15
16	Dy164			=AVERAGE(B16:C16)		=E16-D16	Hf179			=AVERAGE(H16:I16)		=K16-J16	=L16/F16	=G16	=-1*M16	=""&A16
17	Gd160			=AVERAGE(B17:C17)		=E17-D17	Lu175			=AVERAGE(H17:I17)		=K17-J17	=L17/F17	=G17	=-1*M17	=""&A17
18	END FIRST ORDER CORRECTIONS – PUT THESE IN AND REPROCESS DATA FOR SECOND ORDER CORRECTION ELEMENTS LISTED BELOW															
19																
20	2ND ORDER CORRECTION ELEMENTS															
21	Nd146			=AVERAGE(B21:C21)		=E21-D21	Gd160			=AVERAGE(H21:I21)		=K21-J21	=L21/F21	=G21	=-1*M21	=""&A21
22	Nd146			=AVERAGE(B22:C22)		=E22-D22	Dy164			=AVERAGE(H22:I22)		=K22-J22	=L22/F22	=G22	=-1*M22	=""&A22
23	Sm149			=AVERAGE(B23:C23)		=E23-D23	Er166			=AVERAGE(H23:I23)		=K23-J23	=L23/F23	=G23	=-1*M23	=""&A23
24	END SECOND ORDER CORRECTIONS – PUT THESE IN AND REPROCESS DATA FOR THIRD ORDER CORRECTION ELEMENTS LISTED BELOW															
25																
26	THIRD ORDER CORRECTION ELEMENTS															
27	Sm149			=AVERAGE(B27:C27)		=E27-D27	Gd160			=AVERAGE(H27:I27)		=K27-J27	=L27/F27	=G27	=-1*M27	=""&A27
28	Sm149			=AVERAGE(B28:C28)		=E28-D28	Dy164			=AVERAGE(H28:I28)		=K28-J28	=L28/F28	=G28	=-1*M28	=""&A28
29	W184			=AVERAGE(B29:C29)		=E29-D29	Hf180			=AVERAGE(H29:I29)		=K29-J29	=L29/F29	=G29	=-1*M29	=""&A29
30	Dy164			=AVERAGE(B30:C30)		=E30-D30	Hf180			=AVERAGE(H30:I30)		=K30-J30	=L30/F30	=G30	=-1*M30	=""&A30
31																
32																
33	OTHER OXIDE CORRECTIONS															
34	Ca43			=AVERAGE(B34:C34)		=E34-D34	Fe57			=AVERAGE(H34:I34)		=K34-J34	=L34/F34	=G34	=-1*M34	=""&A34
35	Ca43			=AVERAGE(B35:C35)		=E35-D35	Co59			=AVERAGE(H35:I35)		=K35-J35	=L35/F35	=G35	=-1*M35	=""&A35
36	Ca43			=AVERAGE(B36:C36)		=E36-D36	Ni60			=AVERAGE(H36:I36)		=K36-J36	=L36/F36	=G36	=-1*M36	=""&A36
37																
38	Zr90			=AVERAGE(B38:C38)		=E38-D38	Ag107			=AVERAGE(H38:I38)		=K38-J38	=L38/F38	=G38	=-1*M38	=""&A38
39	Nb93			=AVERAGE(B39:C39)		=E39-D39	Ag109			=AVERAGE(H39:I39)		=K39-J39	=L39/F39	=G39	=-1*M39	=""&A39
40																
41	Mo 95			=AVERAGE(B41:C41)		=E41-D41	Cd 111			=AVERAGE(H41:I41)		=K41-J41	=L41/F41	=G41	=-1*M41	=""&A41
42	Mo 98			=AVERAGE(B42:C42)		=E42-D42	Cd 114			=AVERAGE(H42:I42)		=K42-J42	=L42/F42	=G42	=-1*M42	=""&A42