Metals, atomic emission spectrometry, inductively coupled plasma (ICP)

Parameters and Codes:
Metals, dissolved,I-1472-87 (see below)

Parameter	Code	Parameter		Code
Barium (µg/L as Ba)	**01005**	**Magnesium**	**(mg/L as Mg)**	**00925**
Beryllium (µg/L as Be)	**01010**	**Manganese**	**(µg/L as Mn)**	**01056**
Cadmium (µg/L as Cd)	**01025**	**Molybdenum**	**(µg/L as Mo)**	**01060**
Calcium (mg/L as Ca)	**00915**	**Nickel**	**(µg/L as Ni)**	**01065**
Chromium (µg/L as Cr)	**01030**	**Silica**	**(mg/L as $Si0_2$)**	**00955**
Cobalt (µg/L as Co)	**01035**	**Silver**	**(µg/L as Ag)**	**01075**
Copper (µg/L as Cu)	**01040**	**Sodium**	**(mg/L as Na)**	**00930**
Iron (µg/L as Fe)	**01046**	**Strontium**	**(µg/L as Sr)**	**01080**
Lead (µg/L as Pb)	**01049**	**Vanadium**	**(µg/L as V)**	**01085**
Lithium (µg/L as Li)	**01130**	**Zinc**	**(µg/L as Zn)**	**01090**

1. Application

1.1 This method is used only for the determination of dissolved metals in water samples that have a measured specific conductance of less than 2,000 µS/cm at *25°C.* The concentration limits are listed in table 8. Samples containing analyte concentrations greater than the maximum concentration limit can be analyzed for calcium, magnesium, silica, and sodium if the sample is diluted and if, after dilution, the specific conductance is less than 2,000 µS/cm. Trace metals also can be determined after appropriate dilution in samples that have a measured specific conductance greater than 2,000 µS/cm; however, detection levels and sensitivity will change proportionally. This modified method was implemented in the National Water Quality Laboratory In August 1987.

Table *8.--Concentration limits of metals for inductively coupled plasma*

[µg/L, microgram per liter; mg/L, milligram per liter]

Metals	Minimum limit (µg/L, except where noted)	Maximum limit (µg/L, except where noted)	Wavelength
Barium	1	10,000	455.5
Beryllium	.5	10,000	313.0
Cadmium	1	10,000	214.4
Calcium (1)	.02 mg/L	25 mg/L	396.8
Calcium (2)	25 mg/L	400 mg/L	315.8
Chromium	5	10,000	267.7
Cobalt	3	10,000	238.8
Copper	10	10,000	324.7
Iron	3	10,000	259.9
Lead	10	10,000	220.3
Lithium	4	10,000	670.7
Magnesium (1)	.01 mg/L	5 mg/L	279.5
Magnesium (2)	5 mg/L	100 mg/L	382.9
Manganese	1	10,000	257.6
Molybdenum	10	10,000	203.8
Nickel	10	10,000	[1]23l.6
Silica (SiO_2)	.01 mg/L	100 mg/L	288.1
Silver	1	10,000	328.1
Sodium (1)	.2 mg/L	50 mg/L	589.0
Sodium (2)	50 mg/L	400 mgfL	330.2
Strontium	.5	10,000	421.5
Vanadium	6	10,000	292.4
Zinc	3	10,000	[1]206.0

‘Second order.

1.2 Analyze filtered and acidified samples. Water-suspended sediment or bottom material samples cannot be analyzed.

1.3 The inductively coupled plasma (ICP) methods approved for U.S. Geological Survey use are linked to a specific instrument and associated software. This does not imply endorsement of one product over another.

2. Summary of method

All metals are determined simultaneously on a single sample by a direct-reading emission spectrometric method using an inductively coupled argon plasma as an excitation source. Samples are pumped into a crossflow pneumatic nebulizer, and introduced into the plasma through a spray chamber and torch assembly. Each analysis is determined on the basis of the average of three replicate integrations, each of which is background corrected by a spectrumshifting technique except for lithium (670.7 nm) and sodium (589.0 nm). A series of five mixed-element standards and a blank are used for calibration.

3. Interferences

3.1 Several interelement interference effects have been evaluated. Interelement correction factors are programmed into the Thermo Jarrell-Ash system software, and corrections are automatically applied internally to the data before they are printed.

3.2 Samples containing high dissolved solids show a variety of unidentified interference effects. Therefore, analyses need to be limited to samples with a specific conductance of 2,000 µS/cm or less.

4. Apparatus

4.1 *Emission spectrometry system* consisting of the following:

4.1.1 *Autosampler*.

4.1.2 *Computer*, IBM PS/2 or equivalent.

4.1.3 *Peristaltic pump.*

4.1.4 *Quartz torch assembly.*

4.1.5 *Spectrometer*, Jarrell-Ash Plasma Spectrometer, 0.75-m focal curve with spectrum shifter background correction, crossflow pneumatic nebulizer, and radio frequency generator. (See table 8 for element wavelengths.)

4.2 Refer to the Jarrell-Ash instruction manual (ICAP61E) for operating techniques. Operating conditions (see NOTE 1):

NOTE 1. Operating conditions are approximate and will vary from instrument to instrument.

Incident radio frequency power	1.25 kW
Reflected radio frequency power	<10 W
Vertical observation position	16 mm above load coil
Horizontal observation position	Center
Argon head pressure	40 lb/in^2
Sample argon pressure for crossflow nebulizer	17 lb/in^2
Sample argon flow rate for crossflow nebulizer	0.9 L/min
Coolant argon flow rate	18 L/min
Sample pumping rate for crossflow nebulizer	10 percent above aspiration
Refractor plate position	Optimized for Hg profile
Spectrum shifter	0.03 nm on high side of wavelength

5. Reagents

5.1 Use Ultrex grade acids or equivalent to prepare standards.

5.1.1 *Aqua regia:* Cautiously mix three parts concentrated HCl (sp gr 1.19) and one part concentrated HNO_3 (sp gr 1.41) just before use.

5.1.2 *Hydrochloric acid, 6M:* Add 500 mL concentrated HCl (sp gr 1.19) to 400 mL water, and dilute to 1 L.

5.2 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.3 Prepare standard stock solutions from Spex HiPure grade chemicals or equivalent. Dry all salts for 1 h at 105°C unless otherwise specified. Do not dry hydrated salts. Clean all metals thoroughly with the appropriate acid, and dry prior to weighing.

5.3.1 *Barium standard solution 1,* 1.00 mL = 1,000 µg Ba: Dissolve 1.512 g $BaCl_2$ dried at 180°C for 1 h and cooled in a desiccator, in a 1 ,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. After the $BaCl_2$ has dissolved, dilute to 1 ,000 mL with water.

5.3.2 *Beryllium standard solution* 1, 1.00 mL = 1,000 µg Be: Transfer 1.000 g Be flakes into a 1 ,000-mL volumetric flask with minimum water. Use a well-ventilated hood (Caution, see Note 2). Add 90 mL concentrated HNO3 (sp gr 1.41) and 10 mL concentrated HCl (sp gr 1.19). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

NOTE 2. Beryllium is extremely toxic. May be fatal if swallowed or inhaled.

5.3.3 *Cadmium standard solution 1,* 1.00 mL = 1,000 µg Cd: Transfer 1.000 g Cd splatters into a 1 ,000-mL volumetric flask containing 100 mL water. Add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.4 *Calcium (1) standard solution 1,* 1.00 mL = 1,000 µg Ca: Weigh 2.497 3 g $CaCO_3$ dried at 180°C for 1 h and quickly transfer into a 1 ,000-mL volumetric flask containing 100 mL water. Dissolve cautiously with 10 mL concentrated HNO_3 (sp gr 1.41). Cool and dilute the solution to 1,000 mL with water.

5.3.5 Calcium (2) standard solution I, 1.00 mL = 5,000 µg Ca: Dry 12.4865 g $CaCO_3$ at 180°C for 1 h and cool in a desiccator. Weigh quickly, transfer into a 1,000-mL volumetric flask containing 100 mL water, and dissolve cautiously with 10 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water. After cooling, adjust volume to 1,000 mL.

5.3.6 *Chromium standard solution I,* 1.00 mL = 1,000 µg Cr: Transfer 1.000 g Cr metal into a 1 ,000-mL volumetric flask with minimum water. Add 50 mL concentrated HCI (sp gr 1.19) and stir. Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.7 Cobalt standard solution 1, 1.00 mL = 1,000 µg Co: Transfer 1.000 g Co powder into a 1 ,000-mL volumetric flask with minimum water. Add 100 mL concentrated HNO_3 (sp gr 1.41). Place in an ultrasonic bath to increase rate of dissolution. Dilute to 1,000 mL with water.

5.3.8 *Copper standard solution I,* 1.00 mL = 1,000 µg Cu: Transfer 1.000 g Cu powder into a 1 ,000-mL volumetric flask with minimum water. Slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. If necessary, heat to increase rate of dissolution. Dilute to 1,000 mL with water.

5.3.9 Iron standard solution 1, 1.00 mL = 1,000 µg Fe: Transfer 1.000 g Fe powder into a 1,000-mL volumetric flask with minimum water. Place flask in hood and, while stirring, add 15 mL concentrated HCI (sp gr 1.19). Heat to increase rate of dissolution. After dissolution, slowly add 85 mL concentrated HNO_3 (sp gr 1.41). Cool and dilute to 1,000 mL with water.

5.3.10 *Lead standard solution I,* 1.00 mL = 1,000 µg Pb: Transfer 1.000 g Pb powder into a 1 ,000-mL Teflon volumetric flask with minimum water. Place flask into an ultrasonic bath in a well-ventilated hood and add 15 mL concentrated HCI (sp gr 1.19). Slowly add 85 mL concentrated HNOµ3 (sp gr 1.41) while stirring. Dilute to 1,000 mL with water.

5.3.11 *Lithium standard solution I,* 1.00 mL = 1,000 µg Li: Dry $LiCO_3$ in oven at 180°C for 2 h, cool, and transfer 5.3235 g into a 1,000-mL volumetric flask containing 100 mL water. Slowly add 10 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water. .

5.3.12 *Magnesium standard solution I,* 1.00 mL = 1,000 µg Mg: Transfer 1.000 g Mg granules into a 1 ,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.13 *Manganese standard solution I,* 1.00 mL = 1,000 µg Mn: Transfer 1.000 g Mn flakes into a 1,000-mL volumetric flask with minimum water. In a well-ventilated hood, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water.

5.3.14 *Molybdenum standard solution I,* 1.00 mL = 1,000 µg Mo: Transfer 1.000 g Mo powder into a l,000-mL volumetric flask with minimum water. In a well-ventilated hood while stirring, slowly add 10 mL concentrated HNO_3 (sp gr 1.41). After fumes dissipate, add 90 mL concentrated HNO_3 (sp gr 1.41) and 20 mL water. Heat to increase rate of dissolution. If solution turns cloudy and a precipitate appears, turn heat up on hot plate and stir for an additional 15 to 30 minutes until precipitate disappears. Cool and dilute to 1,000 mL with water.

5.3.15 Nickel standard solution I, 1.00 mL = 1,000 µg Ni: Transfer 1.000 g Ni powder into a 1,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood while stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat and stir for 30 minutes or until dissolution is complete. Cool and dilute to 1,000 mL with water.

5.3.16 Silica standard solution I, 1.00 mL = 1,000 µg SiO_2: Transfer 1.7654 g $Na_2SiO_3.5H_2O$ into a 500-mL polypropylene or Teflon volumetric flask and dissolve with small amount of water. Add 50 mL concentrated HNO_3 (sp gr 1.41) and dilute to 500 mL with water.

5.3.17 Silver standard solution I, 1.00 mL = 1,000 µg Ag: Transfer 1.000 g Ag powder into a 1 ,000-mL volumetric flask containing 100 mL water. In a well-ventilated hood while stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution. Cool and dilute to 1,000 mL with water. Store in an opaque bottle.

5.3.18 Sodium standard solution I, 1.00 mL = 5,000 µg Na: Dissolve 12.7107 g NaCI in a l,000-mL volumetric flask containing 100 mL water. Slowly add 100 mL concentrated HNO_3 (sp gr 1.41) while stirring. Cool and dilute to 1,000 mL with water.

5.3.19 Strontium standard solution I, 1.00 mL = 1,000 µg Sr: Dissolve 2.4153 g $Sr(NO_3)_2$ dried for 1 h at 180°C in a 1,000-mL volumetric flask containing 100 mL water. While stirring, add 100 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water.

5.3.20 Vanadium standard solution I, 1.00 mL = 1,000 µg V: Transfer 2.2963 g $NH_4 VO_3$ into a l,000-mL volumetric flask containing 20 mL concentrated HNO_3 (sp gr 1.41). Heat to increase rate of dissolution and continue to heat while stirring for 1 h. Cool and dilute to 1,000 mL with water.

5.3.2 1 Zinc standard solution I, 1.00 mL = 1,000 µg Zn: Transfer 1.0000 g Zn powder into a 1,000-mL volumetric flask containing 200 mL water. While stirring, slowly add 100 mL concentrated HNO_3 (sp gr 1.41). Dilute to 1,000 mL with water.

5.4 Standard solution II, 1.00 mL = 100 µg metal [except calcium (2) and sodium, 1.00 mL = 500 µg]: Dilute 100 mL of each individual metal standard solution I to 1,000 mL with water.

5.5Mixed working standard solutions

5.5.1 Prepare five mixed working standard solutions as follows: Pipet 25.0 mL of each appropriate standard solution II into a 250-mL volumetric flask. Dilute to 250 mL with water. Transfer to acid-rinsed PTFE bottle for storage. Fresh mixed standards need to be prepared weekly. Final concentration will be 1.00 mL = 10.0 µg for all metals with the exception of sodium and calcium (2), which will be 1.00 mL = 50.0 µg. Composition for mixed standard solutions will be as follows:

5.5.2 *Mixed standard solution* I--Iron, cadmium, chromium, lead, and zinc.

5.5.3 *Mixed standard solution* Il--Barium, beryllium, copper, nickel, strontium, vanadium, and cobalt. .

5.5.4 *Mixed standard solution* III--Molybdenum, lithium, silica, silver, and calcium (2).

5.5.5 *Mixed standard solution* IV--Calcium (1), manganese, and sodium.

5.5.6 *Standard solution* V--Magnesium.

5.5.7 *Rinse solution* is prepared by diluting 20 mL concentrated HNO_3 (sp gr 1.41) with 2,000 mL water.

5.6 *Check standard solution:* Pipet 25 mL of each standard solution II into a 500-mL volumetric flask. Dilute to 500 mL with water. Transfer to PTFE bottle for storage. Fresh check standard solution is to be prepared as needed. Final concentration will be 1.00 mL = 5.00 µg for all metals, with the exception of Na, which will be 1.00 mL = 28.83 µg (because of Na in the Si standard solution).

6. Procedure

6.1 Set up instrument with proper operating conditions (paragraph 4.2) and ignite plasma. Warm the instrument for 30 minutes prior to standardization.

6.2 Initiate the *operation* sequence in the software.

6.3 Aspirate a profiling solution or position the mercury pen lamp in front of the entrance slit. Initiate the *profile* computer command and profile the instrument by averaging the micrometer settings obtained at identical intensity positions on each side of the profiling spectral line. Position the micrometer to the average setting.

6.4 Standardize the data system by running a blank and the series of five mixed standard solutions. Pump rinse solution for 30 seconds between standards. Allow 30 seconds for equilibration each time a new solution is introduced.

6.5 Analyze check standard solution described in paragraph 5.6. Concentration values are not to deviate from the actual values by more than 2 percent. If values do deviate more than 2 percent, recalibrate.

6.6 Check standardization by running certified reference samples in natural matrix materials. The determined concentrations need to be within one standard deviation unit of the concentration given for each constituent in the reference material.

6.7 Analyze samples, allowing 30 seconds for equilibration. Pump rinse solution for 30 seconds between samples. Check calibration after analyzing 10 samples by rerunning a reference sample and the check standard solution. The results for the reference sample and check standard solution need to be within one standard deviation unit of the concentration given for each metal in the reference material and less than ±2 percent for each element. If not, the data system has to be restandardized as described starting at paragraph 6.3.

6.8 Reprofile instrument (paragraph 6.3) as necessary. If profile position changes by more than 4 µm units, the instrument will need to be restandardized (starting with paragraph 6.2).

7. Calculations

7.1 All calculations are performed internally by the computer data system. The compound SiO2 will be labeled Si. Headings are used to identify the results.

7.2 If dilutions were performed, multiply the results by the appropriate dilution factor using computer software.

8. Report

8.1 All results are printed out directly in the appropriate reporting units.

8.2 Report the dissolved constituent concentrations as follows:

.8.2.1 Calcium *(00915)*, magnesium *(00925)*, silica *(00955)*, and sodium (00930): less than 10 mg/L, one decimal; 10 mg/L and greater, two significant figures.

8.2.2 Beryllium (01010), cadmium (01025), manganese (01056), silver (01075), and strontium (01080): less than 10 µg/L, nearest microgram per liter; 10 µg/L and greater, two significant figures.

8.2.3 Barium (01005), chromium (01030), cobalt (01035), iron (01046), lithium (01130), vanadium (01085), and zinc (01090): less than 10 µ*g/L*, nearest microgram per liter to the lower limit of detection as specified in table 8; 10 µg/L and greater, two significant figures.

8.2.4 Copper (01040), lead (01049), molybdenum (01060), and nickel (01065): less than 100 µg/L, nearest 10 µg/L; 100 µg/L and greater, two significant figures.

9. Precision

Within its designated range, single-operator precision of the method for each metal can be expressed as listed in table 9. A minimum of 10 replicates was analyzed to obtain each regression equation shown.

Table 9.-- Single-operator precision data for inductively coupled plasma

[µg/L, microgram per liter; mg/L, milligram per liter]

Metal	Slope[1]	Intercept
Barium (µg/L)	0.0061	0.83
Beryllium (µg/L)	.0061	.06
Cadmium (µg/L)	.0203	.30
Calcium (mg/L)	.0044	.30
Cobalt (µg/L)	.0650	.40
Copper (µg/L)	.0039	1.32
Iron (µg/L)	.0071	.059
Lead (µg/L)	.1210	5.0
Lithium (µg/L)	.0240	.076
Magnesium (mg/L)	.0060	.018
Manganese (µg/L)	.0042	.30
Molybdenum (µg/L)	.1220	.18
Silica (mg/L)	.0040	.019
Sodium (mg/L)	.0077	.26
Strontium (µg/L)	.0089	.076
Vanadium (µg/L)	.1000	1.80
Zinc (µ g/L)	.0059	1.24

[1] The standard deviation S_o is calculated by $S_o=mx+b$, where m is slopé of line, x is concentration of constituent in units specified, and b is intercept.

9.3 Single-operator precision for dissolved chromium, nickel, and silver for five samples, expressed as the standard deviation and percentage relative standard deviation, is as follows:

9.3.1 Chromium

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
11	1.1	1.2	109
12	10.9	.76	7
18	16.6	1.0	6
11	19.7	1.4	7
12	24.6	.98	4

9.3.2 Nickel

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
12	10.6	7.0	66
12	12.7	4.1	32
9	19.8	5.3	27
12	25.2	3.3	13
18	46.8	4.2	9

9.3.3 Silver

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
9	0.37	0.38	102
12	2.48	.52	21
12	3.87	.66	17
12	4.95	1.5	30
18	10.4	1.8	17

Reference

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, v. 11.01, p. 45-47.