Chapter F

The determination of twenty-seven elements in aqueous samples by inductively coupled plasma-atomic emission spectrometry

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U.S. Geological Survey Open File Report 02-223-F

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

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Codes: E080 Accepted : 6/21/94

T02 T03 Revised :11/06/01

Principle

Twenty-seven elements are determined in natural waters, acid mine waters, extraction and leachate samples by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Multi-element standards are used to calibrate the instrument for each element. Samples must be acid preserved prior to analysis, but no digestion is required for the determination of the dissolved elements in aqueous samples.

Interferences

ICP-AES interferences may result from spectral interferences, background shifts and matrix effects (Thompson and Walsh, 1989). Inter-element correction factors and background corrections are applied using proprietary data system software (Perkin Elmer, 1999). Matrix effects can generally be negated by proper matching of standard and sample.

Scope

This method is applicable to the analysis of a variety of aqueous samples. All samples must be previously measured for specific conductivity and be acidified prior to submission for analysis. The elements determined, wavelengths used, and operating ranges for this method are shown in table 1. Analysis of elements at higher concentrations may be obtained by dilution of the sample. Approximately 100 sample solutions can be analyzed daily by the ICP-AES system.

Table 1.—ICP-AES elements, wavelengths, and operating ranges for natural and mine waters

Element	*Wavelength, nm*	*Range*	
Aluminum, Al	396.1	0.01	1,000 ppm
Antimony, Sb	217.5	50	10,000 ppb
Arsenic, As	188.9	100	10,000 ppb
Barium, Ba	455.4	1	10,000 ppb
Beryllium, Be	313.0	10	10,000 ppb
Boron, B	249.7	5	10,000 ppb
Cadmium, Cd	226.5	5	10,000 ppb
Calcium, Ca	317.9	0.1	1,000 ppm
Chromium, Cr	205.5	10	10,000 ppb
Cobalt, Co	228.6	10	10,000 ppb
Copper, Cu	324.7	10	10,000 ppb
Iron, Fe	259.9	0.02	1,000 ppm
Lead, Pb	220.3	50	10,000 ppb
Lithium, Li	670.7	1	10,000 ppb
Magnesium, Mg	279.0	0.1	1,000 ppm
Manganese, Mn	257.6	10	10,000 ppb
Molybdenum, Mo	202.0	20	10,000 ppb
Nickel, Ni	231.6	10	10,000 ppb
Phosphorous,P	213.6	0.1	1,000 ppm
Potassium, K	766.4	0.1	1,000 ppm
Silicon, Si	251.6	0.1	1,000 ppm
Silver, Ag	328.0	1	1,000 ppb
Sodium, Na	588.9	0.1	1,000 ppm
Strontium, Sr	421.5	1	10,000 ppb
Titanium, Ti	334.9	50	10,000 ppb
Vanadium, V	292.4	10	10,000 ppb
Zinc, Zn	213.8	10	10,000 ppb

Apparatus

- ICP-AES, Perkin Elmer Optima 3000
- Vortex mixer
- Transfer pipet
- Repeating pipet (Eppendorf)

Reagents

- Lutetium internal standard (Lu*):* 500 μg Lu/mL, as Lu_2O_3 in 5 percent HCl

Safety precautions

All laboratory personnel are required to wear safety glasses, rubber gloves, and lab coats when working in the laboratory. Refer to the *CHP* and *MSDS* for specific precautions, effects of overexposure, and first-aid treatment for reagents used in the preparation procedure and operation of the ICP-AES system.

Procedure

1. Using a transfer pipet weigh 4.00 g sample into a 13X100 mm polypropylene test tube.
2. Add 40 µL Lu as the internal standard with the repeating pipet.
3. Cap sample to store and vortex to mix.
4. Analyze for 27 elements by ICP-AES. (Table 2 shows instrumental operating conditions for the ICP-AES system)

Table 2.—Operating conditions for determination of 27 elements in waters by ICP-AES

RF power to the torch	1300W
Plasma argon flow rate	15 L/min
Auxiliary argon flow rate	0.5 L/min
Nebulizer argon flow rate	0.75 L/min
Sample pump rate	1 mL/min
Observation height above load coil	15 mm
Equilibration time	15s
Auto integration time	0.5 to 20 s
Nebulizer	Modified Babington

Calculations

$$\text{Concentration (ppm or ppb)} = \frac{\text{Final volume (mL) x ICP-AES reading (ppm or ppb)}}{\text{Sample aliquot volume (mL)}}$$

Assignment of uncertainty

The analytical results of 27 elements for selected water reference materials and method blanks are summarized in table 3.

Table 3.—Analytical performance summary for 27 elements in waters by ICP-AES

pv from Water Resources Division, 1987 – 1999, USGS Janzer,1987,OPF 98-391, 99-259, 00-227, and NIST, 1999]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	Description	n	mean	s	pv	%RSD	%R
Aluminum, Al (ppm)							
T-159	**trace constituents**	18	0.028	0.002	0.0319	8	88
T-153	**trace constituents**	18	0.034	0.002	0.035	5	97
M-100	**major constituents**	12	0.040	0.002	-	6	-
T-157	**trace constituents**	18	0.056	0.002	0.0555	4	100
1643d	**trace elements**	17	0.13	0.002	0.1276	2	100
AMW-3	**trace constituents**	6	22.2	0.5	21	2	106
Antimony, Sb (ppb)							
M-100	**major constituents**	12	<50	-	-	-	-
AMW-3	**trace constituents**	6	<50	-	2.7	-	-
T-157	**trace constituents**	18	<50	-	10.8	-	-
T-159	**trace constituents**	18	<50	-	13.9	-	-
T-153	**trace constituents**	18	<50	-	25.7	-	-
1643d	**trace elements**	17	54.7	6	54.1	11	101
Arsenic, As (ppb)							
M-100	**major constituents**	12	<100	-	-	-	-
T-153	**trace constituents**	18	<100	-	0.5	-	-
T-157	**trace constituents**	18	<100	-	25.4	-	-
T-159	**trace constituents**	18	<100	-	28.4	-	-
1643d	**trace elements**	17	<100	-	56.02	-	-
AMW-3	**trace constituents**	6	<100	-	72.5	-	-
Barium, Ba (ppb)							
AMW-3	**trace constituents**	6	3.83	0.3	4.5	8	85
M-100	**major constituents**	12	16.6	0.7	-	4	-
T-159	**trace constituents**	18	37.0	1	38.1	3	97
T-157	**trace constituents**	18	118	2	118	1	100
T-153	**trace constituents**	18	185	2	184	1	100
1643d	**trace elements**	17	513	13	506.5	2	101
Beryllium, Be (ppb)							
M-100	**major constituents**	12	<10	-	-	-	-
T-153	**trace constituents**	18	<10	-	-	-	-
T-159	**trace constituents**	18	10.8	0.3	10.8	3	100
AMW-3	**trace constituents**	6	12.1	0.4	12	3	101
1643d	**trace elements**	17	12.3	0.2	12.53	1	98
T-157	**trace constituents**	18	12.9	0.1	13	1	100
Boron, B (ppb)							
T-159	**trace constituents**	18	25.7	2	26.4	9	97
AMW-3	**trace constituents**	6	26.9	21	153	77	18
T-157	**trace constituents**	18	69.5	2	70.4	3	99
T-153	**trace constituents**	18	99.3	2	99.4	2	100
1643d	**trace elements**	17	144	4	144.8	3	100
M-100	**major constituents**	12	444	17	425	4	104

Table 3.—Analytical performance summary for 27 elements in waters by ICP-AES---Continued

Reference	Description	n	mean	s	pv	%RSD	%R
Cadmium, Cd (ppb)							
M-100	**major constituents**	12	<5	-	-	-	-
T-157	**trace constituents**	18	6.06	0.8	5.8	13	104
1643d	**trace elements**	17	6.12	0.7	6.47	11	95
T-153	**trace constituents**	18	16.1	0.5	16	3	101
T-159	**trace constituents**	18	24.6	1	24	6	103
AMW-3	**trace constituents**	6	117	4	121	4	97
Calcium, Ca (ppm)							
T-157	**trace constituents**	18	6.62	0.2	6.19	2	107
T-159	**trace constituents**	18	25.7	0.6	25.5	2	101
T-153	**trace constituents**	18	27.4	0.6	27.5	2	100
1643d	**trace elements**	17	31.1	0.4	31.04	1	100
M-100	**major constituents**	12	165	9	180	5	91
AMW-3	**trace constituents**	6	333	5	320	1	104
Chromium, Cr (ppb)							
M-100	**major constituents**	12	<10	-	-	-	-
AMW-3	**trace constituents**	6	<10	-	11	-	-
T-153	**trace constituents**	18	15.4	0.9	14.9	6	103
1643d	**trace elements**	17	18.6	1	18.53	5	100
T-159	**trace constituents**	18	27.3	0.9	26.8	3	102
T-157	**trace constituents**	18	31.6	1	31.3	3	101
Cobalt, Co (ppb)							
T-153	**trace constituents**	18	<10	-	-	-	-
T-157	**trace constituents**	18	<10	-	4.03	-	-
M-100	**major constituents**	12	<10	-	-	-	-
T-159	**trace constituents**	18	12.9	2	13.3	14	97
1643d	**trace elements**	17	24.9	2	25	6	100
AMW-3	**trace constituents**	6	147	15	133	10	110
Copper, Cu (ppb)							
M-100	**major constituents**	12	<10	2	-	-	-
1643d	**trace elements**	17	20.5	0.5	20.5	2	100
T-153	**trace constituents**	18	23.5	0.8	24	3	98
T-157	**trace constituents**	18	26.1	0.6	24.8	2	105
T-159	**trace constituents**	18	34.0	1	33.4	3	102
AMW-3	**trace constituents**	6	4840	191	4670	4	104
Iron, Fe (ppm)							
M-100	**major constituents**	12	<.02	0.004	-	-	-
T-159	**trace constituents**	18	0.041	0.003	0.0489	8	85
T-153	**trace constituents**	18	0.068	0.005	0.075	7	91
T-157	**trace constituents**	18	0.071	0.004	0.076	6	93
1643d	**trace elements**	17	0.093	0.003	0.0912	4	102
AMW-3	**trace constituents**	6	150	4	142.65	3	105

Table 3.—Analytical performance summary for 27 elements in waters by ICP-AES---Continued

Reference	Description	n	mean	s	pv	%RSD	%R
Lead, Pb (ppb)							
M-100	**major constituents**	12	<50	-	-	-	-
T-157	**trace constituents**	18	<50	-	6.9	-	-
AMW-3	**trace constituents**	6	<50	-	15.5	-	-
T-159	**trace constituents**	18	<50	-	16.6	-	-
1643d	**trace elements**	17	<50	-	18.15	-	-
T-153	**trace constituents**	18	<50	-	46.2	-	-
Lithium, Li (ppb)							
T-159	**trace constituents**	18	7.94	0.4	8.57	5	93
1643d	**trace elements**	17	16.7	0.4	16.5	2	101
T-157	**trace constituents**	18	32.4	0.5	32.4	1	100
AMW-3	**trace constituents**	6	37.4	1	35	4	107
T-153	**trace constituents**	18	53.6	0.7	53.4	1	100
M-100	**major constituents**	12	109	4	-	4	-
Magnesium, Mg (ppm)							
T-157	**trace constituents**	18	1.05	0.01	1.03	1	102
T-159	**trace constituents**	18	5.38	0.1	5.6	2	96
1643d	**trace elements**	17	8.02	0.1	7.989	2	100
T-153	**trace constituents**	18	8.69	0.1	8.72	2	100
M-100	**major constituents**	12	96.8	4	98	4	99
AMW-3	**trace constituents**	6	112	3	114	2	98
Manganese, Mn (ppb)							
M-100	**major constituents**	12	<10	-	-	-	-
T-159	**trace constituents**	18	22.5	0.6	22	3	102
1643d	**trace elements**	17	37.9	0.7	37.66	2	101
T-153	**trace constituents**	18	73.4	2	74.5	2	99
T-157	**trace constituents**	18	147	3	143	2	103
AMW-3	**trace constituents**	6	82600	1865	82800	2	100
Molybdenum, Mo (ppb)							
M-100	**major constituents**	12	<20	-	-	-	-
T-157	**trace constituents**	18	<20	-	13	-	-
AMW-3	**trace constituents**	6	<20	-	-	-	-
T-159	**trace constituents**	18	25.9	3	41.4	10	63
T-153	**trace constituents**	18	108	7	154	6	70
1643d	**trace elements**	17	108	3	112.9	3	95
Nickel, Ni (ppb)							
M-100	**major constituents**	12	<10	-	-	-	-
T-159	**trace constituents**	18	23.6	2	22.2	8	106
T-157	**trace constituents**	18	30.7	1	30	5	102
T-153	**trace constituents**	18	33.7	2	32.2	6	105
1643d	**trace elements**	17	58.4	2	58.1	3	101
AMW-3	**trace constituents**	6	231	10	206	4	112

Table 3.—Analytical performance summary for 27 elements in waters by ICP-AES---Continued

Reference	Description	n	mean	s	pv	%RSD	%R
Phosphorus,P(ppm							
T-153	**trace constituents**	18	<100	-	-	-	-
T-157	**trace constituents**	18	<100	-	-	-	-
T-159	**trace constituents**	18	<100	-	-	-	-
1643d	**trace elements**	17	<100	-	-	-	-
AMW-3	**trace constituents**	6	<100	-	-	-	-
M-100	**major constituents**	12	<100	-	10	-	-
Potassium, K (ppm)							
T-159	**trace constituents**	18	1.47	0.05	1.52	3	97
T-153	**trace constituents**	18	1.57	0.03	1.6	2	98
1643d	**trace elements**	17	2.38	0.1	2.356	2	101
T-157	**trace constituents**	18	2.53	0.04	2.51	2	101
AMW-3	**trace constituents**	6	3.86	0.2	3.5	5	110
M-100	**major constituents**	12	4.54	0.1	4.5	2	101
Silicon, Si (ppm)							
T-153	**trace constituents**	18	2.73	0.04	2.71	2	101
1643d	**trace elements**	17	2.91	0.1	2.7	2	108
M-100	**major constituents**	12	5.14	0.1	4.77	3	108
T-159	**trace constituents**	18	5.41	0.1	5.37	2	101
T-157	**trace constituents**	18	6.63	0.03	6.64	0	100
AMW-3	**trace constituents**	6	23.7	1	22.4	4	106
Silver, Ag (ppb)							
M-100	**major constituents**	12	<1	-	-	-	-
AMW-3	**trace constituents**	6	<1	-	0.8	-	-
1643d	**trace elements**	17	1.32	0.2	1.27	18	104
T-153	**trace constituents**	18	6.26	0.4	6.24	7	100
T-159	**trace constituents**	18	9.62	0.5	9.67	5	100
T-157	**trace constituents**	18	14.0	0.5	14.5	3	97
Sodium, Na (ppm)							
1643d	**trace elements**	17	21.9	0.4	22.07	2	99
T-153	**trace constituents**	18	28.7	0.3	28.7	1	100
AMW-3	**trace constituents**	6	33.2	1	30.8	4	108
T-157	**trace constituents**	18	59.9	0.9	60.7	2	99
T-159	**trace constituents**	18	98.5	2	100	2	98
M-100	**major constituents**	12	293	10	281	4	104
Strontium, Sr (ppb)							
T-157	**trace constituents**	18	58.0	0.9	59.6	1	97
T-159	**trace constituents**	18	190	6	190	3	100
1643d	**trace elements**	17	301	6	294.8	2	102
T-153	**trace constituents**	18	309	5	311	2	99
AMW-3	**trace constituents**	6	1550	73	1474	5	105
M-100		12	3360	126	3450	4	97

Table 3.—Analytical performance summary for 27 elements in waters by ICP-AES---Continued

Reference	Description	n	mean	s	pv	%RSD	%R
Titanium, Ti (ppb)							
1643d	**trace elements**	17	<50	-	-	-	-
AMW-3	**trace constituents**	6	<50	-	-	-	-
M-100	**major constituents**	12	<50	-	-	-	-
T-153	**trace constituents**	18	<50	-	-	-	-
T-157	**trace constituents**	18	<50	-	-	-	-
T-159	**trace constituents**	18	<50	-	-	-	-
Vanadium, V(ppb)							
M-100	**major constituents**	12	<10	-	11.6	-	-
AMW-3	**trace constituents**	6	<10	-	15	-	-
T-159	**trace constituents**	18	14.1	0.5	14.4	3	98
T-157	**trace constituents**	18	15.9	0.4	15.7	3	101
T-153	**trace constituents**	18	19.2	0.4	19	2	101
1643d	**trace elements**	17	36.5	1	35.1	3	104
Zinc, Zn (ppb)							
M-100	**major constituents**	12	<10	-	-	-	-
T-159	**trace constituents**	18	17.4	2	19.2	10	91
T-157	**trace constituents**	18	23.4	2	23.5	6	100
T-153	**trace constituents**	18	72.9	3	72.6	4	100
1643d	**trace elements**	17	73.2	1	72.48	2	101
AMW-3	**trace constituents**	6	42500	1846	41450	4	102

Table 3.–Continued—Duplicate samples results

Duplicate samples	k	n	Mean	s	%RSD	min	max	< total	< pairs
Ag ppb	7	2	1.75	0.51	29	0.97	3.2	107	53
Al ppm	45	2	2.36	0.24	10	0.01	29	30	15
As ppb	3	2	2667	107	4	1440	3401	114	57
B ppb	31	2	2200	134	6	6.1	37062	58	29
Ba ppb	59	2	54.6	3.5	6	4.5	273	2	1
Be ppb	0	2	-	-	-	-	-	120	60
Ca ppm	59	2	67.9	1.1	2	1.3	693	2	1
Cd ppb	26	2	29.6	1.5	5	4.4	157	69	34
Co ppb	13	2	28.9	2.1	7	5.4	172	95	47
Cr ppb	0	2	-	-	-	-	-	120	60
Cu ppb	27	2	602	16	3	17	2444	66	33
Fe ppm	43	2	3.22	0.12	4	0.02	66	34	17
K ppm	59	2	3.10	0.14	5	0.23	33	2	1
Li ppb	50	2	43.2	1.4	3.2	0.92	1432	21	10
Mg ppm	59	2	18.6	1.4	8	0.25	376	2	1
Mn ppb	43	2	3819	149	4	10	49551	34	17
Mo ppb	3	2	89.6	8.7	10	17	206	115	57
Na ppm	57	2	17.3	0.38	2	0.30	313	6	3
Ni ppb	20	2	29.5	1.3	4	9.0	74	81	40
P ppb	14	2	674	28	4	85	2484	93	46
Pb ppb	16	2	1115	125	11	44	8594	89	44
Sb ppb	0	2	-	-	-	-	-	120	60
Si ppm	59	2	8.09	0.50	6	1.2	38	2	1
Sr ppb	59	2	888	20	2	9.4	19111	2	1
Ti ppb	5	2	125	32	26	70	228	110	55
V ppb	5	2	15.3	0.88	6	12	21	110	55
Zn ppb	38	2	4409	140	3	10	25910	44	22

Table 3.–Continued--Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limits of determination (LLD)

Method blank	n	Mean	s	3s	5s
Ag ppb	30	-0.145	0.16	0.47	0.79
Al ppm	30	-0.007	0.001	0.003	0.005
As ppb	30	14.8	21	64	110
B ppb	30	-1.83	0.28	0.83	1.4
Ba ppb	30	-0.504	0.033	0.099	0.17
Be ppb	30	-0.05	0.006	0.018	0.03
Ca ppm	30	-0.01	0.00009	0.00027	0.00045
Cd ppb	30	-0.695	0.68	2.1	3.4
Co ppb	30	-0.268	2.0	6.1	10
Cr ppb	30	1.61	0.84	2.5	4.2
Cu ppb	30	1.58	0.17	0.51	0.85
Fe ppm	30	-0.0003	0.0004	0.0012	0.002
K ppm	30	-0.019	0.008	0.024	0.04
Li ppb	30	-1.42	0.22	0.66	1.1
Mg ppm	30	-0.005	0.00008	0.00024	0.0004
Mn ppb	30	0.015	0.10	0.30	0.51
Mo ppb	30	-0.72	3.3	9.8	16
Na ppm	30	-0.059	0.0015	0.0045	0.0075
Ni ppb	30	3.1	0.88	2.6	4.4
P ppm	30	0.005	0.005	0.015	0.025
Pb ppb	30	10.7	4.9	15	25
Sb ppb	30	-4.7	4.0	12	20
Si ppm	30	0.023	0.002	0.006	0.01
Sr ppb	30	0.048	0.023	0.069	0.12
Ti ppb	30	0.35	0.14	0.42	0.7
V ppb	30	-1.8	0.15	0.45	0.75
Zn ppb	30	0.45	1.1	3.3	5.5

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