Chapter U

The determination of 30 elements in geological materials by energy-dispersive X-ray fluorescence spectrometry

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Principle

EDXRF spectrometry can be used as both a qualitative and a quantitative technique for the rapid, non-destructive, elemental analysis of liquid and solid samples. Sample preparation is a simple matter of lightly pressing a powdered geologic sample into a Mylar cup fitted with a Prolene foil. Then the sample is bombarded by X-rays of a selected energy and the characteristic X-ray photons of the analytes are detected and measured. By using selected secondary and polarizing targets a greater peak to background ratio for the various peaks are obtained than when using direct tube excitation. With this method 30 trace elements: V, Cr, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Nd, W, Pb, Bi, Th and U are determined routinely. The readers are referred to the literature (E. Bertin, 1975; Johnson and King, 1987; and King,1987) for more details on the use of EDXRF for geologic and geochemical applications.

Interferences

Interferences in X-ray fluorescence consist of spectral-line overlaps, matrix effects, spectral artifacts, and particle size or mineralogical effects.

Peak overlaps occur when a peak of a different element cannot be resolved from the peak of the element of interest. The most significant peak overlaps that occur in this procedure are as follows: Ti Kβ and Ba Lβ overlap the V Kα, V Kβ on Cr Kα, Co Kβ on Ni Kα, Ni Kβ and W Lα on Cu Kα, W Lα on Zn Kα, W Lβ on Ge Kα, Au Lβ and Pb Lα on As Kα, As Kβ on Br Kα, Th Lα and U Lα on Rb Kα, Rb Kβ on Y Kα, Sr Kβ on Zr Kα, Y Kβ on Nb Kα, ZrKβ,ULβ on Mo Kα, Ag Kβ on Sn Kα, Cd Kβ on Sb Kα, Cu Kα and Zn Kα on W Lα , As Kα, Pb Lα and Se Kα on Bi Lα, Rb Kα and Bi Lβ on Th Lα and RbKα and Sr Kα on ULα. These interferences are accounted for using linear and nonlinear fits of Gausian peaks and are removed using the computer algorithms provided with the software. Often an analyte whose concentration is >1000ppm cannot be deconvoluted from an adjacent element whose concentration is 1-5 ppm. These results are denoted by “inf” or interference.

Matrix effects occur when radiation from the analyte element is absorbed or enhanced by other elements in the sample before it reaches the detector. The effects are corrected by a scattered radiation method (Anderman and Kemp, 1958) which has been used for routine trace analyses of geologic materials (R.G. Johnson, 1984 and B.W. King, 1987). The method is based on the principle that the line intensities from the analyte line and the incoherent scatter peak (Compton peak) are effected in the same proportion due to the overall mass absorption coefficient of the sample. The ratio of the analyte line intensity to the Compton peak intensity is constant over a wide range of geologic matrices. This Compton peak method also helps to minimize the effects of particle size, packing density and short term minor drifts in tube current.

Spectral artifacts such as escape peaks, sum peaks, low energy line tailing, pulse pile up lines, and Bremsstralung correction are accounted for with the provided software.

Scope

Analysis by EDXRF for the above listed trace elements is applicable to a wide variety of geochemical samples including rocks, stream sediments, and soils presented as a powder (-120 mesh) packed to 10 foot pounds on a 1 inch diameter die. The analyzed elements and their reporting limits are shown in Table 1.

Table 1. Elements analyzed and the lower limits of determination (LLD) for elemental analysis of geological samples

Element	LLD	Element	LLD	Element	LLD
Vanadium, V	5 ppm	Rubidium, Rb	2 ppm	Cesium, Cs	5 ppm
Chromium, Cr	5 ppm	Strontium, Sr	2 ppm	Barium, Ba	5 ppm
Nickel, Ni	2 ppm	Yttrium, Y	2 ppm	Lanthanum, La	5 ppm
Copper, Cu	2 ppm	Zirconium, Zr	2 ppm	Cerium, Ce	5 ppm
Zinc, Zn	2 ppm	Niobium, Nb	2 ppm	Neodymium, Nd	10 ppm
Gallium, Ga	2 ppm	Molybdenum, Mo	2 ppm	Tungsten, W	5 ppm
Germanium, Ge	2 ppm	Silver, Ag	1 ppm	Lead, Pb	3 ppm
Arsenic, As	2 ppm	Cadmium, Cd	1 ppm	Bismuth, Bi	5 ppm
Selenium, Se	1 ppm	Tin, Sn	2 ppm	Thorium, Th	4 ppm
Bromine, Br	1 ppm	Antimony, Sb	2 ppm	Uranium, U	4 ppm

Apparatus

Spectro X-lab 2000 Energy Dispersive X-ray Spectrometer.
Gresham high purity silicon (**HP Si**rius) liquid nitrogen cooled detector. Resolution at Mn Ka at 10000 counts is 150eV.
X-ray source 400W – Paladium end – window tube
Pana-vise with torque wrench set to 10 foot pounds
Chemplex cups, 32mm
Prolene Film support thickness 4µ (0.16 mil)

Calibration Standards

Table 2. lists the 58 reference standards used for the calibration of this technique. Values are obtained from Govindaraju, 1989 and 1994, National Institute of Standards & Technology (NIST) Certificates of Analysis, U.S. Geological Survey Certificate of Analysis and recommended values obtained on USGS internal laboratory standards.

Table 2. Calibration standards used in the EDXRF method

AGV-1	BCS-375	BHVO-1	BIR-1	BR-N	DR-N	DTS-1	G-2
GH-N	GS-N	GSD-1 thru GSD-12	GSP-1	GSR-1	GSR-4	GSS-1 thru GSS-7	JP-1
MA-N	MAG-1	MICA-FE	MRG-1	NIM-L	NOD-P-1	NBS-88b,278,1646 and 1633a	SY-2
PACS-1	PCC-1	RGM-1	SDO-1	STM-1	SY-3	UB-N	W-2
KRS1-5	KRS-12	KRS3-5	KRS6-5	SQTZ	DGPM-2		

Safety Precautions

The Spectro X-lab 2000 is adequately shielded to prevent X-rays from escaping into the lab area. The system is monitored routinely with a radiation-survey meter at intervals of 6 months. In addition, all laboratory personnel are required to wear a radiation safety badge when operating the X-ray system.

Procedure

A 2- to 3-g portion of the powdered sample or reference material is poured into a 32 mm spectro cup fitted with a bottom of stretched 4μ Prolene film held with a concentric ring. This requires no weighing. The powder is then packed into the cup at approximately 10 lbs/in^2 using the Panavise with torque wrench.

Table 3. Operating conditions for Spectro X-lab 2000 X-ray Spectrometer

Mo secondary target	Determination of Compton and Raleigh Mo Ka peak intensities
Al_2O_3 polarizing target	Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, and Nd determinations - Kα line
Boron Carbide B_4C Polarizing target	Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr and Nb determinations Kα line
	W, Bi,Th, and U determinations – Lα line
	Pb determination – Lβ line
Cobalt secondary target	V and Cr determinations – Kα line
Excitation target voltages	40 kV for Mo, 53kV for Al_2O_3, 44kV for B_4C and 35kV for Co targets
Excitation target current	Current is optimized to reach a dead time of 50%
Acquisition time (live time)	150s Mo target, 300s for B_4C, Al_2O_3 and Co targets.

Up to 20 sample positions can be used in the sample holder. 18 are unknown samples and 2 are selected reference materials for the quality control of the instrument. The sample ID numbers, job numbers and analytical programs are entered into the computer that operates the instrument. A total of 36 samples can be analyzed in a 24-hour period allowing for automatic operation of the instrument overnight.

Spectrum deconvolution:

- Subtraction of escape lines
- Correction of the detector shelf channel per channel
- Subtraction of the pile up lines
- Correction of the Bremsstralung created in the sample
- Subtraction of incomplete polarized scattering radiation or of the scattered radiation of secondary targets
- Correction of the low energy line tailing
- Determination of matrix dependent element specific line ratios
- Recalibration of the channel-energy-calibration and the width-energy-calibration using the zero-peak
- Linear and nonlinear fit of the Gaussian peaks
- Calculation of net peak intensities

The ratios of peak intensity to the Mo Compton scatter intensity are used in a linear least-squares fit of the concentration data for each element.

Calculations

The concentration C_i of element I, in the unknown sample is calculated from the intercept B_o and slope B_i of the best fit line of calibration and the ratio of intensity I_i to Compton scatter radiation C as follows:

$$C_i = B_o + B_i (I_i / C)$$

Assignment of Uncertainty

The counting error σ_N , where σ_N is the standard deviation in terms of the accumulated count N, in X-ray spectroscopy is that error arising only from the random arrival of x-ray photons to the detector. This error is represented by the following equation:

$$\sigma_N = \sqrt{N}$$

σ_N represents the best precision that can be obtained on a particular sample and can be used as a standard against which the actual measured precision can be judged.
The total sources of error are the counting error, the instrument stability error, the specimen preparation error, operational error, and miscellaneous errors.
Table 4. represents the statistical summary for the analysis of 7 geological standard reference materials.

Table 4. Analytical performance summary for elements in geological materials by EDXRF

Reference	Description	n	Mean	σ_N	s	pv	%RSD	%R
Ag ppm								
BHVO-2	Basalt	10	<1	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<1	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<1	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<1	NA	NA	NR	NA	NA
TILL-4	Till	10	<1	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	0.5	NA	NA	<1	NA	NA
NBS-2711	Soil	10	4.6	0.3	0.3	5.9	5.2	78
As ppm								
BHVO-2	Basalt	10	<2	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<2	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<2	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<2	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	42	1.6	0.7	42	1.7	100
NBS-2711	Soil	10	111	4.8	1.9	105	1.7	106
TILL-4	Till	10	117	1.7	0.9	111	0.8	105
Ba ppm								
BHVO-2	Basalt	10	128	1.7	2.7	130	2.1	98
TILL-4	Till	10	391	2.3	4.6	395	1.2	99
STSD-2	Stream sed	10	523	2.7	5.3	540	1.0	97
BCR-2	Basalt	10	646	2.8	6.6	683	1.0	95
NBS-2711	Soil	10	710	2.9	10	726	1.4	98
AGV-2	Andesite	10	1127	3.9	15	1140	1.3	99

Reference	Description	n	Mean	σ_N	s	pv	%RSD	%R
Bi ppm								
BHVO-2	Basalt	10	<5	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<5	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<5	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<5	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	<5	NA	NA	NR	NA	NA
NBS-2711	Soil	10	<5	NA	NA	NR	NA	NA
TILL-4	Till	10	39	1.4	1.0	40	2.5	98
Br ppm								
BHVO-2	Basalt	10	<1	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<1	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<1	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<1	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	3.8	0.4	0.4	4.0	9.3	95
NBS-2711	Soil	10	5.6	0.5	0.5	5.0	9.8	112
TILL-4	Till	10	8.0	0.5	1.0	8.6	2.5	93
Cd ppm								
BHVO-2	Basalt	10	<1	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<1	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<1	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<1	NA	NA	NR	NA	NA
TILL-4	Till	10	<1	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	<1	NA	NA	0.8	NA	NA
NBS-2711	Soil	10	48	0.7	2.9	41	6.0	117
Ce ppm								
BHVO-2	Basalt	10	34	2.4	3.2	38	9.4	89
BCR-2	Basalt	10	48	2.5	2.2	53	4.6	91
AGV-2	Andesite	10	65	2.7	2.8	68	4.3	96
NBS-2711	Soil	10	66	2.6	2.6	69	3.9	96
TILL-4	Till	10	80	2.6	2.5	78	3.2	103
STSD-2	Stream sed	10	87	2.7	3.7	93	4.2	94
GSP-2	Granodiorite	10	468	3.65	4.5	410	1.0	114
Cr ppm								
BCR-2	Basalt	10	14	2.1	2.0	18	11	78
GSP-2	Granodiorite	10	17	1.4	1.2	20	7.1	85
AGV-2	Andesite	10	21	1.2	1.1	17	5.4	124
NBS-2711	Soil	10	48	1.1	1.2	47	2.6	102
TILL-4	Till	10	51	1.1	1.9	53	3.7	96
STSD-2	Stream sed	10	121	1.6	5.1	116	4.2	104
BHVO-2	Basalt	10	314	3.4	3.2	280	1.1	112
Cs ppm								
BHVO-2	Basalt	10	<5	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<5	NA	NA	1.2	NA	NA
BCR-2	Basalt	10	<5	NA	NA	1.1	NA	NA
GSP-2	Granodiorite	10	<5	NA	NA	1.2	NA	NA
STSD-2	Stream sed	10	11	0.9	0.8	12	7.4	92
TILL-4	Till	10	13	0.9	0.6	12	4.9	108
NBS-2711	Soil	10	7.0	0.6	1.1	6.1	15	115

Reference	Description	n	Mean	σ_N	s	Pv	%RSD	%R
Cu ppm								
BCR-2	Basalt	10	17	1.9	2.0	19	11	89
GSP-2	Granodiorite	10	40	1.9	2.0	43	5.1	93
STSD-2	Stream sed	10	45	2.0	3.2	47	7.0	96
AGV-2	Andesite	10	51	2.1	2.0	53	3.8	96
NBS-2711	Soil	10	108	2.7	4.3	114	4.0	95
BHVO-2	Basalt	10	135	3.6	3.5	127	2.6	106
TILL-4	Till	10	248	3.8	5.6	237	2.3	105
Ga ppm								
NBS-2711	Soil	10	13	2.0	1.9	15	14	87
TILL-4	Till	10	17	1.0	1.5	NR	8.5	NA
STSD-2	Stream sed	10	21	1.1	1.5	NR	7.0	NA
BHVO-2	Basalt	10	21	1.3	2.0	22	9.5	95
AGV-2	Andesite	10	21	1.1	1.2	20	5.6	105
GSP-2	Granodiorite	10	22	1.1	0.8	22	3.6	100
BCR-2	Basalt	10	23	1.3	1.0	23	4.3	100
Ge ppm								
BHVO-2	Basalt	10	<2	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<2	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<2	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<2	NA	NA	NR	NA	NA
TILL-4	Till	10	<2	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	<2	NA	NA	NR	NA	NA
NBS-2711	Soil	10	<2	NA	NA	NR	NA	NA
NBS-1633a	Fly Ash	10	39	1.2	1.6	34	4.1	115
La ppm								
BHVO-2	Basalt	10	13	1.7	1.9	15	14	87
BCR-2	Basalt	10	22	1.8	2.2	25	9.8	88
NBS-2711	Soil	10	36	1.9	1.3	40	3.7	90
AGV-2	Andesite	10	38	2.0	1.8	38	4.8	100
TILL-4	Till	10	41	1.9	2.1	41	5.2	100
STSD-2	Stream sed	10	51	2.0	2.4	59	4.7	86
GSP-2	Granodiorite	10	204	2.6	3.1	180	1.5	113
Mo ppm								
NBS-2711	Soil	10	2.4	0.7	0.6	1.6	24	150
AGV-2	Andesite	10	2.6	0.8	0.6	NR	22	NA
GSP-2	Granodiorite	10	4.0	1.0	1.3	2.1	32	190
BHVO-2	Basalt	10	5.3	0.9	0.7	NR	13	NA
STSD-2	Stream sed	10	13	0.9	0.9	13	6.8	100
TILL-4	Till	10	16	1.0	0.9	16	5.9	100
BCR-2	Basalt	10	239	2.9	4.8	248	2.0	96
Nb ppm								
BCR-2	Basalt	10	12	0.5	0.7	NR	6.0	NA
AGV-2	Andesite	10	14	0.4	0.4	15	2.6	93
NBS-2711	Soil	10	14	0.4	0.4	NR	2.8%	NA
TILL-4	Till	10	15	0.4	0.3	15	1.9	100
BHVO-2	Basalt	10	19	0.5	0.7	18	3.5	106

Reference	Description	n	Mean	σ_N	s	pv	%RSD	%R
Nb ppm								
STSD-2	Stream sed	10	20	0.4	0.7	20	3.7	100
GSP-2	Granodiorite	10	26	0.4	0.7	27	2.7	96
Nd ppm								
BHVO-2	Basalt	10	23	5.2	1.8	25	7.2	92
BCR-2	Basalt	10	28	5.8	4.1	28	14	100
NBS-2711	Soil	10	31	5.7	5.2	31	17	100
AGV-2	Andesite	10	31	6.0	6.2	30	20	103
TILL-4	Till	10	34	5.5	4.3	30	13	113
STSD-2	Stream sed	10	44	5.7	8.5	43	19	102
GSP-2	Granodiorite	10	214	6.0	5.6	200	2.6	107
Ni ppm								
BCR-2	Basalt	10	11	1.6	2.0	10	18	110
GSP-2	Granodiorite	10	15	1.7	1.7	17	11	88
TILL-4	Till	10	16	1.6	1.0	17	6.4	94
AGV-2	Andesite	10	18	1.8	1.2	19	6.6	95
NBS-2711	Soil	10	21	1.7	1.1	21	5.4	100
STSD-2	Stream sed	10	59	2.5	1.8	53	3.1	111
BHVO-2	Basalt	10	122	4.1	4.9	119	4.0	103
Pb ppm								
BHVO-2	Basalt	10	3.9	0.9	0.5	NR	12	NA
BCR-2	Basalt	10	12	1.1	1.1	11	9.5	109
AGV-2	Andesite	10	14	1.0	0.8	13	5.3	108
GSP-2	Granodiorite	10	43	1.3	1.0	42	2.3	102
TILL-4	Till	10	52	1.4	1.2	50	2.3	104
STSD-2	Stream sed	10	75	1.6	1.7	66	2.2	114
NBS-2711	Soil	10	1147	5	4.3	1162	0.4	99
Rb ppm								
BHVO-2	Basalt	10	9.9	0.4	0.5	9.8	5.4	101
BCR-2	Basalt	10	49	0.7	1.4	48	2.9	102
AGV-2	Andesite	10	69	0.7	0.9	69	1.3	100
STSD-2	Stream sed	10	100	0.8	0.9	104	0.9	96
NBS-2711	Soil	10	114	0.8	1.0	110	0.9	104
TILL-4	Till	10	166	1.0	1.2	161	0.7	103
GSP-2	Granodiorite	10	245	1.2	1.4	245	0.6	100
Sb ppm								
BHVO-2	Basalt	10	<2	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<2	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<2	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<2	NA	NA	NR	NA	NA
TILL-4	Till	10	<2	NA	NA	1.0	NA	NA
STSD-2	Stream sed	10	3.7	0.2	0.3	4.8	9.2	77
NBS-2711	Soil	10	18	0.4	2.0	19	11	95
Se ppm								
BHVO-2	Basalt	10	<1	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<1	NA	NA	NR	NA	NA

Reference	Description	n	Mean	σ_N	s	pv	%RSD	%R
Se ppm								
BCR-2	Basalt	10	<1	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<1	NA	NA	NR	NA	NA
STSD-2	Stream sed	10	<1	NA	NA	NR	NA	NA
TILL-4	Till	10	1.2	.5	0.2	NR	14	NA
NBS-2711	Soil	10	1.4	0.7	0.3	1.5	24	93
Sn ppm								
AGV-2	Andesite	10	2.3	0.1	0.4	2.3	17	100
BHVO-2	Basalt	10	2.4	0.2	0.2	1.9	8.1	126
BCR-2	Basalt	10	2.6	0.2	0.4	NR	15	NA
STSD-2	Stream sed	10	3.4	0.2	0.2	5.0	6.6	68
NBS-2711	Soil	10	4.6	0.2	0.6	NR	14	NA
GSP-2	Granodiorite	10	6.8	0.2	0.7	NR	10	NA
TILL-4	Till	10	12	0.3	0.9	NR	7.1	NA
Sr ppm								
TILL-4	Till	10	115	0.7	1.2	109	1.0	106
NBS-2711	Soil	10	222	1.0	0.8	245	0.4	91
GSP-2	Granodiorite	10	238	1.1	10	240	4.2	99
BCR-2	Basalt	10	343	1.5	2.3	346	0.7	99
BHVO-2	Basalt	10	394	1.7	3.2	389	0.8	101
STSD-2	Stream sed	10	417	1.4	4.2	400	1.0	104
AGV-2	Andesite	10	654	1.9	5.7	658	0.9	99
Th ppm								
BHVO-2	Basalt	10	<4	NA	NA	1.2	NA	NA
AGV-2	Andesite	10	4.2	0.3	0.6	6.1	9.8	69
BCR-2	Basalt	10	4.6	0.3	0.7	6.2	11	74
NBS-2711	Soil	10	8.8	0.5	0.8	14	8.8	63
STSD-2	Stream sed	10	17	0.5	0.8	17	4.9	100
TILL-4	Till	10	23	0.8	0.7	17	3.3	135
GSP-2	Granodiorite	10	111	1.0	0.9	105	0.8	106
U ppm								
BHVO-2	Basalt	10	<4	NA	NA	NA	NA	NA
AGV-2	Andesite	10	<4	NA	NA	1.9	NA	NA
BCR-2	Basalt	10	<4	NA	NA	1.7	NA	NA
NBS-2711	Soil	10	4.6	1.4	0.6	2.6	14	177
GSP-2	Granodiorite	10	5.2	1.6	1.0	2.4	20	217
TILL-4	Till	10	6.0	1.6	0.7	5.0	12	120
STSD-2	Stream sed	10	18	1.4	1.1	19	6.4	95
V ppm								
GSP-2	Granodiorite	10	51	3.0	2.5	52	4.9	98
TILL-4	Till	10	67	2.7	3.3	67	4.9	100
NBS-2711	Soil	10	72	2.7	2.9	82	4.1	88
STSD-2	Stream sed	10	100	3.4	4.8	101	4.6	99
AGV-2	Andesite	10	109	3.9	12	120	11	91
BHVO-2	Basalt	10	308	7.8	5.7	317	1.5	97
BCR-2	Basalt	10	429	8.2	12	416	2.9	103

Reference	Description	n	Mean	σ_N	s	pv	%RSD	%R
W ppm								
BHVO-2	Basalt	10	<5	NA	NA	NR	NA	NA
AGV-2	Andesite	10	<5	NA	NA	NR	NA	NA
BCR-2	Basalt	10	<5	NA	NA	NR	NA	NA
GSP-2	Granodiorite	10	<5	NA	NA	NR	NA	NA
NBS-2711	Soil	10	<5	NA	NA	3.0	NA	NA
STSD-2	Stream sed	10	5.1	2.7	2.0	7.0	39	73
TILL-4	Till	10	190	4.6	5.9	204	3.1	93
Y ppm								
AGV-2	Andesite	10	20	0.5	0.6	20	3.2	100
NBS-2711	Soil	10	NR*	NA	NA	25	NA	NA
BHVO-2	Basalt	10	27	0.5	1.2	26	4.3	104
GSP-2	Granodiorite	10	27	0.7	0.7	28	2.7	96
TILL-4	Till	10	30	0.6	0.8	33	2.6	91
BCR-2	Basalt	10	41	0.6	3.6	37	8.9	111
STSD-2	Stream sed	10	37	0.6	0.6	37	1.5	100
Zn ppm								
TILL-4	Till	10	71	1.9	2.3	70	3.3	101
AGV-2	Andesite	10	91	2.1	2.1	86	2.4	106
BHVO-2	Basalt	10	106	2.6	6.0	103	5.8	103
GSP-2	Granodiorite	10	124	2.3	2.8	120	2.3	103
BCR-2	Basalt	10	129	2.8	2.6	127	2.0	102
STSD-2	Stream sed	10	260	3.3	4.0	246	1.5	106
NBS-2711	Soil	10	360	3.7	4.2	350	1.2	103
Zr ppm								
BHVO-2	Basalt	10	172	1.2	11	172	6.4	100
STSD-2	Stream sed	10	174	1.0	3.4	185	2.0	94
BCR-2	Basalt	10	187	1.2	1.2	188	0.6	99
AGV-2	Andesite	10	229	1.2	1.4	230	0.6	100
NBS-2711	Soil	10	267	1.0	1.9	230	0.7	116
TILL-4	Till	10	350	1.1	6.6	385	1.9	91
GSP-2	Granodiorite	10	541	1.5	7.6	550	1.4	98

* When Pb is greater than 500 ppm, Y is reported as "inf" or interference.

n = number of samples
pv = proposed value taken from published reference material compilation
BHVO-2, AGV-2, BCR-2, and GSP-2 (U. S. Geological Survey Certificates of Analysis)
TILL-4 (CCRMP, 1995)
STSD-2 (Lynch, 1990) and (Govindaraju, 1994)
NBS-1633a (Govindaraju, 1989)
σ_N = 1–sigma standard deviation in terms of accumulated count or the best standard deviation to be expected
s = 1-sigma standard deviation

See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Table 4.—Continued—Duplicate samples results

Duplicate samples	k	n	mean	s	%RSD	Concentration range	No. of < (total)	No. of < (pairs)
Antimony	13	2	10.3	0.37	3.59	2 to 33	28	13
Arsenic	18	2	153	3.47	2.26	3 to 1240	18	9
Barium	28	2	881	6.00	0.72	13 to 2510	0	0
Bromine	9	2	3.11	0.45	14.5	1 to 7	36	17
Cadmium	8	2	20.2	0.28	1.36	3 to 53	40	20
Cerium	27	2	79.5	1.98	2.50	9 to 442	1	0
Cesium	18	2	18.4	0.72	3.92	4 to 107	17	6
Chromium	26	2	243	3.50	1.44	7 to 2050	4	2
Copper	27	2	172	3.78	2.20	2 to 2960	2	1
Gallium	21	2	15.3	1.08	7.04	3 to 24	0	0
Lanthanum	26	2	51.2	1.29	2.52	11 to 203	3	1
Lead	26	2	332	1.24	0.37	5 to 5520	4	2
Molybdenum	24	2	18.2	1.89	10.4	1 to 230	5	1
Neodymium	25	2	48.1	4.00	8.33	12 to 213	5	2
Nickel	28	2	146	3.69	2.54	3 to 2220	0	0
Niobium	25	2	15.7	0.66	4.18	3 to 65	5	2
Rubidium	27	2	89.1	1.01	1.13	3 to 248	2	1
Selenium	10	2	25.5	0.30	1.18	1 to 141	36	18
Silver	8	2	7.96	0.31	3.87	1 to 34	39	19
Strontium	27	2	288	1.89	0.66	7 to 1360	2	1
Thorium	21	2	15.1	1.86	12.3	3 to 110	13	6
Tin	13	2	4.73	0.26	5.52	2 to 8	29	14
Uranium	22	2	9.47	0.93	9.85	2 to 48	10	4
Vanadium	28	2	205	3.53	1.72	6 to 2270	0	0
Yttrium	21	2	41.7	0.83	1.98	5 to 170	5	2
Zinc	28	2	540	4.77	.88	7 to 6820	0	0
Zirconium	27	2	218	6.41	2.94	12 to 543	2	1

Bibliography

Anderman, G., and Kemp, J.W., 1958, Scattered X-rays as internal standards in X-ray emission Spectroscopy: Analytical Chemistry, 30, 8, p. 1306-1309.

Arbogast, Belinda, F. *editor*, 1996, Analytical methods manual for the Mineral Resource Surveys Program, U.S. Geological Survey: U.S. Geological Survey Open File Report 96-525 248p.

Bertin, Eugene P., 1975, Principals and practice of X-ray spectrometric analysis: Plenum Press.

Canadian Certified Reference Materials Project, 1995, Certificate of Analysis, Till-1, Till-2 Till-3, and Till-4.

Govindaraju, K., 1989, 1989 Compilation of working values and sample description for 272 geostandards: Geostandards Newsletter, v. 8, Special Issue, 113p.

Govindaraju, K., 1994, 1994 Compilation of working values and sample description for 383 geostandards: Geostandards Newsletter, v. 18, Special Issue, 158p.

Johnson, R.G., 1984, Trace element analysis of silicates by means of energy-dispersive X-ray Spectrometry: X-ray Spectrometry, 13, p. 64-68.

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Johnson, R.G. and B.-S.L. King, 1987, Energy-dispersive X-ray fluorescence spectrometry, *in* Baedecker, P.A., Methods for geochemical analyses: U.S. Geological Survey Professional Paper 1770, P. F1-F5.

King, B.W., 1987, Determination of trace elements in eight Chinese stream sediment reference samples by Energy-dispersive X-ray spectrometry: Geostandards Newsletter, 11, p. 193-195.

National Institute of Standards & Technology, 1993, Montana Soil, 2711: Certificate of Analysis.

Taggart, Joseph E., Jr., Lindsey, J.R., Scott, B.A., Vivit, D.V., Bartel, A.J., and Stewart, K.C., 1987, Analysis of geologic materials by wavelength-dispersive X-ray fluorescence spectrometry, *in* Baedecker, P.A., Methods for geochemical analyses: U.S. Geological Survey Professional Paper 1770, P. E1-E19.

U.S. Geological Survey, 1998, Andesite, AGV-2: Certificate of Analysis (Preliminary).

U.S. Geological Survey, 1998, Basalt, Columbia River, BCR-2: Certificate of Analysis.

U.S. Geological Survey, 1998, Basalt, Hawaiian Volcanic Observatory, BHVO-2: Certificate of Analysis.

U.S. Geological Survey, 1998, Granodiorite, Silver Plume, Colorado, GSP-2: Certificate of Analysis.

Wilson, S., 2000, U.S. Geological Survey analysis of DGPM-2, KRS1-5, KRS-12, KRS3-5, KRS6-5.