

U.S. GEOLOGICAL SURVEY CIRCULAR 996



A Modification of the U. S. Geological Survey
One-Sixth Order Semiquantitative
Spectrographic Method for the
Analysis of Geologic Materials that
Improves Limits of Determination of some
Volatile to Moderately Volatile Elements

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By David E. Detra and Elmo F. Cooley

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A MODIFICATION OF THE U.S. GEOLOGICAL SURVEY ONE-SIXTH ORDER SEMIQUANTITATIVE SPECTROGRAPHIC METHOD FOR THE ANALYSIS OF GEOLOGIC MATERIALS THAT IMPROVES LIMITS OF DETERMINATION OF SOME VOLATILE TO MODERATELY VOLATILE ELEMENTS

By David E. Detra and Elmo F. Cooley

ABSTRACT

A modification of the one-sixth order semiquantitative emission spectrographic method for the analysis of 30 elements in geologic materials (Grimes and Marranzino 1968) improves the limits of determination of some volatile to moderately volatile elements. The modification uses a compound-pendulum-mounted filter to regulate the amount of emitted light passing into the spectrograph. One hundred percent transmission of emitted light is allowed during the initial 20 seconds of the burn, then continually reduced to 40 percent over the next 32 seconds using the pendulum-mounted filter, and followed by an additional 68 seconds of burn time. The reduction of light transmission during the latter part of the burn decreases spectral background and the line emission of less volatile elements commonly responsible for problem-causing interferences. The sensitivity of the method for some geochemically important trace elements commonly determined in mineral exploration (Ag, As, Au, Be, Bi, Cd, Cr, Cu, Pb, Sb, Sn, and Zn) is improved up to five-fold under ideal conditions without compromising precision or accuracy

INTRODUCTION

The semiquantitative emission spectrographic method for the analysis of 30 elements in geologic materials described by Grimes and Marranzino (1968) has been used almost exclusively by the U.S. Geological Survey over the last decade to provide a foundation for the assessment of mineral resource potential of Federal lands. A modification of the method increasing the sensitivity for trace elements provides a broader data base which will allow the geochemist to make more comprehensive geochemical interpretations without supplemental acid dissolution and solvent extractions of samples analyzed by atomic absorption spectroscopy. Data generated using the modification allow the geochemist to make interpretations with greater confidence at low element concentration levels.

The use of a compound-pendulum-mounted filter adapted to the existing instrumentation (Jarrell-Ash¹ 1.5-m optical-emission spectrograph, D.C.-Arc) increases the sensitivity of the method for 12 elements (Ag, As, Au, Be, Bi, Cd, Cr, Cu, Pb, Sb, Sn, and Zn), while the sensitivity of only one element (W) is comprised and the sensitivity for the remaining 17 elements is unchanged. Ideal operating conditions are required to obtain the best results. Therefore, production rates are less than those that can be anticipated using the method described by Grimes and Marranzino, limiting the utility of the adaption to specific research requiring better sensitivity

INSTRUMENTATION ADAPTATION

The modification uses a compound pendulum-mounted filter to regulate the amount of emitted light passing into the spectrograph. A compound pendulum is defined as any friction damped "real" pendulum having a mass distributed over its entire body, a calculable center of gravity.

The pendulum used in the modification has an aluminum arm with an adjustable brass counterweight. The arm is attached to a Teflon hub, and the hub of the pendulum is mounted on a 6-in. rod extending out from an aluminum base which is attached directly onto the arc stand (fig. 1). To maintain frictional consistency over time, a Teflon sleeve is placed on the rod on which the Teflon hub rotates. A 97° arc of 8-in. radius is attached to the end of the aluminum pendulum in such a way that the arc extends 48.5° on each side of the attachment point. A 1-in. filter is centered on the 0°

¹Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS

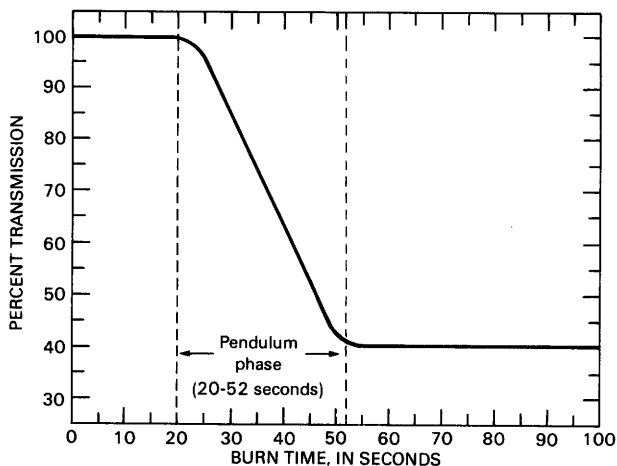


FIGURE 1.—Compound-pendulum-mounted filter modification for the optical-emission spectrograph.

position of the arc so that the emitted light path is centered vertically on the filter. A series of three 100-percent transmission ports and four 0-percent transmission spokes extend outward on both sides from the 0° position of the arc. This configuration allows for smooth, continuous filtering transition of emitted light. The filter is made from a section of exposed film (Kodak SA-1)¹ providing for 40-percent transmission of light above 270.0 nanometers (nm). The pendulum is set in a horizontal position at the start of each burn and held in place by a low-voltage plunger solenoid which is wired to a timer and is automatically activated 20 seconds after the arc is struck, releasing the pendulum. Listed below are the instrumentation and analytical parameters used in the development of the modification.

Spectrograph: 1.5-m Wadsworth-mounted Jarrell-Ash, equipped with a 15,000 lines/in. (590 grooves/mm) lined grating blazed for 310.0 nm, providing for a dispersion of 5.45 angstroms/mm over a spectral range of 210.0 nm to 480.0 nm in the second order, slit width of 10 micrometers.

Source: Direct-current 220 volts with maximum arc current of 13 amperes

Electrodes:

Upper: preformed 1/8-in. diameter with 8° taper (UltraCarbon 5001)

Lower: preformed graphite 1/4-in. diameter, crater wall thickness of 0.04 in., crater diameter of 0.144 in., and crater depth of 0.313 in. (UltraCarbon 7075)

Film: 35-mm Spectrum Analysis No. 1 (SA-1) emulsion, processed with D-19 Kodak developer for 2.5 minutes at 20°C, fixed for 3 minutes, rinsed in cold water and air dried

Arc parameters:

Electrode gap: 4 mm

Exposure: 120 seconds

0–20 seconds at 100-percent transmission

20–52 seconds transition from 100-percent transmission to 40 percent transmission

52–120 seconds at 40-percent transmission for wavelengths of 270.0 nm and above

52–120 seconds at 0-percent transmission for wavelengths below 270.0 nm

Current: Initial excitation of 6 amperes increased to 13 amperes immediately

MODIFIED METHOD

The method allows for 100-percent transmission of light for the initial 20 seconds of the burn. During these initial 20 seconds, the majority of the 12 elements (Ag, As, Au, Be, Bi, Cd, Cr, Cu, Pb, Sb, Sn, and Zn) are volatilized. After 20 seconds have elapsed, a solenoid releases the pendulum-mounted filter from a horizontal position, so that it swings freely through the light path with an average period of 0.80 seconds. As the volatile elements are consumed during the 32-second pendulum phase, the distillation of the elements into the arc decreases, and the refractory elements begin to volatilize more rapidly. When the pendulum has stopped, all emitted light is filtered to 40-percent transmittance for the remaining 68 seconds of the burn. During the last phase of the burn, when the 40-percent filter is in place, the majority of the refractory elements are volatilized. Since the free-swinging compound-pendulum bob passes through the optical-emission light path with a decreasing amplitude, it provides for a transitional period of 32 seconds in which the emitted light will be filtered from 100- to 40-percent transmission (fig. 2). Therefore, the period the filter is in the light path increases with time as a function of the decreasing amplitude of the pendulum. The resulting smooth, continuous increase in filtration as expressed by the curve in figure 2 is aided by the configuration of the pendulum bob. Without the transmission ports and spokes on the bob extensions, the curve would be relatively flat over the first 20 seconds and extremely steep over the last 10 seconds of the pendulum phase.

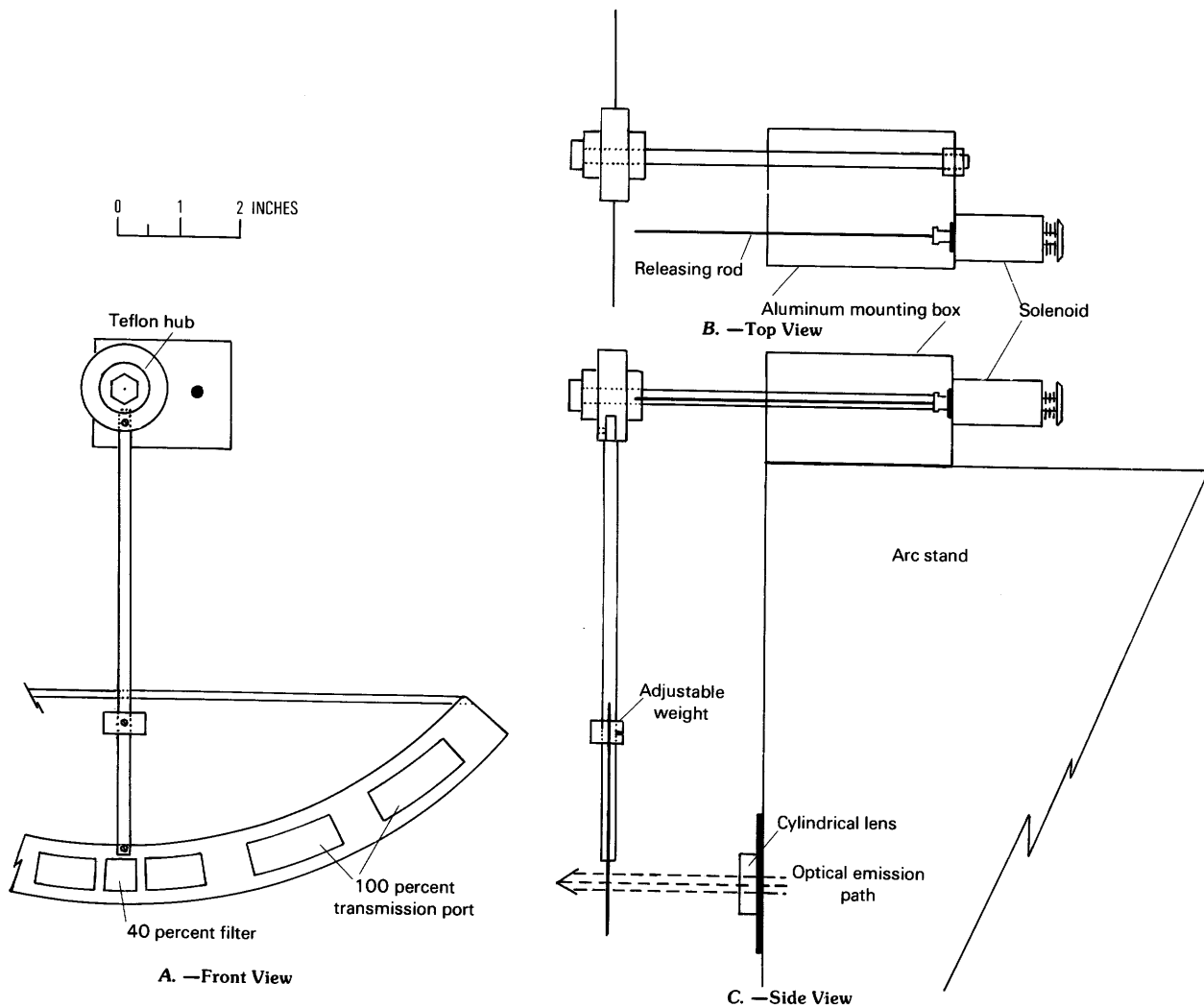


FIGURE 2.—Transitional transmission curve. (Percent transmission was calculated by exposing the spectrographic film to a constant UV light source for continuous 10-second intervals. Three densitometric readings were taken for each 10-second interval and averaged.)

The effect of the modification is an increase in sensitivity of the method for the 12 elements: Ag, As, Au, Be, Bi, Ca, Cr, Cu, Pb, Sn, and Zn by a factor of up to 5 (table 1) while the sensitivity of tungsten decreased as a direct response to the filtering process.

DISCUSSION

Geologic materials have complex and variable matrices. Refractory elements which commonly make up the matrices of these geologic materials cause difficulty in the interpretation of the resulting spectrum by producing line interferences on the volatile-element emission lines. In addition, large

changes in matrix composition of samples can cause changes in line intensities in the spectrum. These variations in composition characteristically cause changes in arc temperatures and the distillation rates of specific elements into the arc. Thus, the change in percent transmittance from 100 to 40 percent must be a gradual transition (fig. 2) rather than a single or multistep transition. This transition helps reduce the effects of matrix variations by providing a relatively long period of time compared to the total burn over which the change in transmittance takes place, and yet, it still produces the desired effects of increasing sensitivity of specific elements while maintaining a good line-to-background ratio.

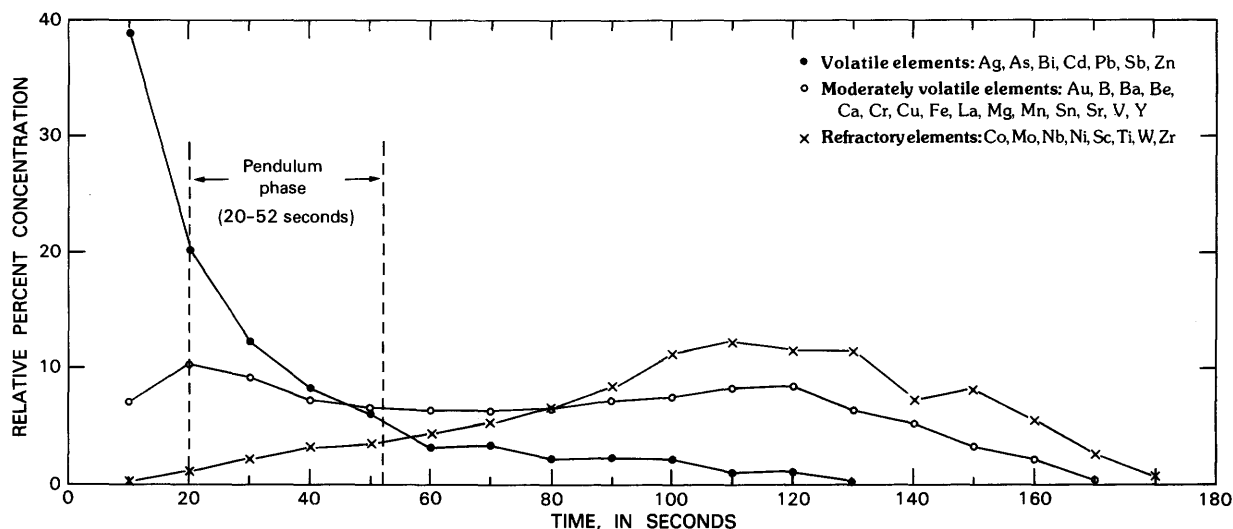


FIGURE 3.—Selective volatilization curves for 30 elements in GSE standard from the USGS Trace Element glass standards (Filter conditions: 100% transmission for 180 seconds.)

TABLE 1.—Lower limits of determination for unmodified and pendulum methods

Element	Grimes and Marranzino, (1968) (parts per million)	Filtered pendulum modification (parts per million)
Ag	0.5	0.1
As	200	50
Au	10	2
Be	1	.5
Bi	10	2
Cd	20	5
Cr	10	2
Cu	5	1
Pb	10	2
Sb	100	20
Sn	10	5
W	50	100
Zn	200	50

In order to better understand and effectively eliminate or reduce interference problems, selective volatilization rates (SVRs) have been studied for the 30 elements analyzed routinely in geologic samples. The U.S. Geological Survey Trace Element Glass Standards sample, GSE, was utilized because its uniform concentration range for the major elements is comparable to silicate matrices found in the natural environment.

The SVRs of each of the selected elements in the standard were determined by racking the camera at 10-second intervals during a 180-second excita-

tion period. The 30-element semiquantitative spectrographic method (Grimes and Marranzino, 1968) was used to determine the emission concentration for each element at each 10-second interval, and the value was recorded. From these data the 30 elements were grouped into three subsets: volatile, moderately volatile, or refractory. The emission concentrations for all elements within each subset were added for each 10-second interval, and the resulting values were then changed to relative percent concentration, which was rounded to the nearest whole percent. Plots of selective volatilization rates for the three subsets were calculated and are shown in figure 3.

The visual determination of line intensity is accurate to within ± 30 percent of the correct value (Ahrens and Taylor, 1961). This accuracy is adequate for the intended purpose of the SVRs in demonstrating general volatilization rates of volatile and refractory elements. We compared visual determination versus densitometric readings for several elements and found the visual determinations were accurate within the limits set forth by Ahrens and Taylor (1961).

The spectrographic conditions under which the SVRs in figure 3 were determined are shown in table 2. However, 100-percent transmission was used for the entire 180-second burn. It was determined from the SVRs that the most effective filtering design is one in which the pendulum phase ends approximately at the intersect point of the volatile and refractory curves.

TABLE 2.—Description of USGS GXR Reference Samples and USGS Trace-Element Glass Standards

Geochemical Exploration Reference Samples	
Standard designation	Description and source
GXR-1	Jasperoid: Drum Mountains, Utah
GXR-2	Soil: Park City, Utah
GXR-3	Fe-Mn-W-rich Hot Spring Deposit: Humboldt County, Nevada
GXR-4	Porphyry Copper Mill Heads: Utah
GXR-5	Soil (B zone): Somerset County, Maine
GXR-6	Soil (B zone): Davidson County, North Carolina

USGS Trace-Element Glass Standards	
Standard designation	Additive element concentration
GSB	0.5 ppm
GSC	5.0 ppm
GSD	50 ppm
GSE	500 ppm

Approximate matrix composition:

SiO ₂ - 62%	CaO - 5%
Al ₂ O ₃ - 14%	Na ₂ O - 4%
Fe ₂ O ₃ - 7%	K ₂ O - 4%
Mgo - 4%	H ₂ O - ?

Additive elements:

Ti	B	Ce	Eu	La	Pb	Rh	Ta	W	F
Mn	Ba	Cs	Gc	Li	Pd	Sb	Te	Y	
Ag	Be	Co	Hf	Mo	Pt	Sc	Tl	Zn	
As	Bi	Cr	In	Nb	Rb	Sn	U	Zr	
Au	Cd	Cu	Ir	Ni	Rc	Sr	V	Cl	

ANALYSES AND RESULTS

The pendulum method was used to analyze two different sets of reference samples with each analysis being replicated 10 times. The reference materials included the Geochemical Exploration Reference samples (GXR 1-6), which consist of six rock and soil samples representing the broad range

of matrices found in geologic materials, and four USGS Trace-Element Glass Standards synthetically produced by Corning Glass Works, which are composed of approximately 0.5, 5.0, 50, and 500 parts per million of 46 additive elements (table 2). The resulting reference material spectra were compared to spectra for the six-step prepared standards (Grimes and Marranzino, 1968). Results reported on table 3

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards

[Results listed by element showing sample designation, range, median, mean, relative standard deviation (RSD) (reported as percent), and accepted value. Values reported in parts per million (ppm) except Fe, Mg, Ca, and Ti which are reported in percent. Accepted values for GXR Reference samples obtained from Gladney (1980) except for Nb, Sn, and Y whose values were obtained from Allcott and Lakin (1978) and Ag, Au, Bi, and Cd whose values were obtained from Viets (1978). Accepted values for the USGS Trace-Element Glass Standards were obtained from Myers and others (1976). An L indicates the element was detected but below the level of determination. The symbol N or < specifies the element was not detected. When an L was used in calculating the median, mean, and RSD, it was given a real value equal to the next lower reporting interval below the value of the lower limit of determination for that element.]

Sample	Range	Median	Mean	RSD	Accepted value
Fe%					
GXR-1	G20	G20	G20	0.00	24.7 ± 1.8
GXR-2	3- 5	3	3.8	25.78	1.9 ± .23
GXR-3	20	20	20	0	18.6 ± 1.8
GXR-4	3- 5	5	4.8	12.50	2.97 ± .43
GXR-5	5- 7	5	5.4	14.81	3.19 ± .29
GXR-6	7-15	10	9.3	25.47	5.58 ± .42
GSB	5- 7	5	5.8	16.89	
GSC	2- 7	5	5.7	27.23	
GSD	5- 7	5	5.4	14.81	
GSE	3- 7	5	5.4	22.22	
Mg%					
GXR-1	.2 - .3	.3	.29	10.34	.21 ± .01
GXR-2	1 - 2	2	1.80	18.43	.88 ± .05
GXR-3	.7 - 2	1.5	1.52	30.41	.64 ± .05
GXR-4	2 - 3	2	2.4	20.41	1.65 ± .05
GXR-5	1.5 - 2	2	1.95	7.69	1.22 ± .05
GXR-6	1 - 2	1.5	1.55	17.37	.65 ± .04
GSB	2 - 3	3	2.9	10.34	
GSC	2 - 3	3	2.9	10.34	
GSD	3	3	3.0	0	
GSE	3	3	3.0	0	

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Ca%					
GXR-1	1 - 1.5	1	1.05	14.29	.87 ± .08
GXR-2	1	1	.97	9.28	.82 ± .04
GXR-3	7 -10	10	9.1	15.11	14.1 ± .6
GXR-4	1	1	1	0	.9 ± .05
GXR-5	.5 - .7	.5	.58	16.89	.75 ± .06
GXR-6	.07- .15	.01	.099	20.92	.095 ± .01
GSB	3 - 5	4	4.0	25.00	
GSC	2 - 5	3	3.5	29.28	
GSD	2 - 3	3	2.9	10.34	
GSE	3	3	3	0	
Ti%					
GXR-1	.02 -.05	.03	.033	27.27	.06 ± .005
GXR-2	.2 -.5	.3	.34	32.75	.28 ± .03
GXR-3	.05 -.1	.07	.071	16.00	.10 ± .02
GXR-4	.15 -.3	.2	.21	23.33	.26 ± .03
GXR-5	.15 -.2	.2	.195	7.69	.21 ± .03
GXR-6	.3 -.15	.5	.48	22.44	.5 ± .04
GSB	L(.022)-.002	L(.002)	.0016	12.5	.0006
GSC	L(.002)	L(.002)	L(.002)	0	.0011
GSD	.005 -.01	.007	.0072	22.22	.0044
GSE	.03 -.05	.05	.048	12.50	.049

are identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, etc., but are reported arbitrarily as midpoints of

these brackets, 1., 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, etc. Precision and accuracy of the pendulum method are best demonstrated in table 3, which presents

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Ag					
GXR-1	30 - 50	30	38	25.78	32.6
GXR-2	20	20	20	0	17.4
GXR-3	N(.1)	N(.1)	N(.1)	0	.06
GXR-4	2	2	2	0	3.6
GXR-5	.5 - 1	1	.89	19.75	.82
GXR-6	.1 - .2	.2	.19	15.79	.29
GSB	.5 - 1	.5	.55	27.20	.5
GSC	5	5	5	0	4
GSD	50	50	50	0	37
GSE	500	500	500	0	380
As					
GXR-1	300 -500	300	380	25.78	460 ± 30
GXR-2	N(50)	N(50)	N(50)	0	31 ± 5
GXR-3	2,000	2,000	2,000	0	4,000 ± 450
GXR-4	100	100	100	0	98 ± 10
GXR-5	N(50)	N(50)	N(50)	0	12 ± 3
GXR-6	300	300	290	10.34	340 ± 30
GSB	N(50)	N(50)	N(50)	0	.3
GSC	N(50)	N(50)	N(50)	0	6
GSD	N(50)	N(50)	N(50)	0	42
GSE	300	300	300	0	450

the range of the 10 replicate analyses for each element, the mean value, median value, percent relative standard deviation (RSD), and the accepted

value of that element for the particular reference material. A general indication of accuracy can be obtained by comparing the median and mean

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Au					
GXR-1	L(2)	L(2)	L(2)	0.00	3.7
GXR-2	N(2)	N(2)	N(2)	0	.05
GXR-3	N(2)	N(2)	N(2)	0	.06
GXR-4	N(2)	N(2)	N(2)	0	.60
GXR-5	N(2)	N(2)	N(2)	0	<.05
GXR-6	N(2)	N(2)	N(2)	0	.1
GSB	N(2)	N(2)	N(2)	0	.1
GSC	N(2)	N(2)	N(2)	0	1.2
GSD	10	10	10	0	14
GSE	30-50	30	32	18.75	50
B					
GXR-1	20-30	20	21	14.28	15.3 ± .5
GXR-2	100	100	100	0	44 ± 1
GXR-3	200	200	200	0	180 ± 20
GXR-4	10	10	10	0	4.3 ± .4
GXR-5	50	50	50	0	25 ± 2
GXR-6	10-20	20	17	26.96	11 ± 1
GSB	50	50	50	0	18
GSC	50	50	50	0	20
GSD	70	70	70	0	50
GSE	500	500	500	0	500

values from the replicate analyses to the accepted values. Even though it is not acceptable to make a statistical comparison between quantitative and

semiquantitative data that are reported as interval midpoints, a visual comparison will show excellent agreement between the experimental

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Ba					
GXR-1	700-1,000	1,000	970	9.28	560 ± 120
GXR-2	1,500-3,000	2,000	2,050	17.07	2,000 ± 400
GXR-3	5,000	5,000	5,000	0	4,700 ± 800
GXR-4	1,500-2,000	1,500	1,550	9.68	1,350 ± 330
GXR-5	1,500-2,000	2,000	1,900	10.52	1,800 ± 500
GXR-6	1,000-2,000	1,500	1,550	17.37	1,100 ± 300
GSB	30- 50	40	40	25.00	31
GSC	20- 50	50	43	25.58	39
GSD	70- 150	100	102	17.97	90
GSE	500	500	500	0	500
Be					
GXR-1	1 - 2	1.5	1.65	19.40	1.12 ± .17
GXR-2	1 - 2	1.5	1.55	22.58	1.64 ± .09
GXR-3	30 -100	50	55	27.27	26 ± 1
GXR-4	2	2	2	0	2.1 ± .2
GXR-5	.5 - 1	1	.84	24.51	1.19 ± .16
GXR-6	.7 - 1	1	.97	9.28	1.1 ± .1
GSB	N(.5)	N(.5)	N(.5)	0	--
GSC	5	5	5	0	3.5
GSD	30 - 50	50	46.0	17.39	44
GSE	500	500	500	0	500

values and the acceptable values. Specific attention is drawn to the test studies of Ag, Bi, Cd, Sb, and Zn in table 4 where the accepted value in a reference sample is at the stated limit of determination and the pendulum method is detecting the elements at these low levels with excellent precision.

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Bi					
GXR-1	1,500-2,000	2,000	1,800	18.43	1725
GXR-2	N(2)-L(2)	L(2)	--	--	.4
GXR-3	N(2)	N(2)	N(2)	0	<.2
GXR-4	20- 30	20	21	14.29	21.2
GXR-5	N(2)	N(2)	N(2)	0	.4
GXR-6	N(2)	N(2)	N(2)	0	.2
GSB	N(2)	N(2)	N(2)	0	
GSC	5	5	5	0	
GSD	50	50	50	0	
GSE	500	500	500	0	
Cd					
GXR-1	N(5)	N(5)	N(5)	0	3.0
GXR-2	L(5)- 7	4	4.2	31.59	3.9
GXR-3	N(5)	N(5)	N(5)	0	.4
GXR-4	N(5)	N(5)	N(5)	0	.3
GXR-5	N(5)	N(5)	N(5)	0	.14
GXR-6	N(5)	N(5)	N(5)	0	.11
GSB	N(5)	N(5)	N(5)	0	--
GSC	5	5	5	0	3
GSD	50- 70	50	56.0	16.37	30
GSE	500	500	500	0	420

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Co					
GXR-1	10	10	10	0.00	9.3 ± 1.1
GXR-2	10- 20	15	16.5	19.40	9 ± 2
GXR-3	30-100	85	75	35.40	48 ± 5
GXR-4	15- 20	20	18	13.61	16 ± 2
GXR-5	30- 70	50	50	17.89	30 ± 5
GXR-6	15- 50	17.5	22.5	47.92	14 ± 3
GSB	N(5)	N(5)	N(5)	0	2
GSC	5- 10	10	9.5	15.79	6
GSD	30- 50	30	38	25.78	35
GSE	300-500	500	480	12.50	450
Cr					
GXR-1	10- 15	10	10.5	14.29	10 ± 2
GXR-2	50	50	50	0	37 ± 10
GXR-3	10- 15	10	10.5	14.29	19 ± 1
GXR-4	50- 70	70	68	8.82	64 ± 10
GXR-5	100	100	100	0	100 ± 5
GXR-6	70-100	70	76	15.79	96 ± 10
GSB	5- 7	5	5.2	11.54	3
GSC	5- 10	7	8.3	34.52	7
GSD	50	50	50	0	47
GSE	500	500	500	0	490

The precision of the method is also shown by the relative standard deviations (RSD) in table 4. The RSDs obtained range in magnitude from 0 to 77

percent with an average of 9.85 percent. Commonly acceptable RSDs for the semiquantitative emission spectrographic method range from 10 to

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Cu					
GXR-1	1,000-1,500	1,000	1,050	14.28	1,300 ± 100
GXR-2	100- 150	150	145	10.34	69 ± 2
GXR-3	10- 20	17.5	17	19.51	10.8 ± 0.8
GXR-4	5,000-7,000	7,000	6,800	8.82	6,500 ± 200
GXR-5	300- 500	300	340	23.53	360 ± 20
GXR-6	100- 150	100	110	18.18	105 ± 12
GSB	3- 5	5	4.2	23.33	5
GSC	5- 10	7	7.1	15.99	9
GSD	50- 70	50	54.0	14.81	45
GSE	300- 500	500	480	12.50	500
La					
GXR-1	L(20)	L(20)	L(20)	0	6.1 ± .3
GXR-2	L(20)	L(20)	L(20)	0	25 ± 1
GXR-3	L(20)	L(20)	L(20)	0	8.5 ± 1
GXR-4	70- 100	70	82	17.92	64 ± 5
GXR-5	50	50	50	0	18 ± 4
GXR-6	L(20)	L(20)	L(20)	0	14 ± 2
GSB	L(20)	L(20)	L(20)	0	--
GSC	L(20)	L(20)	L(20)	0	5
GSD	50	50	50	0	47
GSE	500	500	500	0	550

30 percent (Mosier, 1972). Of the 10 RSDs greater than 30 percent, 5 can be attributed to analyses of nickel and cobalt. These two elements show less

precision because of the poor background-to-line ratios on the upper end of the spectrum where the nickel and cobalt lines that were used are located

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Mn					
GXR-1	700-1,000	1,000	970	9.28	--
GXR-2	1,000-1,500	1,500	1,300	18.84	960 ± 100
GXR-3	65,000	65,000	65,000	0	22,300 ± 2,000
GXR-4	150- 300	200	215	27.61	140 ± 20
GXR-5	200- 500	300	330	35.98	280 ± 20
GXR-6	1,000	1,000	1,000	0	1,000 ± 50
GSB	200- 300	200	210	14.29	190
GSC	200	200	200	0	200
GSD	200- 300	200	210	14.29	210
GSE	700	700	700	0	600
Mo					
GXR-1	L(5)	L(5)	L(5)	0.00	10 ± 2
GXR-2	N(5)- 10	N(5)	--	--	1.5 ± .5
GXR-3	N(5)-L(5)	L(5)	--	--	<6
GXR-4	200-300	300	260	18.84	310 ± 25
GXR-5	30- 50	40	40	25.00	30 ± 4
GXR-6	N(5)- 20	N(5)	--	--	1.7 ± .4
GSB	N(5)	N(5)	N(5)	0	2
GSC	L(5)- 7	5	5.2	20.71	6
GSD	50	50	50.0	0	46
GSE	300-500	500	480	12.50	500

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Nb					
GXR-1	L(20)	L(20)	L(20)	0	<10
GXR-2	L(20)	L(20)	L(20)	0	<10
GXR-3	L(20)- 20	20	18	13.61	<20
GXR-4	L(20)	L(20)	L(20)	0	<20
GXR-5	L(20)	L(20)	L(20)	0	<10
GXR-6	L(20)	L(20)	L(20)	0	<10
GSB	L(20)	L(20)	L(20)	0	--
GSC	L(20)	L(20)	L(20)	0	5
GSD	20	20	20	0	40
GSE	100-150	150	145	10.34	500
Ni					
GXR-1	20- 30	20	24	20.41	42 ± 10
GXR-2	20- 50	20	25	36.88	18 ± 3
GXR-3	30- 70	50	46	26.09	55 ± 5
GXR-4	30- 70	50	46	26.09	38 ± 4
GXR-5	50- 150	70	76	40.43	63 ± 7
GXR-6	15- 100	20	33	77.61	22 ± 4
GSB	10- 15	10	11.0	18.18	14
GSC	10- 15	15	13.5	16.97	18
GSD	50	50	50	0	55
GSE	500	500	500	0	500

(Ni, 341.4 nm; Co, 345.3 nm). To help improve the spectrum at the high end, a glass plate, which provided an additional 10 to 15 percent light filtration below 400.0 nm, was placed in the light path

between the grating and the spectrum film, as close to the film as possible. The plate was positioned in such a way that it covered the wavelengths of light between 340.0 nm and 350.0 nm.

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Pb					
GXR-1	300- 500	400	400	25.00	670 ± 20
GXR-2	700-1,000	1,000	880	16.70	615 ± 15
GXR-3	10- 20	10	13	30.77	15 ± 2
GXR-4	50- 70	70	64	14.32	
GXR-5	20	20	20	0	22 ± 2
GXR-6	100	100	100	0	110 ± 10
GSB	10- 15	15	14.5	10.34	13
GSC	10- 15	15	13.5	16.97	15
GSD	50- 70	50	56.0	16.37	52
GSE	300- 500	500	460	17.39	500
Sb					
GXR-1	100-150	100	105	14.29	124 ± 6
GXR-2	50	50	50	0	48 ± 5
GXR-3	20- 30	30	26	18.84	40 ± 3
GXR-4	L(20)-N(20)	N(20)	--	--	4.4 ± .8
GXR-5	N(20)	N(20)	N(20)	0	2 ± 1
GXR-6	N(20)	N(20)	N(20)	0	3.8 ± .7
GSB	N(20)	N(20)	N(20)	0	--
GSC	N(20)	N(20)	N(20)	0	--
GSD	30	30	30	0	37
GSE	500	500	500	0	470

CONCLUSIONS

Semiquantitative analytical data for some volatile to moderately volatile elements used in the

assessment of mineral resource potential in regional geochemical exploration study areas can be improved by utilizing a modification to the one-sixth order semiquantitative emission spectrographic

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Sc					
GXR-1	L(5)	L(5)	L(5)	0	1.7 ± .1
GXR-2	7- 10	10	9.4	12.77	6.8 ± .2
GXR-3	20- 30	20	23	19.92	18 ± 1
GXR-4	10- 15	10	10.5	14.29	8.3 ± .4
GXR-5	10	10	10	0	7.8 ± .4
GXR-6	20- 50	20	26	35.25	31 ± 1
GSB	N(5)	N(5)	N(5)	0	--
GSC	N(5)	N(5)	N(5)	0	--
GSD	N(5)	N(5)	N(5)	0	3
GSE	20- 30	20	22	18.18	30
Sn					
GXR-1	50	50	50	0.00	63
GXR-2	N(5)	N(5)	N(5)	0	<(10)
GXR-3	N(5)	N(5)	N(5)	0	<(10)
GXR-4	15- 20	15	17	14.41	<(10)
GXR-5	N(5)	N(5)	N(5)	0	<(10)
GXR-6	N(5)	N(5)	N(5)	0	<(10)
GSB	N(5)	N(5)	N(5)	0	.6
GSC	5	5	5	0	5
GSD	50	50	50	0	43
GSE	500	500	500	0	440

method described by Grimes and Marranzino (1968). The modification uses a compound-pendulum-mounted filter to provide a transitional change for the filtering of emitted light from 100

to 40 percent over 32 seconds after the initial 20 seconds of the burn at 100 percent. Filtering more light during the latter part of the burn improves the sensitivity of the method for 12 trace elements

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Sr					
GXR-1	500-700	700	660	12.12	280 ± 60
GXR-2	100-150	100	105	14.29	160 ± 23
GXR-3	1,000	1,000	1,000	0	1,140 ± 100
GXR-4	200-300	200	210	14.29	220 ± 30
GXR-5	100	100	100	0	120 ± 20
GXR-6	N(100)	N(100)	N(100)	0	42 ± 9
GSB	N(100)	N(100)	N(100)	0	26
GSC	N(100)	N(100)	N(100)	0	27
GSD	N(100)	N(100)	N(100)	0	64
GSE	500	500	500	0	500
V					
GXR-1	70- 100	85	88	16.70	88 ± 9
GXR-2	50- 100	70	74	19.30	57 ± 20
GXR-3	30- 50	30	32	18.75	39 ± 10
GXR-4	70- 100	100	97	9.28	92 ± 15
GXR-5	50- 70	70	66	12.12	60 ± 20
GXR-6	150- 200	200	180	13.61	180 ± 20
GSB	L(10)	L(10)	L(10)	0	2
GSC	L(10)	L(10)	L(10)	0	6
GSD	50	50	50	0	45
GSE	500	500	500	0	500

commonly used in mineral exploration by reducing spectral background and the line emission of elements commonly responsible for problem-

causing interferences without compromising precision and accuracy. Using this modification greatly reduces the capacity of the method in terms of

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
W					
GXR-1	L(100)- 100	1(100)	76	15.79	
GXR-2	N(100)	N(100)	N(100)	0	1.8 ± .2
GXR-3	10,000-G10,000	10,000	10,500	14.29	10,800 ± 600
GXR-4	N(100)-L(100)	N(100)	--	--	28 ± 5
GXR-5	N(100)	N(100)	N(100)	0	.5 ± .2
GXR-6	N(100)	N(100)	N(100)	0	.88 ± .18
GSB	N(100)	N(100)	N(100)	0	--
GSC	N(100)	N(100)	N(100)	0	--
GSD	N(100)	N(100)	N(100)	0	50
GSE	150	150	150	0	420
Y					
GXR-1	30- 70	50	48	22.44	57 ± 11
GXR-2	15- 30	20	21.5	20.93	16 ± 1
GXR-3	20- 30	30	26	18.84	16 ± 2
GXR-4	10- 15	15	13	18.84	12 ± 3
GXR-5	10- 20	15	14.5	18.57	16 ± 3
GXR-6	15- 30	15	18	25.46	14 ± 3
GSB	N(10)	N(10)	N(10)	0	4
GSC	N(10)	N(10)	N(10)	0	8
GSD	50	50	50	0	46
GSE	500	500	500	0	490

TABLE 3.—Results from 10 replicate analyses of 30 elements of the USGS GXR Reference Samples and USGS Trace-Element Glass Standards—Continued

Sample	Range	Median	Mean	RSD	Accepted value
Zn					
GXR-1	1,000	1,000	1,000	0	740 ± 110
GXR-2	500-1,000	850	830	21.59	500 ± 60
GXR-3	150- 200	200	180	13.61	220 ± 70
GXR-4	100	100	100	0	64 ± 10
GXR-5	50	50	50	0	50 ± 5
GXR-6	100	100	100	0	120 ± 20
GSB	N(50)	N(50)	N(50)	0	3
GSC	N(50)	N(50)	N(50)	0	12
GSD	50	50	50	0	43
GSE	500	500	500	0	500
Zr					
GXR-1	20	20	20	0.00	66 ± 20
GXR-2	150-300	200	225	22.77	200 ± 40
GXR-3	30- 50	50	44	20.83	<200
GXR-4	150-200	150	165	13.89	200 ± 40
GXR-5	150-200	150	165	13.89	140 ± 20
GXR-6	70-200	100	116	36.21	106 ± 8
GSB	N(10)	N(10)	N(10)	0	4
GSC	N(10)	N(10)	N(10)	0	6
GSD	50	50	50	0	48
GSE	300-500	500	460	17.39	480

TABLE 4.—Analytical lines and sensitivities

Element	Lines used (nm)	Limit of determination (ppm)
Ag	328.068	0.1
	338.280	.5
As	286.045	50
	278.020	50
Au	267.595	2
B	249.773	10
Ba	455.404	20
Be	313.042	.5
Bi	312.107	2
Cd	3221	5
	326.106	5
Co	345.351	5
Cr	425.435	2
	284.325	10
Cu	327.396	1
Fe	305.909	<50
La	333.749	50
Mg	278.142	<200
Mn	293.930	10
	307.027	
Mo	317.035	5
	319.397	10
Nb	316.340	20
	319.498	20
Ni	341.477	5
Pb	366.347	5
	283.307	2

TABLE 4.—Analytical lines and sensitivities—Continued

Element	Lines used (nm)	Limit of determination (ppm)
Sb	259.806	50
	287.792	20
Sn	317.502	5
Sc	335.373	5
Sr	346.446	100
Ti	316.852	20
V	345.344	10
W	294.738	100
	324.228	10
Y	332.788	10
	330.259	50
Zn	334.502	50
	327.926	10
Zr	339.198	10

sample throughput. However, this study should provide a basis for the design of an automated mechanism allowing for greater production.

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