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X-ray Fluorescence Determination of Chromium, Gallium, Niobium, Lead, Rubidium, Strontium, Yttrium, Zinc and Zirconium in Rocks

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Abstract

Nine trace elements were determined with high accuracy by the proposed x-ray fluorescence method. Pellets were prepared by taking 1.5 g of powdered rock sample, and mixed with 1.5 g of panorak, a plastic binder. The mixture was filled in an aluminium ring and pressed between two steel plates at 1850 kg/cm². Matrix effect was eliminated by using the background as an internal standard for most elements. The method is satisfactorily applied to the variety of standard rocks.

1. Introduction

For the determination of trace elements in silicates, spectrophotometric and other chemical methods are used conventionally, but the chemical procedure is time-consuming in general. Atomic absorption method is relatively sensitive and accurate, but the sensitivity for gallium, niobium, yttrium and zirconium is not so high as to apply the method to common rock samples.

X-ray fluorescence method has high sensitivity for the above mentioned elements, and the analytical procedure is rather simple. HATTORI and SHIBATA (1969), FAIRBAIRN and HURLEY (1971) demonstrated the advantages of the method for the determination of rubidium and strontium in rocks. FABBI (1971), FABBI and ESPOS (1972) applied the method to analyses of barium, strontium, arsenic, antimony, nickel, rubidium, scandium, vanadium and zinc. MURAD (1973) described different correction techniques for matrix effects in trace elements analyses.

In this study, chromium, gallium, niobium, lead, rubidium, strontium, yttrium, zinc and zirconium in standard rocks were determined after some examinations in the preparation of sample and standard, and correction of spectral interference and matrix effects.

2. Experimental

2.1 Apparatus and Reagents

The instrument used is the Toshiba AFC-202 F automatic x-ray fluorescence spectrograph with a rhodium target tube. The instrument parameters in this work are given

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Table 1 Instrument parameters for Toshiba AFC-202 F spectrometer of this study.

Elements	Crystal	Line	Angle		Pulse height analyser		
			Peak	Background	Gain	Upper	Lower
Cr	LiF	Kα	69.35°	71.00°	0.17	700	300
Ga	LiF	Kα	38.90°	39.80°	0.77	700	200
Nb	LiF	Kα	21.43°	21.75°	1.00	800	300
Pb	LiF	Lβ	28.23°	29.50°	1.00	800	300
Rb	LiF	Kα	26.62°	27.30°	1.00	800	300
Sr	LiF	Kα	25.14°	25.85°	1.00	800	300
Y	LiF	Kα	23.80°	24.50°	1.00	700	300
Zn	LiF	Kα	41.81°	42.50°	1.00	800	300
Zr	LiF	Kα	22.58°	23.30°	1.00	700	300

(Rh tube, 40Kv, 30mA, Fine collimeter, Scintillation counter)

in Table 1.

Panorak BA-223 (a powdered plastic binder), silicon oxide (SiO_2), iron oxide (Fe_2O_3), potassium chromate (K_2CrO_4), gallium oxide (Ga_2O_3), niobium oxide (Nb_2O_5), strontium carbonate ($SrCO_3$), zinc oxide (ZnO) and zirconyl nitrate ($ZrO(NO_3)_2 \cdot 2H_2O$) were used for making synthetic standard samples.

2.2 Procedure

Few papers described the way of sample preparation in trace elements analyses (HATTORI and SHIBATA, 1969; FABBI, 1971; MURAD, 1973). HATTORI and SHIBATA (1969) used a powdered plastic binder. Their method is simple and the procedure is more rapid than those proposed in other papers, so the method of HATTORI and SHIBATA (1969) was adopted in this work. Although the details of the sample preparation were described in their original paper, the outline is given below.

Take out 1.5 g of finely ground rock sample (under 200 mesh) in a 10 ml mixing bottle and add 1.5 g of panorak, shake the bottle for 15 min using the spex 8000 mixer mill. Fill the mixture in a ϕ 35 mm aluminium ring and press between two steel plates at around 1850 kg/cm².

Calibration curves were prepared using USGS standard rocks GSP-1 and PCC-1 for lead, GSP-1 and DTS-1 for rubidium, and DTS-1 and BCR-1 for yttrium. For the other elements, such as zirconium, chromium, gallium, niobium, strontium and zinc, reagent materials were mixed with powders consisting of 85% silicon oxide and 15% iron oxide. The outline of the procedure for zirconium is described below as an example.

Prepare a 5% zirconium standard material by taking 1.465 g of zirconyl nitrate and 8.535 g of silicon oxide into an agate sample mill and grind for about 30 minutes. Dilute the 5% zirconium standard material with silicon oxide and make a 0.5% zirconium standard material. Take out 0.015, 0.030, 0.060, 0.090, 0.120, 0.150 and 0.300 g of the 0.5% zirconium standard material into seven mixing bottles. After adding 0.15 g of iron oxide to each of the bottles, adjust the total weight of the mixture to 1.5 g with silicon oxide. Add 1.5 g of the panorak and make a pellet.

Irradiate samples for 80 seconds, count both peak intensity and background intensity

and subtract background from the peak intensity. Relate the net intensity of each element for all samples and standards to appropriate calibration curves. Make corrections for matrix effects when necessary.

3. Results and Discussion

3.1 Correction for spectral interference

Several important x-ray lines cannot be completely separated from neighbouring lines. Prominent examples are the coincidence of Zr Kα with Sr Kβ and of Y Kα with Rb Kβ (Figure 1). If one of these lines is to be used for the determination of an element,
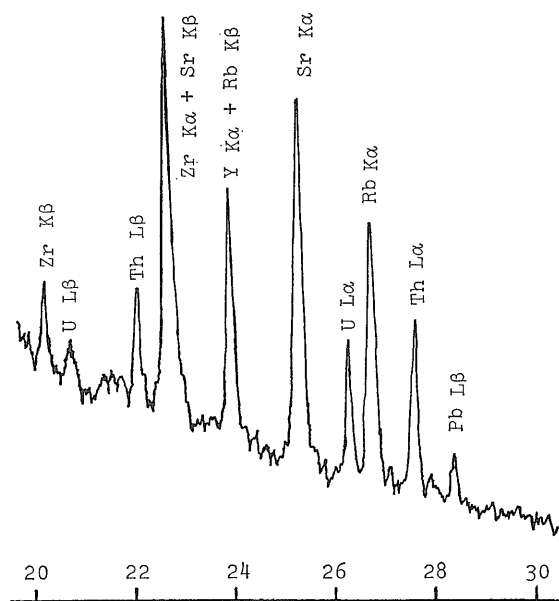

Fig. 1 Qualitative analysis of SY-2 syenite.

a correction for the interfering peak is essential. In this study, the zirconium and yttrium values were corrected by the strontium and rubidium content of the samples, respectively. In the determination of lead, the Pb Lβ line was used to avoid the interference of As Kα over Pb Lα line. Nb Kα line is interfered by various lines of yttrium, uranium and thorium, if their amounts are more than about 200 ppm. The interferences could not be corrected easily.

3.2 Correction for matrix effects

Matrix effects may depend upon i) the intensity of x-ray emission on the grain size of the sample, ii) the orientation of the mineral grains, iii) absorption or enhancement of the radiation by other elements, and iv) the mineral species in which the element is

bounded. The proposed methods for correction of matrix effects can be divided into four major categories.

1. Dilution or fusion procedures with or without a heavy absorber.

2. Addition of known amounts of the investigated element to the sample.

3. Internal standard procedures, (a) addition of a suitable element or use of an element of known concentration in the sample, (b) use of a scattered tube line or of the background radiation as an internal standard.

4. Computation of correction factors on the basis of mass absorption or empirically determined coefficients.

MURAD (1973) made ditail investigations on the correction method. His recommendation on routine works is to use the internal standard procedure: Cr Kα and W Lα from the scattered tube line for chromium and zinc, respectively, and the background radiation for rubidium, strontium, zirconium, barium and lead.

To use the background as an internal standard for correction of matrix effects was first described by ANDERMANN and KEMP (1958). The theoretical consideration and its application to geochemical materials were reported in several papers (KALMAN and HELLER, 1962; PRICE and ANGELL, 1968; FAIRBAIRN and HURLEY, 1971, and TANAKA et al., 1972). The correction method is the simplest and no further measurements are required other than those essential to determine the net peaks of the elements.

Table 2   X-ray fluorescence determination of chromium, gallium, niobium, lead, rubidium,

	Cr		Ga		Nb		Pb	
	XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.
USGS								
G-2 Granite	6	7	24	22.9	11	13.5	29	31.2
GSP-1 Granodiorite	11	12.5	23	22	25	29	[b]	51.3[b]
AGV-1 Andesite	10	12.2	20	20.5	14	15	35	35.1
PCC-1 Peridotite	2990	2730	<3	0.4	<3	<2	[b]	13.3[b]
DTS-1 Dunite	4060	4000	<3	0.2	<3	<3	12	14.2
BCR-1 Basalt	19	17.6	22	20	13	13.5	16	17.6
CSRM								
MRG-1 Gabbro	416		16		20		7	
SY-2 Syenite	6		28		—		75	
SY-3 Syenite	4		27		—		126	
NIM								
NIM-D Dunite	3210	2900	<3	<3	<3	3	<5	<10
NIM-G Granite	10	12	31	32	53	50	35	38
NIM-L Lujavrite	8	20	45	55	1020	980	42	45
NIM-N Norite	33	40	16	19	<3	2	<5	<10
NIM-P Pyroxenite	24150[a]		6	13	<3	3	<5	<10
NIM-S Syenite	10	13	13	11	<3	3	<5	13
GSJ								
JG-1 Granodiorite	51	50	20	20	13		25	24
JB-1 Basalt	415	417	19	17	33		14	14

XRF: Average of this study (n=5), Ref.: Values reported by FLANAGAN (1973)
   a: Determined after diluting with SiO_2 and Fe_2O_3.   b: Samples used as calibration standard.
   c: ANDO et al. (1974).

In this study, the appropriate measurement was made by subtracting scattered background intensity from peak intensity and working curves were constructed based on the relationship:

$$\text{Concentration (ppm)} \propto \frac{(\text{Peak I.} - \text{Background I.})}{\text{Background I.}}$$

The background correction method is not well applicable to light elements ($\sim$chromium) and high content ($\sim$1%) elements. Therefore, chromium was not corrected by the background method. Zirconium in NIM-L lujavrite, and chromium in NIM-P pyroxenite were expected to be high in concentration and determined after diluting to one per ten with silicon oxide and iron oxide.

3.3 Analytical results

The results of this study and recommended values by FLANAGAN (1973) for zirconium in selected standard rocks are shown in Figure 2. The values corrected by both the Sr Kβ and the background agree with those of the recommended values.

Analytical results of this study on seventeen standard rock samples and some reference values for chromium, gallium, niobium, lead, rubidium, strontium, yttrium, zinc and zirconium are given in Table 2. The results for all the elements approximate to the reference values. The limit of detection for lead is 5 ppm, and for other elements are

strontium, yttrium, zinc and zirconium in ppm of standard rocks and some reference values.

| Rb		Sr		Y		Zn		Zr	
XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.	XRF	Ref.
173	168	483	479	10	12	84	85	304	300
b	254[b]	240	233	29	30.4	101	98	515	500
71	67	655	657	21	21.3	79	84	234	225
<3	0.06	<3	0.41	<3	<5	41	36	<3	7
b	0.05[b]	<3	0.35	b	0.05[b]	39	45	<3	3
49	46.6	323	330	b	37.1[b]	108	120	189	190
9		256		15		180		101	
217		278		144		238		290	
196		303		745		224		325	
<3	<3	<3	5	<3		80	90	3	50
327	274	11	13	159	100	51	60	288	300
190	183	4473	4480	41	30	388	320	11900[a]	
6	9	266	254	9	7	55	80	14	25
4	4	36	40	5		94	100	13	20
538	550	67	76	<3	<5	9	21	18	30
182	185.5	185	184	31	30.8[c]	39	36	109	111[c]
42	41	427	438	24	25.5[c]	75	83	141	153[c]
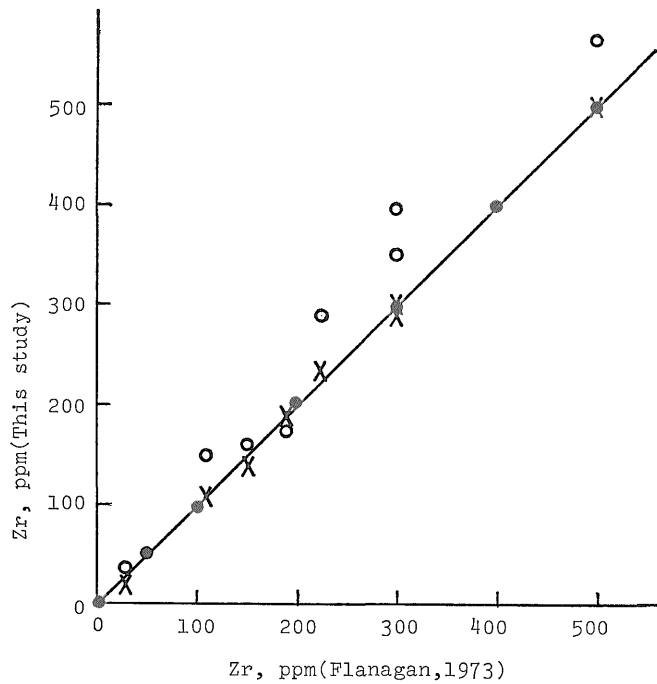
Fig. 2 Comparison of results for zirconium in selected standard rocks.
Open circle—uncorrected
Cross—corrected
Solid circle-synthetic calibration standard

3 ppm at the 2 σ confidence level. The method is proved to be very rapid and allows to determine nine elements in ten samples per day.

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けい光 X 線分析法による岩石中の Cr, Ga, Nb, Pb, Rb, Sr, Y, Zn, Zr の定量

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要　旨

けい光 X 線分析法による岩石中の微量成分の定量における近接線の干渉およびマトリックスの影響の補正方法，検量線の作製などについて検討し，定量法を確立した．

粉末試料 1.5 g とパノラック 1.5 g をプラスチック容器にはかりとり，約 15 分間振動混合する．アルミニウムリングを用い，全圧約 21 トンで加圧成型し，ペレットを作製した．検量線は，鉛，ルビジウム，イットリウムについては含有量既知の試料を，その他の成分については純試薬を用いて合成した試料を用いて作製した．

イットリウムについてはルビジウム，ジルコニウムについてはストロンチウムの Kβ 線の重なりを差引き，また，クロムを除くすべての成分についてバックグラウンドによるマトリックスの補正方法を適用することにより，各種標準岩石中のクロム，ガリウム，鉛，ルビジウム，ストロンチウム，イットリウム，亜鉛，ジルコニウムが良好な精度で定量できた．検出限界は鉛 5 ppm，その他の成分 3 ppm で，一日に 10 試料中 9 成分の定量が可能である．