

Application of X-Ray Fluorescence Spectrometry to the Analysis of Geochemical Prospecting Samples in China

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The application of x-ray fluorescence analysis to multi-element determination in geochemical prospecting samples has been discussed in this paper. It consists of seven parts: introduction; sample preparation; instrument and analytical conditions; standardization and standardized sample; matrix effect correction; correction of spectral overlap; and conclusion.

INTRODUCTION

The application of x-ray fluorescence analysis (XRFA) to multi-element determinations in geochemical prospecting samples has the advantage of simple sample preparation, rapid analysis, good reproducibility and low cost. It has already proved an effective means for the multi-element analysis of geochemical samples and has been widely used in China and elsewhere.¹⁻⁷ According to the detection limits attained for elemental analysis in XRFA, the elements analysed for a regional geochemical survey in China at present include Na, Mg, Al, Si, P, K, Ca, Ti, Cr, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Sn, Ba, La, Ce, Pb, Th and U (30 elements); 25 min are required for each sample analysis. This is about half the time needed for the analysis of 22 elements published in the literature.⁶ Regarding sample preparation, a pressed-powder pellet in a bed of low-pressure polyethylene is more practical and more effective than a pressed-powder pellet with corn powder as the adhesive.⁶ For the determination of major elements, influence coefficients or theoretical coefficients are used for the correction of matrix effects. For the determination of trace elements (Zr, Y, Sr, Rb, etc.), Compton scattering is used as the internal standard for these corrections. The detection limits, precision and accuracy are satisfactory.

SAMPLE PREPARATION

In regional geochemical surveys, a large number of samples must be analyzed for many elements. Therefore, a simple, rapid sample preparation method, with reasonable cost and low detection limits, is necessary. The pressed-powder pellet method meets this requirement.

The sample should be ground to 200 mesh prior to pelleting. In this method, either adding a portion of adhesive to the sample and mixing well to make the pressed pellet or preparation in a bed of adhesive is adequate.

Mixing with adhesive

Owing to the poor binding behaviour of rock powders, it is difficult to make a compact pellet by simply pressing the powder; folding, layering and splitting will make the analysis difficult. Therefore, mixing a dried and accurately weighed sample with the appropriate adhesive is necessary.

Pellet pressed in a bed of adhesive

This method has been reported in the literature,⁸ in many cases using boric acid. However, boric acid is successful in producing a stable pellet in only about 80% of the preparations. Fabbi⁹ discussed the problem of contamination of the instrument and suggested the use of chromatographic-grade or methane-cellulose. Lichtfuss *et al.*¹⁰ used paraffin whereas Zyi *et al.*¹¹ adopted a mixture of paraffin and styrene. Chai *et al.*³ used methane-cellulose M20 and M450, to which a fixed amount of paraffin was added. They found that (1) the amount of paraffin must be sufficient or the pellet will not hold together, but (2) too much paraffin makes the pellet difficult to remove from the mould, decreasing the efficiency of the sample preparation; (3) the pressed pellet is not stable and breaks easily; (4) M450 is better than M20, producing a more compact pellet; (5) methane-cellulose is more hygroscopic than boric acid, so the pellet absorbs moisture easily and can be distorted and even broken; (6) the time of vacuum pumping is long, particularly at high humidity, often

approaching 1 h, thus decreasing the working efficiency dramatically; and (7) moisture in the spectrometer causes hydrolytic decomposition of some analysing crystals. When using starch as the adhesive, it is difficult to remove the pellet from the mould and the compactness of the compressed pellet is poor; when stored in the atmosphere, the specimen frequently separates from the bed owing to its hygroscopic nature, and it is impossible to make measurements.

Low-pressure polyethylene is an ideal adhesive, being composed of only carbon and hydrogen. It is a small-grain white powder, and does not contaminate the instrument. The pellet is more compact, less hygroscopic and requires less time for vacuum pumping. For drainage sediments and soil samples, the success rate for sample preparation is 100%; for rock samples it is above 90%. The pressed pellet can be preserved for a long period without distortion. Moreover, the cost of the reagent is low.

INSTRUMENT AND ANALYTICAL CONDITIONS

Chai *et al.*³ carried out the determination of 24 elements in geochemical prospecting samples using the empirical coefficient and the Compton scattering methods for correction of the matrix effects; good results were obtained. Chen⁵ determined 30 major and minor elements in geological samples using empirical coefficients. Dong *et al.*² accomplished the determination of 19 trace elements in geochemical prospecting samples and Yang *et al.*¹ carried out the XRFA of 25 major and minor elements in rocks. The particular feature of their analytical procedure was to use LiF (200) as the analysing crystal and adopt $2\theta = 19^\circ$ (scattered intensity) as the background (for Sr, Rb, Zr, Nb, Y, etc., the background is 0.2–0.3 at the peak value). With the Lucas-Tooth and Pye equation, it enables $Z < 15$ and $Z > 15$ elements to be corrected for matrix effects by Rh $L\alpha$, Rh $K\alpha$ Compton-scattered and Fe $K\alpha$ intensities, respectively (for Sr, Rb, Zr, Y and Nb, the Rh Compton intensity is used as the internal standard).

Li *et al.*⁴ analysed drainage sediments for 25 major and trace elements. In their procedure, they used the Rh $K\alpha$ Compton-scattered intensity as the internal standard for correction of inter-element matrix effects for elements with wavelengths shorter than the Fe K absorption edge. For samples with high concentrations of Fe and Ca, it is necessary to correct for Fe and Ca interferences. For other elements, matrix effects were corrected using empirical coefficients based on the matrix elemental correction sequence calculated by Plesch discrimination.¹² The analytical methods adopted in this work are commonly used spectral measuring methods in China, as listed in Table 1.

STANDARDIZATION AND STANDARDIZED SAMPLE

In order to overcome the influence of instrumental drift, it is necessary to make drift corrections, either by the

relative intensity method or by the intensity correction method. Both methods require standardized samples.

Relative intensity method

When analysing a standard sample, the ratio of the intensity of the analytical line of the standard sample to that of a standardized specimen is calculated. The relative intensity of the analytical line is used for the calibration graph or for further calculations. When analysing an unknown specimen, the standardized specimen is also analysed simultaneously in order to obtain the relative intensity for the unknown specimen, so that the content of the element of interest can be determined.

Intensity correction method

When analysing a standard sample, a standardized specimen is also measured. The intensity of the analytical line of the element to be analysed in the standardized specimen is given as I_s and is stored on a computer disk. The absolute intensity of the standard sample is used to construct the calibration graph, or for further calculations. When analysing an unknown specimen, the standardized specimen is also analysed. The intensity of the analytical line of the element to be measured in the standardized specimen is I_m , and the intensity calibration coefficient is $\alpha = I_s/I_m$. The intensity from the unknown specimen is multiplied by the calibration coefficient α , giving the calibrated intensity. Hence it can be seen that the standardized specimen must contain all the elements to be determined, and all the interfering elements. Each element should be present at a high enough concentration to minimize counting errors. Further, the physical and chemical properties of the standardized specimen must be stable.

MATRIX EFFECT CORRECTION

The calibration graph constant of each element and the inter-element matrix effect coefficient (and also the spectrum overlap correction coefficient, see below) can be obtained by regression analysis of standard samples. Therefore, the standard samples utilized must have accurate analytical (chemical) data. The range of concentrations of each element in the standard samples must match that of the samples to be analysed. The distribution of the concentration of each element in the standard samples should be independent of each other, i.e. there should be a random distribution. Table 2 shows the concentration range of the various elements in 50 natural standard samples, including GSD 1–12, GSR 1–6, GSS 1–8 and some secondary standards. This set of standards can meet the requirements for the concentration range for the determination of drainage sediments and rocks. Table 3 lists the elements analysed, overlapping spectra and influence elements.

For the analysis of major elements (Na_2O , MgO , Al_2O_3 , SiO_2 , K_2O , CaO and Fe_2O_3) and minor elements (P, Ti, Mn, V, Cr, La and Ba), the inter-element

Table 1. Analytical conditions

Element or oxide	Spectral line	Crystal	Detector	Collimator	Absorber	Pulse- height analyser	2θ angle		Counting time (s)	
							Spectral line	Back- ground	Spectral line	Back- ground
Na ₂ O	Kα	TAP	F-PC	C	1	100-350	55.11	58.00	40	20
MgO	Kα	TAP	F-PC	C	1	100-350	45.17	48.00	20	10
Al ₂ O ₃	Kα	PE	F-PC	C	1	100-350	144.65		10	
SiO ₂	Kα	InSb	F-PC	F	2	100-350	144.54		10	
K ₂ O	Kα	PE	F-PC	C	1	100-350	50.60		10	
CaO	Kα	LiF200	F-PC	F	1	90-180	113.08		10	
Fe ₂ O ₃	Kα	LiF200	Sc	F	1	100-350	57.51		10	
P	Kα	Ge	F-PC	C	1	100-350	140.93	143.50	20	10
Ti	Kα	LiF200	Sc	C	1	100-350	86.13	85.00	20	10
V	Kα	LiF200	F-PC	C	1	90-180	76.92	80.60	20	10
Cr	Kα	LiF200	F-PC	C	1	90-180	69.32	70.50	20	10
Mn	Kα	LiF200	Sc	C	1	100-350	62.98	64.50	20	10
Mn	Kα	LiF220	Sc	C	1	100-350	95.22	96.50	20	10
Co	Kα	LiF200	F-PC	C	1	90-180	52.76	55.50	20	20
Ni	Kα	LiF200	Sc	C	1	100-300	48.65	49.65	20	20
Cu	Kα	LiF200	Sc	C	1	100-350	45.02	47.00	20	20
Zn	Kα	LiF200	Sc	C	1	100-350	41.79	42.79	20	10
Ga	Kα	LiF200	Sc	C	1	100-300	38.91	39.60	20	10
As	Kα	LiF200	Sc	C	1	100-300	34.00	34.70	20	10
Rb	Kα	LiF200	Sc	C	1	100-300	26.59	29.70	20	10
Sr	Kα	LiF200	Sc	C	1	100-300	25.14	29.70	20	10
Y	Kα	LiF200	Sc	C	1	100-300	23.79	24.50	20	10
Zr	Kα	LiF200	Sc	C	1	100-300	22.54	23.20	20	10
Nb	Kα	LiF200	Sc	C	1	100-300	21.39	23.20	20	10
Sn	Kα	LiF200	Sc	C	1	100-300	14.03	13.20	40	10
								14.90		
Ba	Kα	LiF200	Sc	C	1	100-300	11.01	9.98	20	10
								11.90		10
Ba	Lα ₁	LiF200	F-PC	C	1	90-180	87.16	88.50	20	20
Ba	Lβ ₁	LiF200	F-PC	C	1	90-180	73.29	74.40	60	30
La	Lα ₁	LiF200	F-PC	C	1	90-180	82.90	84.50	20	20
Ce	Lα ₁	LiF200	F-PC	C	1	90-180	79.02	80.50	20	20
Pb	Lβ ₁	LiF200	Sc	C	1	100-300	28.24	29.70	20	20
Th	Lα ₁	LiF200	Sc	C	1	100-300	27.45	29.70	20	20
U	Lα ₁	LiF200	Sc	C	1	100-300	26.14	29.70	20	20
Rh-R		LiF200	Sc	C	1	100-350	17.56		20	
Rh-C		LiF200	Sc	C	1	100-350	18.43		20	
Bi	Lα ₁	LiF200	Sc	C	1	100-300	33.01	34.70	20	20

matrix effects can be corrected using influence coefficients, obtained by performing regression analysis on the 50 standard samples, using the equations

$$X_k = a_k I^2 + b_k I + c_k \tag{1}$$

$$W_i = X_i \left(1 + K + \sum_j A_{ij} F_j + \sum_j B_{ij} F_j + \sum_{jk} D_{ij} K F_j F_k + C_i \right) \tag{2}$$

where
 X_k and X_i are the uncorrected concentrations of the elements to be analysed;
 I is the x-ray intensity (or internal standard ratio);
 a_k , b_k and c_k are the correction curve constants (the subscript k is the divisional mark for the calibration graphs);
 W_i is the corrected concentration of element i ;
 F_j and F_k are the concentrations of the concomitant elements (or the x-ray intensity);
 K , A , B , C and D are correction constants.
Based on Plesch discrimination,¹² preliminary influ-

ence coefficients are chosen and substituted in turn in Eqn (2). A_{ij} is calculated by regression, W_i is then calculated for each A_{ij} , and the residual standard deviation is used to measure the result of the inter-element effect to

Table 2. Range of contents of various elements in standard samples

Component	Content range	Component	Content range
Na ₂ O	0.043-4.49 (%)	Rb	2-490
MgO	0.11-33.61 (%)	Sr	25.4-1090
Al ₂ O ₃	1.73-29.22 (%)	Y	4.6-67
SiO ₂	15.56-90.34 (%)	Zr	64-490
K ₂ O	0.12-5.19 (%)	Nb	3.1-95
CaO	0.089-35.69 (%)	Ba	120-3340
Fe ₂ O ₃	0.96-18.84 (%)	La	13.4-606
P	67-4140 (ppm)	Pb	5.8-640
Ti	420-20100 (ppm)	Th	2.7-70
Mn	175-2500 (ppm)	Zn	20.72-745
Co	2.6-99 (ppm)	Cr	7.6-3243
Ni	2.7-2138 (ppm)	V	16.5-574
Cu	3.1-1230 (ppm)		

Table 3. Elements analysed, overlap spectra and influence elements

Element analysed	Analytical line	Overlap spectra	Influence elements
Na	K α		Mg, Al, Si, K, Ca, Ti, Fe
Mg	K α		Na, Al, Si, K, Ti, Fe, Ca
Al	K α		Na, Mg, Si, Ca, Fe
Si	K α		Na, Mg, Al, Si, K, Ca, Fe
P	K α		Na, Mg, Al, Si, K, Ca, Fe
K	K α		Na, Mg, Al, Si, K, Ca, Fe
Ca	K α		Na, Mg, Al, Si, K, Ca, Fe
Mn	K α	Cr K β_1	Ti, Fe, Ca
Ti	K α	Ba L α_1	Al, Si, K, Ca, Fe
Fe	K α		Mg, Al, K, Ca, Fe
Ba	L α_1		Na, Al, Si, Ca, Fe
Cr	K α	V K β_1	Ca, Fe
V	K α	Ti K β_1	Fe, Ca
Co	K α	Fe K β_1	Si, Al, Mg, Ca
La	L α_1		Mg, Al, Si, Ca, Fe
Cu	K α		Fe, Ca
Ni	K α	Y K α II, Rb K β_1 II	Fe, Ca
Zn	K α		
Y	K α	Rb K β_1	Fe, Ca
Th	L α_1	Bi L β_1	Fe, Ca
Bi	L α_1		
Zr	K α	Sr K β_1	Fe, Ca
Sr	K α		
Nb	K α	Y K β_1	
Pb	L β_1		
Rb	K α		
As	K α	Pb L α_1	
U	L α_1	Rb K α	Fe, Ca

be corrected by each coefficient:

$$\sigma_d^2 = \frac{\sum_{i=1}^n (C_{cal} - C_{chem})^2}{n - m}$$

(3)

where

C_{cal} and C_{chem} are the calculated concentration and recommended value of element i in the standard sample;

n is the number of standard samples;

m is the number of calculated coefficients.

The influence coefficient for the correction of the inter-element effect is chosen to be that for which the influence element of σ_d is minimized.

The analysis of trace elements utilizes the scattered line internal standard method for the correction of matrix effects. For a wavelength of the analytical line shorter than the Fe K absorption edge, i.e. Nb, Zr, Y, Sr, Th, Pb, Zn, Ga, As, Cu, Ni, etc., the Compton- or Rayleigh-scattered Rh K α (from the x-ray tube target) is used as an internal standard. If the contents of Fe and Ca vary significantly, the empirical coefficient method should be adopted for the correction of Fe and Ca.

CORRECTION OF SPECTRAL OVERLAP

The following two methods can be used to correct for spectral overlap.

Intensity correction method

First, measure the total net intensities of the element to be analysed (I_i) and the interfering element (j) in a series of standard samples at the 2θ angle for the element to be analysed. Then, measure the net intensity of a non-interference line of element j (I_j). From the equation

$$X_i = AI_i^2 + BI_i + C + \sum B_{ij}I_j$$

(4)

regression analysis permits the calibration graph constants A , B and C and the overlap coefficient B_{ij} to be obtained.

Concentration correction method

First, using a standard sample without any interfering element, construct the calibration graph. Then, measure the total net intensity I_i of the element to be analysed and the interfering element j in a series of standard samples at the 2θ angle for the element of interest. From the calibration graph without the interfering element, the concentration X_i of the element analysed prior to overlap correction can be determined. From the equation

$$W_i = X_i + \sum B_{ij}W_j$$

(5)

where W_i and W_j are the concentrations of the element to be analysed and the interfering element, the overlap coefficient B_{ij} can be obtained by regression. When using the scattered line internal standard method for

correction of the matrix effect, this approach is more convenient. When using the influence coefficient method, the calibration graph for artificial standard samples without interfering elements is used to combine with Eqn (2). Utilizing the multi-element standard sample with regression, the overlap coefficient B_{ij} and the inter-element coefficient α_{ij} are obtained simultaneously.

Measurement of the intensity

The prepared sample pellets are placed in the automatic sample changer; the analytical conditions are set and the computer software chooses the necessary coefficients. When the intensities are measured, the computer calculates automatically the background subtraction, the interference subtraction, the matrix correction, etc., according to the quantitative program stored in the memory, and prints out the results. After a batch of samples have been measured, an analytical report of various element concentrations will be printed out according to the form compiled.

Detection limit, precision and accuracy

Based on the measuring time of each element in Table 1 and Eqn (5), Table 4 lists the detection limits of various elements and the detection-limit requirements for regional geochemical prospecting. The detection limit is calculated according to the standard equation

$$C_{DL} = \frac{3}{m} \sqrt{\frac{I_b}{T}}$$
 (6)

where m is the counting rate, I_b is the background counting rate and T is the total counting time.

The data in Table 4 show that the detection limits for most elements are better than required for regional geochemical prospecting. However, the detection limits for Co, Cu, As and U do not meet those requirements; therefore, this method is only useful for those samples in which the concentrations of those elements are relatively high.

Twenty specimen pellets of the same sample were prepared and measured according to the analytical conditions in Table 1. Statistical analysis of the results is shown in Table 5, where it can be seen that the relative standard deviation of all elements is generally within 10%, and mostly better than 5%, i.e. similar to data published elsewhere.

In the multi-element XRFA of 1:200 000 regional geochemical prospecting samples, usually a batch of 50 samples are analysed; four different provincial-grade standard samples are analysed with a secret code for each batch. For each 1:200 000 map, national first-grade standard samples are analysed four times, and each time eight (GSD 1-8) standard samples are included. The logarithmic deviations of the determined value and recommended value are calculated. The quality of analysis is controlled by the requirements listed in Table 6.

Table 4. Detection limits in multi-element analysis of regional geochemical survey samples

Element or oxide	Measuring time (s)	Detection limit (ppm)	Approximate requirement for the detection limits in geochemical prospecting samples (ppm)
Na ₂ O	60	100	
MgO	30	53	
Al ₂ O ₃	10	52	
SiO ₂	10	178	
K ₂ O	10	21	
CaO	10	21	
Fe ₂ O ₃	10	22	
P	30	5.1	100
Ti	30	12.3	100
V	30	3.6	10
Cr	30	3.3	10-20
Mn	30	4.8	10
Co	40	2.3	1
Ni	40	2.5	5-10
Cu	40	2.2	1
Zn	30	2.0	10
Ga	30	2.0	
As	30	1.6	1
Rb	30	1.3	
Sr	30	1.2	5-50
Y	30	1.1	10
Zr	30	1.1	10
Nb	30	1.0	5
Sn	60	5.2	1-3
Ba	40	18.6	50
La	40	12.5	30
Ce	40	11.7	
Pb	40	3.4	1-10
Th	40	3.7	4
U	40	3.3	1

Table 5. Twenty replicate sample preparations and reproducibility of determinations

Element or oxide	Average value of determinations (n = 20)	Standard deviation	Coefficient of variation (%)
Na ₂ O (%)	1.75	0.041	2.34
MgO (%)	1.55	0.023	1.48
Al ₂ O ₃ (%)	12.74	0.098	0.77
SiO ₂ (%)	57.32	0.247	0.43
K ₂ O (%)	2.49	0.008	0.32
CaO (%)	2.28	0.007	0.30
Fe ₂ O ₃ (%)	5.33	0.013	0.24
P (ppm)	1411	24.5	1.74
Ti (ppm)	4654	50.1	1.08
V (ppm)	86	8.4	9.73
Cr (ppm)	74	4.8	6.50
Mn (ppm)	888	10.7	1.21
Co (ppm)	16	1.1	6.89
Ni (ppm)	32	2.7	8.29
Cu (ppm)	29	1.4	4.87
Zn (ppm)	100	2.2	2.15
Rb (ppm)	108	1.1	0.98
Sr (ppm)	322	1.4	0.42
Y (ppm)	28	1.0	3.51
Zr (ppm)	269	2.6	0.99
Nb (ppm)	20	0.7	3.66
Ba (ppm)	649	25.3	3.90
Pb (ppm)	39	2.8	7.14
Th (ppm)	14	1.5	7.17

Table 6. Quality monitoring standard

Concentration range	Second-grade standard sample ^a		First-grade standard sample, ^a
	$\Delta \log \bar{C}(\text{GRD}) = \frac{\sum_{i=1}^4 (\log C_i - \log C_{Ri})}{4}$	$\sigma(\text{GRD}) = \sqrt{\frac{\sum_{i=1}^4 (\Delta \log C_i - \Delta \log C^2)}{4-1}}$	$\Delta \log C(\text{GSD}) = \log C - \log C_s$
Within three times the detection limit	$\leq \pm 0.2$	≤ 0.34	$\leq \pm 0.40$
Above three times the detection limit	$\leq \pm 0.1$	≤ 0.17	$\leq \pm 0.20$
1-5%	$\leq \pm 0.1$	≤ 0.17	$\leq \pm 0.20$
>5%	$\leq \pm 0.05$	≤ 0.085	$\leq \pm 0.10$

^a Means of display and monitoring limits.

Table 7. Comparison of analytical results for standard samples

Element or oxide determined	GSD-1			Standard sample GSD-2			GSD-3		
	This method	Recommended value	$\Delta \log C$	This method	Recommended value	$\Delta \log C$	This method	Recommended value	$\Delta \log C$
Al ₂ O ₃ (%)	14.49	14.83	-0.0101	16.61	15.72	0.0239	11.94	12.04	-0.0036
SiO ₂ (%)	58.66	58.43	0.0017	70.43	69.90	0.0033	73.44	71.28	0.0130
MgO (%)	4.17	4.14	0.0031	0.20	0.21	-0.0212	0.66	0.70	-0.0256
Na ₂ O (%)	3.38	3.50	-0.0152	3.12	3.04	0.0113	0.32	0.34	-0.0263
K ₂ O (%)	2.69	2.77	-0.0127	5.29	5.19	0.0083	2.46	2.19	0.0505
CaO (%)	4.43	4.60	-0.0164	0.25	0.25	0.0000	0.21	0.22	-0.0202
Fe ₂ O ₃ (%)	6.80	7.35	-0.0338	1.83	1.89	-0.0140	6.64	6.51	0.0086
Ba (ppm)	875	950	-0.0357	139	185	-0.1242	578	615	-0.0269
Co (ppm)	20	20.4	-0.0086	3	2.6	0.0621	16	11.7	0.1359
Cr (ppm)	189	194	-0.0113	11	12.2	-0.0450	91	87	0.0195
La (ppm)	36	43	-0.0772	72.4	90	-0.0945	39	39	0.0000
Mn (ppm)	837	920	-0.0411	288	240	0.0792	439	400	0.0404
P (ppm)	1532	1490	0.0121	198	200	-0.0044	641	630	0.0075
V (ppm)	121	121	0.0000	8	16.5	-0.3144	118	120	-0.0073
Ti (ppm)	5597	5870	-0.0207	1391	1380	0.0034	6382	6360	0.0015
Cu (ppm)	28	21.8	0.1087	4	4.9	-0.0831	169	177	-0.0201
Nb (ppm)	35	35	0.0000	86	95	-0.0432	17	16	0.0263
Pb (ppm)	28	24.4	0.0598	42	32	0.1181	39	40	-0.0110
Rb (ppm)	123	116	0.0254	458	470	-0.0112	77	79	-0.0111
Sr (ppm)	515	525	-0.0084	27	28	-0.0158	86	90	-0.0197
Th (ppm)	30	23	0.0300	63	70	-0.0458	9	9.2	-0.0095
Y (ppm)	24	22.5	0.0280	55	67	-0.0857	21	22	-0.0202
Zn (ppm)	87	79	0.0419	35	44	-0.0994	46	52	-0.0532
Zr (ppm)	31.3	310	0.0042	410	460	-0.0500	209	220	-0.0223
Ga (ppm)	23.7	23	0.0130	28.2	27.4	0.0125	16.7	15.9	0.0213
As (ppm)	1.3	2.0	-0.1871	9.0	6.2	0.1899	17.7	17.6	0.0025
Ni (ppm)	91	70	0.0732	8	55	0.1627	23	25.0	-0.0465

t analysis is used for detecting whether there is systematic error in the determination:

$$t = \frac{\Delta \log C}{s} \sqrt{n} \tag{7}$$

When $\alpha = 0.05$, $n = 8$, $t_{0.05} = 2.365$. For $t < t_{\alpha}$, there is no systematic error in the determination of the element. Two pairs of repeated samples should be analysed in each batch. The analytical quality is also monitored by the requirements listed in Table 6 in order to test whether the sampling, preparation and analytical errors will cover the geochemical variance.

This method was used for a single determination of the eight GSD first-grade standard samples and the four

second-grade samples from Shanxi province. A comparison of some analytical results is shown in Table 7. The results of this method are in good agreement with the analytical values for standard samples; hence the analytical quality is in the high rank laid down by the Chinese Ministry of Geology and Mineral Resources.

CONCLUSION

XRFA has been combined with some other analytical techniques for analysing geochemical prospecting samples in many laboratories in geological departments, and the results are satisfactory. The great advantage of

XRFA for the multi-element determinations in geochemical prospecting samples is the reproducibility, and XRFA in fact provides a good basis for the accomplishment of a geochemical prospecting map on a national scale.

Using an automatic x-ray spectrometer, 30 major and trace elements can be determined in one preparation of the sample, and 20 samples can be analysed in 24 min, illustrating the speed of the technique. The procedure is simple and possible errors introduced in the process are minimized. Analytical results are accurate and reliable. The method is especially suitable for the large number of samples required for geochemical prospecting.

For major element analysis, the matrix effect is corrected by the use of empirical coefficients. The accuracy of measurement is improved in the concentration range of the element analysed. For trace elements whose wavelengths are shorter than the Fe K absorption edge, the scattered line internal standard method is used for the correction of the matrix effect. When the concentrations of Fe and Ca are significant, influence coefficients

are used to correct for their effect on the analysis. Hence the accuracy of trace element analysis is improved.

Low-pressure polyethylene is the best adhesive for the pressed-pellet method (or plastic-ring method). It is less hygroscopic and does not contaminate the instrument. The cost is low and sample preparation is rapid; also, the specimen pellets can be preserved for a long period of time.

The sample preparation module has been modified and improved and, accordingly, the labour requirements are decreased; the quality of sample preparation is improved, providing 100% efficiency.

The procedures for drawing maps of abnormalities and geological sections¹ are programmed. After samples from the geological map have been analysed, the maps of abnormalities and sections can be drawn.

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