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A FAST PROCEDURE TO ANALYZE SULPHATE-RICH WEATHERED MATERIALS USING X-RAY FLUORESCENCE SPECTROMETRY

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This paper describes a fast method for the simultaneous determination of the main major (Si, Al, Fe, K, S, Mg), minor (Ca, Zn, Pb, Ti, As, Mn, Na) and trace elements (Ba, Cd, Sb, Ag, Sr, Cu, Sn, Rb, and Ge) by X-ray fluorescence (XRF) spectrometry in weathered materials containing natural hydrated sulphates. Fourteen synthetic standards with a fixed matrix and different amounts of the analytes have been prepared. Correlations between elements as well as the reproducibility of the analytical data and the validity of the method have been studied. The values of theoretical minimum detection and quantification limits from As, Ge, Sn, Cd, Ag and Sb have been calculated.

KEY WORDS: X-ray spectrometry, weathering, geochemistry, hydrated sulphates.

INTRODUCTION

Weathering processes of sulphide deposits significantly contribute to the pollution of surface and underground waters used in agriculture, because elements such as Pb, Zn, Cd and Ge are dissolved. These processes are very important with wastes of old mining districts. For this reason it is necessary to devise a fast method to analyze these materials.

The chemical composition of weathered materials in the Mazarron mining district (Murcia, Spain) presents a large complexity due to the presence of a variable sulphate-rich mineralogy involving hydrated sulphates of Fe, Al, Mn, Mg and Zn, as a result of weathering of wall-rocks (dacites and rhyodacites) and primary mineralization of sphalerite-pyrite-galene type. Several authors^{1,2} have studied the course of the intense weathering processes in this area, which are favoured by the lixiviation of materials by highly acidic waters. These processes are more important in the old mining wastes, where the water acidity is higher. For this reason our interest is focused on the latter type of materials.

A complementary chemical and mineralogical study using atomic absorption spectrometry (AAS) and X-ray diffraction (XRD) has also been reported². However, the analytical procedures used were time-consuming due to the need for a dissolution

step; besides, the lengthy sample manipulation process led to contamination problems and the desirable accuracy was sometimes hardly reached. From a practical point of view, a more reliable and faster method appears to be needed.

At present, X-ray fluorescence (XRF) is widely used to analyze geological materials because manipulation of the sample is minimal^{4,5}. The aim of this paper was to develop a rapid procedure for the determination of both major and minor components in the above quoted samples using XRF. Because the dissolution step is avoided, no problems from acids or fluxes are encountered and results useful for mineralogical purposes can be rapidly achieved. Despite the advantages of XRF, problems due to the matrix, particle size and/or surface roughness can affect the results and a careful calibration must therefore be performed. Since the main problem is the nature of the matrix, a logical approach is to use a synthetic matrix with a chemical composition similar to that of the samples or a standard addition method.

In this paper, Si, Al, Fe, K, S and Mg were selected as major elements, Ca, Zn, Pb, Ti, As, Mn, and Na as minor ones and Ba, Cd, Sb, Ag, Sr, Cu, Sn, Rb and Ge as traces to develop a rapid XRF method using synthetic standards, which allows the simultaneous determination of these elements. The procedure here reported, which is essentially an application of XRF to geochemical analysis, describes in detail a fast way to obtain analytical data useful for geochemical purposes.

EXPERIMENTAL

Apparatus

All X-ray measurements were done with a Philips PW-1400 wavelength-dispersive X-ray spectrometer interfaced to a Digital PDP 11/23 computer. A scandium target X-ray tube was used for excitation; vacuum was used throughout. Table 1 summarizes the instrumental conditions. Interference problems by line overlap ($\text{AsK}_\alpha/\text{PbL}_\alpha$; SnK_α (2nd order)/ PbL_β) were resolved using other alternative lines.

The selection of measurement time for each element was done taking into account sensitivity and sample concentration criteria.

Reagents

All chemicals used for the preparation of standards were of analytical reagent grade quality and were used without further purification. Granite NIM-G and basalt SRM 688 were also used.

Preparation of standards and samples

Taking into account the previously reported chemical composition of weathered samples from the area², a matrix was prepared by mixing granite and basalt standards with known quantities of chemicals to give the composition summarized in Table 2. Next, standards were prepared by mixing various amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$,

Table 1 Instrumental conditions for XRF.

Element	Line	Collimator*	Detector**	Crystal	2 θ	kV/mA
Sb	K α	F	S	FLi ₂₀₀	13.415	60/40
Sn	K α	F	S	FLi ₂₀₀	13.995	60/40
Cd	K α	F	S	FLi ₂₀₀	15.270	60/40
Ag	K α	F	S	FLi ₂₀₀	15.970	60/40
Sr	K α	F	FS	FLi ₂₀₀	25.125	60/40
Rb	K α	F	FS	FLi ₂₀₀	26.605	60/40
As	K β	F	FS	FLi ₂₀₀	30.450	60/40
Pb	L α	F	FS	FLi ₂₀₀	33.930	60/40
Ge	K α	F	FS	FLi ₂₀₀	36.320	60/40
Zn	K α	F	FS	FLi ₂₀₀	41.795	60/40
Cu	K α	F	FS	FLi ₂₀₀	45.030	60/40
Fe	K α	F	F	FLi ₂₀₀	57.535	50/50
Mn	K α	F	F	FLi ₂₀₀	62.980	50/50
Ba	L β	F	F	FLi ₂₀₀	79.265	50/50
Ti	K α	F	F	FLi ₂₀₀	86.170	50/50
Ca	K α	F	F	FLi ₂₀₀	113.160	50/50
K	K α	F	F	FLi ₂₀₀	136.730	50/50
Si	K α	C	F	PE	109.125	40/60
Al	K α	C	F	PE	144.960	40/60
Mg	K α	C	F	PX ₁	22.605	40/60
Na	K α	C	F	PX ₁	27.295	40/60
S	K α	C	F	Ge	110.720	40/60

* F, fine (150 μ m); C, coarse (550 μ m).

** F, flow counter with PR gas (90% Ar-10% CH₄); S, scintillation; FS, flow plus scintillation counters. Sc target X-ray tube; 28 mm diameter mask; vacuum.

ZnSO₄ · 7H₂O, MgSO₄ · 7H₂O, MnSO₄ · H₂O, and Al₂O₃ with different quantities of the matrix. In this way, fourteen standards covering a wide range of concentrations of the various analytes (Table 3) were obtained.

2 g of each standard were weighed, ground (<270 mesh) and mixed with 3 ml of acetone containing 20% w/v of Elvacite 2044⁶. This mixture was converted to a 31-mm diameter double layer pellet (with backing pellet of boric acid) in a Herzog hydraulic press under a total weight of 30 tons. Samples were prepared in the same

Table 2 Chemical composition (%) of matrix.

Granite	41.4670
Basalt	39.9404
3CdSO ₄ · 8H ₂ O	0.9968
SnCl ₂ · 2H ₂ O	0.6037
AgNO ₃	1.7166
GeO ₂	0.3591
Sb ₂ O ₃	1.6212
As ₂ O ₃	3.5136
Pb(NO ₃) ₂	2.6793
SrSO ₄	1.9321
CuSO ₄ · 5H ₂ O	2.3746

Table 3 Variation range (%) for each element in standards.

<i>Element</i>	<i>Min.</i>	<i>Max.</i>
Zn	0.0020	8.5240
Mn	0.0105	4.1960
Ti	0.0152	0.5050
K	0.0647	2.1440
Ca	0.1560	5.1840
Si	1.5300	50.7220
Mg	1.7300	5.3750
S	2.5880	21.5580
Fe	3.2290	16.7490
Al	5.4850	34.8340
Rb	0.0004	0.0135
Ge	0.0075	0.2490
Sn	0.0096	0.3170
Cd	0.0132	0.4370
Cu	0.0184	0.6090
Sr	0.0280	0.9290
Ag	0.0329	1.0900
As	0.0401	1.3310
Sb	0.0408	1.3540
Ba	0.0502	1.6640
Pb	0.0506	1.6780
Na	0.0679	2.2520

way, i.e., they were ground, sieved and Elvacite was added. Next, they were pelletized and submitted to analysis using the above quoted standards for calibration.

Standard addition was performed by mixing a carefully weighed amount of sample with known quantities of the analyte. The net intensity was plotted against the amount of analyte added and the concentration of the unknown was obtained from the *X* axis intersection.

RESULTS

Statistical treatment of the experimental data illustrates the performance of the method using synthetic standards. As Tables 4 and 5 demonstrate, the correlation coefficients for analyzed elements are significant ($r > 0.98$) and only for Na and Mg the values are close to 0.90. All of them show a correct behaviour of different elements inside the concentration range used for the standards³. The procedure was applied to natural samples collected in the Mazarron mining district in order to determine the reproducibility of the analytical data. Two random natural samples (2-2 and 1-B4) were studied. Ten pellets from each were prepared and measured with the direct method using the synthetic standards for calibration. The results shown in Table 6 indicate a good reproducibility.

In order to calculate both detection and concentration limits⁷⁻⁹ of the elements absent from the granite-basalt mixture itself and which were added to prepare the

Table 4 Regression equations for major elements

$$(Y = A + B \cdot X)$$

<i>Element</i>	<i>A</i>	<i>B</i>	<i>r*</i>
Zn	4.39E-02	7.10E-2	0.996
Fe	1.72	6.89E-02	0.983
Mn	-2.31E-02	1.01E-01	0.999
Ca	-3.81E-01	3.71E-02	0.997
K	-1.26E-01	3.26E-02	0.998
Si	-3.25E-01	3.94E-01	0.997
Al	4.07E-01	4.15E-01	0.990
Mg	8.01E-01	2.29E-01	0.905
Na	-1.68	1.25	0.900
S	1.05	1.11E-01	0.990

* *r*, regression coefficient.

above matrix, a blank test without Sn, Ag, Sb, Ge, As and Cd was performed. The theoretical minimum detection limits were calculated for the six elements on the basis of net counts for three concentration levels using the criterion of three times the theoretical standard deviation of the background counts. Detection limits of 23, 18, 31, 6, 20 and 20 ppm were found for Sn, Ag, Sb, Ge, As and Cd, respectively.

As Table 6 demonstrates, the results for the two natural samples with direct calibration agree with those obtained using standard addition giving reliability to the procedure here reported.

CONCLUSIONS

The use of synthetic standards in XRF here proposed appears to be a useful approach for the mineralogical routine determination of 22 elements in sulphate-rich weathered

Table 5 Regression equations for minor elements

$$(Y = A + B \cdot X)$$

<i>Element</i>	<i>A</i>	<i>B</i>	<i>r*</i>
Sb	-8.66E-02	1.86E-01	0.991
Sn	-1.79E-02	1.49E-01	0.995
Cd	-2.24E-02	1.25E-01	0.993
Ag	-6.34E-02	1.15E-01	0.995
Sr	-2.62E-02	8.96E-02	0.996
Rb	-2.99E-04	8.91E-02	0.997
As	1.28E-02	2.22E-01	0.995
Pb	5.86E-03	4.69E-02	0.994
Ge	4.78E-03	7.42E-02	0.996
Cu	-1.39E-02	6.58E-02	0.992
Ba	-3.71E-01	1.32	0.993
Ti	-4.79E-02	7.00E-01	0.994

* *r*, regression coefficient.

Table 6 XRF results for two real samples (in %)*, **.

Element	Sample 2-2		Sample 1-B4	
	A	B	A	B
Sn	—	—	0.17 (10.3)	0.022
Rb	0.005 (4.0)	0.007	0.011 (3.7)	0.008
As	0.024 (7.0)	0.021	0.027 (1.8)	0.033
Pb	0.109 (2.2)	0.115	0.246 (1.2)	0.251
Ge	0.004 (8.2)	0.006	0.003 (12.0)	0.005
Zn	0.957 (1.5)	0.948	0.542 (0.7)	0.553
Cu	0.014 (7.2)	0.018	0.006 (10.6)	0.008
Mn	0.794 (1.7)	0.802	0.079 (1.9)	0.071
Ti	0.621 (0.9)	0.615	0.714 (1.2)	0.727
Ca	2.626 (1.4)	2.635	3.131 (1.0)	3.210
K	1.028 (2.0)	1.042	1.501 (1.5)	1.571
Si	32.382 (2.6)	32.365	37.297 (5.6)	37.283
Al	13.256 (0.8)	13.267	10.263 (1.2)	10.281
S	11.250 (1.6)	11.262	16.120 (2.4)	16.133
Mg	2.978 (2.0)	2.966	0.974 (1.0)	0.987
Fe	15.660 (0.4)	15.649	11.266 (0.6)	11.321
Na	0.231 (0.9)	0.242	0.229 (1.0)	0.240

* A, direct procedure using synthetic standards (mean of three different pellets); B, standard addition method.

** Values in brackets are CV values.

materials. The procedure is fast and its reliability is validated by the standard addition results. The advantages over wet classical methods are apparent: no dissolution step is needed and considerable saving of time and efforts is achieved.

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