

APPLICATION OF THE BACKSCATTER FUNDAMENTAL PARAMETER METHOD WITH SIMULTANEOUS EXCITATION BY ⁵⁵Fe AND ¹⁰⁹Cd RADIOISOTOPE SOURCES

Dariusz Wegrzynek^{1,2)}, Andrzej Markowicz^{1,2)}, Ernesto Chinea-Cano¹⁾, Samuel Bamford¹⁾, Philip J. Potts³⁾

¹⁾ *International Atomic Energy Agency Laboratories, Physics, Chemistry, and Instrumentation (PCI) Laboratory, A-2444 Seibersdorf, Austria*

²⁾ *On leave from: Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Krakow, Poland*

³⁾ *Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom*

ABSTRACT

The backscatter fundamental parameter (BFP) method has been applied for determination of elements in loose powder samples utilizing double excitation with ⁵⁵Fe and ¹⁰⁹Cd radioisotope sources. The method has been used for laboratory determination of element concentrations in soil and geological samples. The combined excitation with ⁵⁵Fe and ¹⁰⁹Cd sources allows for improved detection limits of low-Z elements as compared to the excitation with ¹⁰⁹Cd source alone. The utilization of silver *K*-series scattered radiation allows correcting the influence of the so-called "dark matrix" of the analyzed sample. The measurements have been performed with a portable spectrometer system consisting of two annular excitation sources, a thermoelectrically cooled Si-PIN photodiode detector, and a battery operated power supply/amplifier/multichannel analyzer connected to a laptop computer for data acquisition and evaluation. A modified BFP algorithm has been implemented in a computer program, and this program was used to calculate the concentrations of elements in the analyzed samples. The calibration of the BFP method was performed with a set of samples prepared from pure elements, element oxides, or element compounds. Several standard reference materials have been analyzed showing a good agreement between the concentrations of elements calculated by BFP method and the certified/recommended values.

INTRODUCTION

The X-ray fluorescence method (XRF) is known for its versatility and multielemental capability for over 50 years [1]. Nowadays there are two main areas of development: the micro-beam techniques utilizing brilliant synchrotron beams, and portable/bench-top instruments utilizing low power X-ray tubes or radioisotope excitation sources. The synchrotron based XRF is aimed at ultra trace analysis and imaging elemental distributions with micrometer spatial resolution while the portable/bench-top instruments are suitable for *in-situ* element screening [2], geological prospecting [3], preliminary assessment of hazardous element concentrations in the contaminated sites [4], etc. Generally speaking, the portable XRF spectrometers are particularly useful for the applications where the analysis is performed at a site of event with minimum or no sample preparation. Thanks to the recent developments and miniaturization of the excitation sources (X-ray tubes), and the availability of compact liquid nitrogen-free detectors (Si-PIN photodiodes, silicon drift detector), the portable XRF spectrometers became truly portable (hand

held/battery operated units). The versatility of the XRF method combined with miniaturization of equipment made the XRF a method of choice for *in-situ* analysis of the composition of the extraterrestrial surface rocks. The USA National Aeronautics and Space Administration (NASA) has pioneered the extraterrestrial applications of the X-ray spectrometry during its manned APOLLO missions to the Moon and the unmanned Mars exploration [5-7]. In June 2003 the European Space Agency (ESA) is expected to launch Mars Express Mission sending the BEAGLE2 lander, a British led project, to Mars surface [8]. On board of the BEAGLE2 lander, besides other instruments, there will be an X-ray fluorescence spectrometer for analysis of the composition of Martian rocks and soil. The primary goal is to measure the potassium content for age dating purposes and quantify major elements like Mg, Al, Si, S, Ca, Ti, Cr, and Fe to help in identifying rock types. For efficient excitation of low and high-Z elements the spectrometer has been equipped with two radioisotope excitation sources: ^{55}Fe and ^{109}Cd . The two sources irradiate the analyzed sample simultaneously. This paper presents the results obtained with the $^{55}\text{Fe}/^{109}\text{Cd}$ dual-excitation X-ray fluorescence spectrometer.

EXPERIMENTAL

All the measurements were performed with a portable XRF spectrometer system consisting of AMPTEK XR-100CR Si-PIN detector, 300 μm thickness, $\frac{1}{2}$ mil Be window, 7 mm^2 active area, FWHM = 220 eV at 5.9 keV, AMPTEK PX2CR/MCA800A power supply-amplifier, and multichannel analyzer coupled to a laptop computer for data acquisition and evaluation. Two annular excitation sources were used: ^{55}Fe (230 MBq) and ^{109}Cd (740 MBq). In order to simulate the excitation conditions which are to be used in the XRF spectrometer on Martian rocks (simultaneous excitation by the two sources) the standards and the analyzed samples were first irradiated with ^{109}Cd source following irradiation for the same live time with ^{55}Fe source. The irradiation times varied from 250 s to 1000 seconds per irradiation depending on sample type. The cumulative spectra were stored and processed by AXIL spectra deconvolution program [9], which is a part of the IAEA quantitative X-ray analysis software (QXAS) package [10]. The three calibration standards consisted of one thick loose powder sample prepared by mixing SiO_2 and Na_2CO_3 in proportion 4:1, a titanium foil with 6 μm thickness, and an aluminum foil with 40 μm thickness. Three reference materials: IAEA Soil-7 (uncontaminated soil), NIST SRM 2710 (highly contaminated soil), and MINTEK SARM-69 (clay potsherd material) were prepared as thick loose powder and next analyzed by using the portable XRF spectrometer.

THEORY

The quantitative analysis method should be capable of determining the element concentrations in samples containing unknown fraction of low-Z elements not detectable by XRF spectrometry (so-called "dark matrix"). Once calibrated, the method must be applicable for analyzing substances with different matrices. It must also be considered that when the measurements are performed *in-situ*, the measuring geometry may vary from sample to sample, and the method should be able to compensate for the variations. It has been found that the backscatter fundamental parameter (BFP) method can meet the requirements [11]. In our recent publication [12] we presented an application of the BFP method for *in-situ* element determination in soil. In the same paper the details of the BFP algorithm can be found. In this work we describe the modifications introduced to BFP algorithm in order to apply the method for element

determination with dual ^{55}Fe and ^{109}Cd excitation. When two sources irradiate the sample simultaneously, the number of counts per second under p -th characteristic peak of the determined element, R_p , can be expressed by the following equation:

$$R_p = q\varepsilon_p \sum_{s=1,2} G_s K_{p,s} F_{p,s} H_{p,s} \quad (1)$$

where q is the mass per unit area of the determined element, ε_p is the detection efficiency for the characteristic peak, G_s is the semi-geometrical constant, $K_{p,s}$ is the product of fundamental parameters or a mass cross-section for production of the characteristic radiation of determined element, $F_{p,s}$ is absorption factor, and $H_{p,s}$ is the enhancement factor. The index s denotes the radioisotope source, and the index p denotes the characteristic peak of the element determined. Similar equations are formulated for the coherently and incoherently scattered peaks of Ag- $K\alpha$ radiation originating from ^{109}Cd source:

$$R_{Coh} = \varepsilon_{Coh} G_{Coh} \left[\sum_{j=1}^M q_j \sigma_{Coh,j} + q_A \sigma_{Coh,A} + q_B \sigma_{Coh,B} \right] F_{Coh} \quad (2)$$

$$R_{Inc} = \varepsilon_{Inc} G_{Inc} \left[\sum_{j=1}^M q_j \sigma_{Inc,j} + q_A \sigma_{Inc,A} + q_B \sigma_{Inc,B} \right] F_{Inc} \quad (3)$$

where R_{Coh} and R_{Inc} are the number of counts per second under coherently and incoherently scattered Ag- $K\alpha$ peaks, G_{Coh} and G_{Inc} are the semi-geometrical constants for coherently and incoherently scattered radiation, ε_{Coh} and ε_{Inc} are the respective detection efficiencies, q_j is the mass per unit area of the j -th element in the analyzed sample, the $\sigma_{Coh,j}$ and $\sigma_{Inc,j}$ are the mass-cross sections for coherent and incoherent scattering of Ag- $K\alpha$ radiation on j -th element, F_{Coh} and F_{Inc} are the respective absorption factors, q_A and q_B are the masses per unit area of the two elements selected to represent the average composition of the “dark matrix” of the sample with $\sigma_{Coh,A}$, $\sigma_{Coh,B}$ and $\sigma_{Inc,A}$, $\sigma_{Inc,B}$ denoting the respective mass-scattering cross-sections. In the BFP algorithm the elements A and B are selected to fulfill the following inequality:

$$\frac{\sigma_{Coh,A}}{\sigma_{Inc,A}} < \frac{\frac{R_{Coh}}{\varepsilon_{Coh} G_{Coh} F_{Coh}} - \sum_{j=1}^M q_j \sigma_{Coh,j}}{\frac{R_{Inc}}{\varepsilon_{Inc} G_{Inc} F_{Inc}} - \sum_{j=1}^M q_j \sigma_{Inc,j}} < \frac{\sigma_{Coh,B}}{\sigma_{Inc,B}} \quad (4)$$

The Eqns. (1)-(4) make up the basis of the BFP algorithm. In order to apply the method for element determination in unknown sample the method has to be calibrated using standard samples. In Eqns. (1)-(3) there are four factors: G_1 , G_2 , G_{Coh} , G_{Inc} that have to be known. Since radioisotope sources are used for excitation the values of these factors will change with time; nevertheless we will use the term “constant” when referring to them. The constants G_{Coh} and G_{Inc} can be determined independently by measuring a standard sample of known total composition preferably made of low- Z elements. If one performs the measurement for the standard sample at a given moment in time denoted by t_0 , the following set of equations can be used to calculate the values the semi-geometrical constants at a given time, t :

$$R_{Coh} = \varepsilon_{Coh} G_{Coh} F_{Coh} \sum_j q_j \sigma_{Coh,j} \quad (5a)$$

$$R_{Inc} = \varepsilon_{Inc} G_{Inc} F_{Inc} \sum_j q_j \sigma_{Inc,j} \quad (5b)$$

$$G_{Coh} = G_{0Coh} \exp\{-(t-t_0) \ln 2 / T_2\} \quad (5c)$$

$$G_{Inc} = G_{0Inc} \exp\{-(t-t_0) \ln 2 / T_2\} \quad (5d)$$

Summation in Eqns. (5a)-(5b) includes all elements present in the standard sample. The G_{0Coh} , G_{0Inc} are the values of the semi-instrumental constants for coherently and incoherently scattered Ag- $K\alpha$ radiation corresponding to the moment t_0 (the time the measurement of the standard sample was performed), T_2 is the half-life time of the ^{109}Cd isotope. In order to simplify calculation of the semi-geometrical constants for the fluorescence radiation, G_1 and G_2 , let's rewrite Eqn. (1) in the following form:

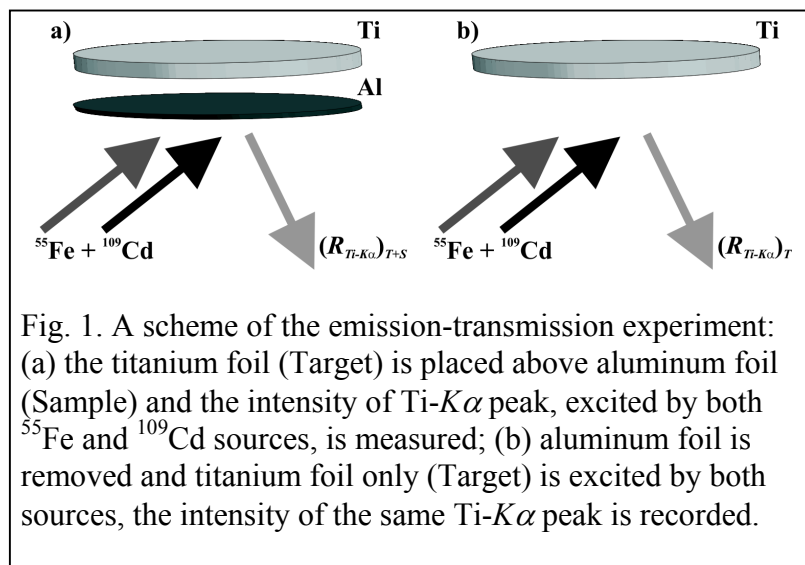
$$R_p = q\varepsilon_p G_2 (rK_{p,1}F_{p,1}H_{p,1} + K_{p,2}F_{p,2}H_{p,2}) \quad (6)$$

In Eqn. (6) only the semi-geometrical constant G_2 is explicitly present. The G_1 constant has been hidden in the term r . This term stands for the ratio of G_1/G_2 . It has been already mentioned, due to the decay of ^{55}Fe and ^{109}Cd isotopes, the values of the semi-geometrical factors vary in time as follows:

$$G_2 = G_{02} \exp\{-(t-t_0) \ln 2 / T_2\} \quad (7)$$

$$r = r_0 \exp\{-(t-t_0) \ln 2(1/T_1 - 1/T_2)\} \quad (8)$$

If the characteristic peak of an element is excited only by ^{109}Cd source then the value of the ratio $r = 0$. The T_1 is the half-life time of the ^{55}Fe isotope. The G_{02} is the value of the semi-geometrical constant G_2 at the moment t_0 and r_0 is the value of the ratio r at the same moment of time. The same reference time moment denoted by t_0 has been used for all constants G_{Coh} , G_{Inc} , G_2 , and r , but in principle different reference moments could also be applied. Providing that the ratio r is known, the value of the factor G_2 as a function of time can be obtained from measurement of a



single standard sample of known total composition featuring at least one element which characteristic radiation is effectively excited by ^{109}Cd or by both ^{55}Fe and ^{109}Cd sources. In order to determine the value of the ratio r the emission-transmission measurement has been performed. A scheme of the emission-transmission experiment is shown in Fig. 1. The recorded intensities of the Ti- $K\alpha$ peaks obtained from "Target+Sample" and "Target" measurements were used to

calculate the r_0 value:

$$r_0 = \frac{(R_{Ti-K\alpha})_T}{(R_{Ti-K\alpha})_{T+S}} \frac{A_{Ti-K\alpha,2} - 1}{1 - \frac{(R_{Ti-K\alpha})_T}{(R_{Ti-K\alpha})_{T+S}} A_{Ti-K\alpha,1}} \times \frac{K_{Ti-K\alpha,2} F_{Ti-K\alpha,2}}{K_{Ti-K\alpha,1} F_{Ti-K\alpha,1}} \quad (9)$$

The factors $A_{Ti-K\alpha,1}$ and $A_{Ti-K\alpha,2}$ account for absorption of the primary and characteristic photons in the aluminum foil and the factors $F_{Ti-K\alpha,1}$ and $F_{Ti-K\alpha,2}$ are the absorption factors associated with 5.9 keV (average photon energy from ^{55}Fe source) and 22.5 keV (average photon energy from

^{109}Cd source) photons and Ti- $K\alpha$ radiation emerging from the titanium foil. The masses per unit area of Al and Ti foils were known allowing calculating the values of these factors. In the next step the value of the r_0 was calculated from Eqn. (9). From the same measurement, using the recorded intensity of the Ti- $K\alpha$ peak excited in the titanium foil, with aluminum foil removed – case (b) in Fig. 1, the value of the G_{02} was calculated using Eqn. (6). Therefore, all constants, G_{Coh} , G_{Inc} , G_2 , and r , necessary to perform analysis of unknown samples have been established. To summarize, the calibration procedure was accomplished by performing three measurement: 1) measurement of a standard sample composed of low- Z elements to obtain G_{Coh} and G_{Inc} , 2) measurement of a titanium foil alone, and 3) measurement of the titanium foil with aluminum foil placed in the front of the titanium foil, to obtain r and G_2 . All the obtained calibration constants vary with time according to Eqns. (5c), (5d), (7), and (8).

RESULTS AND DISCUSSION

The BFP method has been tested in the analysis of three reference materials: IAEA Soil-7, NIST SRM 2710, and MINTEK SARM-89. A comparison of the results obtained by BFP method with the certified/recommended and information values is shown in Table 1.

Table 1. The determined and given values of element concentrations in analyzed samples.

El.	IAEA SOIL-7 RM		NIST SRM 2710		MINTEK SARM-69	
	Determined ^{a)}	Given ^{b)}	Determined	Given	Determined	Given
	[%]		[%]		[%]	
K	1.47 ± 0.07	1.13÷1.27	2.06 ± 0.05	2.00÷2.22	1.56 ± 0.06	1.59÷1.66
Ca	14.4 ± 0.1	15.7÷17.4	1.2 ± 0.1	1.22÷1.28	1.60 ± 0.05	1.67÷1.72
Ti	0.30 ± 0.02	0.26÷0.37	0.26 ± 0.07	0.273÷0.293	0.42 ± 0.01	0.46÷0.47
Fe	2.69 ± 0.04	2.52÷2.63	3.38 ± 0.08	3.28÷3.48	4.73 ± 0.08	4.97÷5.07
	[mg/kg]		[mg/kg]		[mg/kg]	
Cu	< DL	9÷13	3180 ± 90	2820÷3080	< DL	43÷48
Zn	66 ± 20	101÷113	6600 ± 60	6861÷7043	40 ± 20	65÷70
As	< DL	12.5÷14.2	1090 ± 300	588÷664	< DL	-
Rb	57 ± 7	47÷56	113 ± 10	120	59 ± 7	66
Sr	117 ± 6	103÷114	340 ± 20	330	107 ± 7	109
Y	25 ± 6	15÷27	< DL	23	35 ± 20	29
Zr	197 ± 9	180÷201	130 ± 10	-	302 ± 8	271
Nb	6 ± 5	7÷17	< DL	-	11 ± 5	9
Pb	122 ± 20	55÷71	4900 ± 400	5452÷5612	< DL	14

^{a)} the uncertainties (one standard deviation) due to counting statistics are shown

^{b)} 95% confidence interval for certified/recommended values or only information values

As can be noticed in most cases the obtained results are in good agreement with the given values. There are few exceptions, for example due to overlap of As- $K\alpha$ and Pb- $L\alpha$ peaks the calculated

arsenic and lead concentrations differ significantly from the certified values for NIST SRM 2710. The results obtained for Zn and Pb in IAEA Soil-7 and for Zn in MINTEK SARM-69 also show some bias. This is likely due to fact that the concentrations of the elements in these materials are close to detection limits (30-40 mg/kg). Additionally, in the case of the IAEA Soil-7 trace amount of arsenic is also present.

CONCLUSION

The BFP method, combined with two-excitation sources approach, performs well when applied to loose powder samples. A minimum number of standards with a quite different composition from the analysed samples, is required to calibrate the method. The next step in the method development will be to apply the scattered radiation from ^{55}Fe source, in order to reduce the variation of the calibration factors. This should allow applying the method for analysis of irregularly shaped/not flat samples, especially when the measurements are to be performed at reduced atmospheric pressure which guarantees that the majority of scatter occurs on the sample surface [13].

REFERENCES

1. Friedman, H., Birks, L.S., Analysis by Fluorescent X-Ray Excitation, 1948, USA Patent 2,449,066.
2. Piorek, S., Nucl. Instr. Meth., 1994, A353, 528-533.
3. Potts, P.J., Williams-Thorpe, O., Webb, P.C., Geostandards Newsletter, 1997, 21, 29-41.
4. Bernick, M.B., Kalnicky, D.J., Prince, G., Singhvi, R., J. Hazardous Materials, 1995, 43, 101-110.
5. Rieder, R., Economou, T., Wänke, H., Turkevich, A., Crisp, J., Brückner, J., Dreibus, G., McSween Jr, H.Y., Science, 1997, 278, 1771-1774.
6. Radchenko, V., Andreichikov, B., Wänke, H., Gavrilov, V., Korchuganov, B., Rieder, R., Ryabinin, M., Economou, T., App. Radiat. Isotop., 2000, 53, 821-824.
7. Solomon, S.C., McNutt, R.L., Gold, R.E., Acuna, M.H., Baker, D.N., Boynton, W.V., Chapman, C.R., Cheng, A.F., Gloeckler, G., Head III, J.W., Krimigis, S.T., McClintock, W.E., Murchie, S.L., Peale, S.J., Phillips, R.J., Robinson, M.S., Slavin, J.A., Smith, D.E., Strom, R.G., Trombka, J.I., Zuber, M.T., Planetary and Space Science, 2001, 49, 1445-1465.
8. Beagle 2, The British Led Exploration of Mars Website, 2002: <http://www.beagle2.com> [11 June 2002].
9. Van Espen, P., Janssens, K., Nobels, J., Chemom. Intell. Lab. Sys., 1987; 1, 109.
10. IAEA Manual: IAEA, QXAS Quantitative X-Ray Analysis System, 1996, Vienna.
11. Nielson, K.K., Anal. Chem., 1977, 49, 641.
12. D. Wegrzynek, A. Markowicz, E. Chinea-Cano, accepted for publication in X-Ray Spectrometry Journal, 2002.
13. Potts, P.J., Webb, P.C., Williams-Thorpe, O., J. Anal. Atomic Spectr., 1997, 12, 769-776.