

# QUANTITATIVE ANALYSIS BY ENERGY DISPERSIVE X-RAY FLUORESCENCE BY THE TRANSMISSION METHOD APPLIED TO GEOLOGICAL SAMPLES<sup>1</sup>

S.M. SIMABUCO

*Hydraulics and Sanitation Department, FEC/UNICAMP - P.O. Box 6021 - CEP: 13083-970 - Campinas, SP - Brasil*

V.F. NASCIMENTO FILHO

*Department of Physics and Meteorology - ESALQ/USP - P.O.Box 9 - CEP:13418-900 and Center for Nuclear Energy in Agriculture, CENA/USP - P.O. Box 96 - CEP: 13400-970 - Piracicaba, SP - Brasil*

**ABSTRACT:** Three certified samples of different matrices (Soil-5, SL-1/IAEA and SARM-4/SABS) were quantitatively analysed by energy dispersive X-ray fluorescence with radioisotopic excitation. The observed errors were about 10-20% for the majority of the elements and less than 10% for Fe and Zn in the Soil-5, Mn in SL-1, and Ti, Fe and Zn in SARM-4 samples. Annular radioactive sources of Fe-55 and Cd-109 were utilized for the excitation of elements while a Si(Li) semiconductor detector coupled to a multichannel emulation card inserted in a microcomputer was used for the detection of the characteristic X-rays. The fundamental parameters method was used for the determination of elemental sensitivities and the irradiator or transmission method for the correction of the absorption effect of characteristic X-rays of elements on the range of atomic number 22 to 42 (Ti to Mo) and excitation with Cd-109. For elements in the range of atomic number 13 to 23 (Al to V) the irradiator method cannot be applied since samples are not transparent for the incident and emergent X-rays. In order to perform the absorption correction for this range of atomic number excited with Fe-55 source, another method was developed based on the experimental value of the absorption coefficients, associated with absorption edges of the elements.

**Key words:** quantitative analysis, X-ray fluorescence, geological samples, energy dispersive.

## ANÁLISE QUANTITATIVA POR FLUORESCÊNCIA DE RAIOS X COM DISPERSÃO POR ENERGIA PELO MÉTODO DA TRANSMISSÃO APLICADA À AMOSTRAS GEOLÓGICAS

**RESUMO:** Foi realizada a análise quantitativa de três amostras certificadas de diferentes matrizes (Soil-5/IAEA, SL-1/IAEA e SARM-4/SABS) através da fluorescência de raios X por dispersão de energia e excitação radioisotópica. Os erros observados foram em torno de 10 a 20% para a maioria dos elementos e inferiores a 10% para Fe e Zn na amostra Soil-5, Mn na amostra SL-1 e Ti, Fe e Zn na amostra SARM-4. Para a excitação dos elementos presentes foram empregadas as fontes radioativas anelares de Fe-55 e Cd-109, enquanto que na detecção dos raios X característicos utilizou-se um detector de Si(Li), acoplado a uma placa analisadora de pulsos multicanal, inserida em um microcomputador. O método dos parâmetros fundamentais foi utilizado na determinação da sensibilidade elementar e o método do irradiador ou da transmissão na correção dos efeitos de absorção dos raios X característicos de elementos de número atômico entre 22 e 42 (Ti ao Mo) e excitação com Cd-109. Para elementos na faixa de número atômico entre 13 e 23 (Al ao V), o método do irradiador não pode ser aplicado, pois a amostra não é transparente aos raios X incidentes e emergentes, e um outro método baseado nas medidas experimentais dos coeficientes de absorção com Cd-109, associados aos saltos de absorção e excitação com Fe-55 foi então desenvolvido a fim de se efetuar a correção da absorção para esta faixa de número atômico.

**Descritores:** Análise quantitativa, fluorescência de raios X, amostras geológicas, energia dispersiva.

### INTRODUCTION

The X-ray fluorescence analysis is a multielemental and simultaneous technique based

on the measurement of the X-ray intensities emitted by the elements contained in a sample, when it is excited by low-energy X or  $\gamma$  rays. This technique, when applied as quantitative, needs calibration

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methods to convert the data intensities in elemental concentrations. This can be accomplished through empirical curves, involving the preparation of a reasonable number of standards, with similar composition in relation to the matrix.

Another quantitative method, called method of fundamental parameters, developed recently, is based on mathematic relationships derived from physical properties of the elements and physical characteristics of the detection system, and takes into account the matrix effect. The main advantage of this method consists of the utilization of a small number of standards prepared from elements and pure chemical compounds (YAP *et al.*, 1987).

However, in the analysis of unknown samples, it is necessary to establish the absorption correction factor and for this several techniques have been presented, among them the transmission technique for intermediate thickness samples (LEROUX & MAHMUD, 1966).

The aim of this work was to establish the best experimental conditions for quantitative analysis of geological samples, with a special reference to soils, using the fundamental parameters method for the determination of elemental sensitivity and carrying out absorption correction factors by the transmission method (HALLAK & SALEH, 1983).

## THEORY

For the excitation with monoenergetic photons, the relationship between the fluorescence intensity of a characteristic  $K_{\alpha}$  or  $L_{\alpha}$  lines and the concentration of an element present in the sample, is given by:

$$I_i = S_i W_i (\rho_M D) A_i \quad (1)$$

where  $S_i$  is the X-ray sensitivity of the spectrometer for the element  $i$ ,  $W_i$  the weight fraction of the element  $i$ ,  $\rho_M D$  the superficial density of the matrix ( $\text{g}\cdot\text{cm}^{-2}$ ) and  $A_i$  the absorption correction factor for the matrix effects, which is given by the equation:

$$A_i = \frac{1 - \exp(-\chi_i \rho_M D)}{\chi_i \rho_M D} \quad (2)$$

In this expression  $\chi_i$  is the total mass absorption coefficient, defined by:

$$\chi_i = \mu_M(E_o)/\sin \phi_1 + \mu_M(E_i)/\sin \phi_2 \quad (3)$$

where:

$\phi_1$  = radiation incident angle (between the incident beam direction and surface sample),

$\phi_2$  = radiation emergent angle (between the surface sample and emergent beam direction),

$\mu_M(E_o)$  = mass absorption coefficient of the matrix in the excitation energy  $E_o$ , and

$\mu_M(E_i)$  = mass absorption coefficient of the matrix in the X-ray characteristic energy  $E_i$ .

The sensitivity  $S_i$  could be related with the fundamental parameters constant  $K_i$  and the detection efficiency  $\varepsilon_i$  through a proportional constant called geometry factor  $G_i$ :

$$S_i = G_i \varepsilon_i K_i \quad (4)$$

This geometry factor must remain constant for the whole range of energies in order to obtain the average geometry factor, which is used for the sensitivity calculation of each element, including those not measured.

In the expression 4 the detection efficiency  $\varepsilon_i$  is determined by:

$$\varepsilon_i = \exp[-\mu_{\text{air}}(\rho D)_{\text{air}} - \mu_{\text{Be}}(\rho D)_{\text{Be}} - \mu_{\text{Au}}(\rho D)_{\text{Au}} - \mu_{\text{Si}}(\rho D)_{\text{Si,DL}}] \cdot [1 - \exp(-\tau_{\text{Si}}(\rho D)_{\text{Si,CR}})] \quad (5)$$

The first term in brackets takes into consideration the absorption of the characteristic X-rays with energy  $E_o$  in the total absorption path, i. e., by the air, beryllium window detector, gold and silicon dead layers. The second term describes the intrinsic efficiency of the detector for the X-ray energy  $E_i$ .

In this expression  $\mu_{\text{air}}$ ,  $\mu_{\text{Be}}$ ,  $\mu_{\text{Au}}$  and  $\mu_{\text{Si}}$  represent the mass absorption coefficients for air, beryllium, gold and silicon, and  $\tau_{\text{Si}}$  the mass absorption coefficient for the photoelectric effect of the silicon, at the characteristic energy  $E_i$  of each element  $i$ .

The fundamental parameters constant  $K_i$  is given by:

$$K_i = \tau_i (E_o) \omega_{ki} \left(1 - \frac{1}{J_{ki}}\right) f_i \quad (6)$$

where:

$\tau_i(E_o)$  = mass absorption coefficient for the photoelectric effect in relation to the element  $i$  in the excitation energy  $E_o$ ,

$\omega_{ki}$  = K fluorescence yield,

$J_{ki}$  = K absorption-edge jump, and

$f_i$  = fraction of the K photons emitted as  $K_{\alpha}$  photons.

The elemental sensitivity is usually determined by the measurement of the characteristic X-rays emitted by thin film standards, containing only one element, where the absorption and enhancement effects are negligible (ESPEN & ADAMS, 1981). These standards, however, are extremely expensive and they can be damaged very easily.

The standard is considered thin when its absorption and enhancement effects are negligible, these effects depending mainly on the excitation energy and on the characteristic X-ray energy. Usually, these effects do not occur for standards with superficial density in the 1 to 10 mg.cm<sup>-2</sup> range, containing elements with atomic number between 22 (Ti) and 40 (Zr), when excited with a Cd-109 radioactive source.

The utilization of standards prepared in laboratory with commercially available pure elements or compounds has shown to be efficient for the determination of the elemental sensitivity in X-ray fluorescence systems, because they are cheaper than thin film standards and can be easily acquired.

## MATERIALS AND METHODS

**1. Equipment:** The nuclear instrumentation for the energy dispersive X-ray fluorescence analysis consisted of the Si(Li) semiconductor detector, with a 6.0 mm active diameter and a 5.1 mm sensible thickness, and annular excitation sources of Fe-55 (3.7 GBq) and Cd-109 (0.37 GBq). The pulse spectra were obtained with a multichannel emulation card inserted in a IBM PC AT microcomputer and interpreted with the AXIL software (Analysis of X-Ray Spectra by Iterative Least Squares Fitting, ESPEN *et al.*, 1977).

**2. Standards and samples preparations:** The standards utilized for the elemental sensitivity

determinations were prepared in 2.5 cm diameter pellet form, pressed for 5 minutes at 203 MPa.

The pellets of intermediate standards of Ti, V, Cr, Mn, Cu, Zn, Sr and Zr were prepared by dilution of pure elements or simple compounds, in boric acid, at a ratio of 1:4, obtaining a superficial density around 100 mg.cm<sup>-2</sup>. The compounds were selected in order to avoid the enhancement effect for the X-ray intensities measured.

To evaluate the accuracy of the proposed method, Soil-5/IAEA certified samples were prepared as the standards, in three replications. Two other certified samples, SL-1/IAEA and SARM-4/SABS, were also prepared and analysed.

The measuring time for the standards changed between 300 and 1200 s, however this time can be reduced if the standards are not diluted with boric acid.

The measuring time for the certified samples was fixed to obtain a total significant count, minimizing the deviation of area calculation under the characteristic X-ray peaks. The samples excited by Cd-109 were measured for four hours, and for one hour when excited by Fe-55.

**3. Source-sample-detector arrangement:** A source-sample-detector arrangement was made in transparent acrylic, which is constituted of one base on which the radioactive source and the sample are placed, and one cover, which serves as radiologic protection to the X-rays emitted by the source. Excitation/detection can be performed under vacuum condition, through a vacuum pump coupled to the bottom of the base. The system is placed in the upper part of the vertical cryostat.

The distance between the sample and the detector can be changed by using transparent acrylic spacers. The best distance was obtained using a 0.5cm spacer.

An Al conical collimator was used between the sample and the detector for the Cd-109 excitation to obtain a large beam of emergent radiation and to avoid the interaction of the X-rays emitted by the component elements of the radioactive capsule and detector. This collimator has an external diameter of 22.45 mm and it was placed in the internal diameter of the radioactive source (22.50 mm).

A Cd foil (0.75 mm thickness, 5.6 cm external diameter, with a central hole of 9 mm diameter) was also placed between the detector and the holder to avoid the interaction by Compton

effect of the 88 keV gama radiation emitted by this radionuclide, directly with the detector, which would produce a very high base line (*continuum*).

**4. Absorption correction by the transmission method:** This method is based on the measurement of the X-rays emitted by component elements of a target placed in an adjacent position to the sample. Initially, the fluorescent radiation at several energies emitted by the target (irradiator) was measured and afterwards the target was measured by placing the sample between the excitation source and the target (GIAUQUE *et al.*, 1973). Thus, this method can be used only for the analysis of intermediate samples, transparent to the characteristic X-rays (BERTIN, 1975, p. 624-625) of different origin matrices (biological, geological, etc.).

The sample attenuation of the X-rays produced by the element present in the target is given by:

$$R_i = \frac{I_i^{S+T} - I_i^S}{I_i^T} = \exp(-\chi_i \rho_M D) \quad (7)$$

where:

$R_i$  = sample attenuation of the X-rays produced by the element present in the target, and  
 $I_i^{S+T}, I_i^S$  and  $I_i^T$  = sample X-ray intensities with the target, without the target and only for the target, respectively.

A multielemental thick target, containing V, Mn, Cu, As, Br, Sr and Zr, in pellet form, was also prepared for the transmission measurements. The relationship between the  $\chi_i$  and the energy  $E_i$  of the X-rays is not a simple mathematic function, and its use for estimating  $\chi_i$  values for the other elements not present in the target, but present in the sample, is very difficult. On the other hand, the mathematic function between the mass absorption coefficient  $\mu_M$  and the X-ray energy  $E$  of the different elements is very simple, and can be expressed by the following equation:

$$\mu_M(E) = \alpha E^{\beta} \quad (8)$$

In this way, estimatives of  $\mu_M$  values are searched for the elements contained in the target. Afterwards interpolary values of this function are

performed for the elements contained in the sample. This estimation can be made as follows:

1. the mass absorption coefficient  $\chi_i$  is obtained experimentally for different energies  $E_i$ , through transmission measurements (equation 7):

$$\chi_i = \frac{-\ln R_i}{\rho_M D} \quad (9)$$

2. using  $\alpha$  and  $\beta$  values obtained by linear regression of  $\ln \chi_i$  vs  $\ln E$ . A first estimation of  $\mu_M(E_0)$  (equation 3), is obtained as the mean of the whole experimental points, i.e.:

$$\mu_M(E_0) = \frac{1}{n} \sum (\chi_i - \frac{\alpha E_i^{\beta}}{\sin \phi_2}) \sin \phi_1 \quad (10)$$

3. the next value of  $\mu_M(E_i)$  is calculated by using the estimated value of  $\mu_M(E_0)$  through expression 3;

4. with these values a linear regression between  $\ln \mu_M(E_i)$  and  $\ln E_i$  is estimated, obtaining a new estimation of  $\alpha$  and  $\beta$ , and,

5. through a iterative process, the procedure is repeated from item 2 to item 5, until the difference between two successive values  $\mu_M(E_0)$  is smaller than 1%.

This procedure allows to determine the absorption correction factor for the energy range of 5 to 20 keV, with Cd-109 excitation, and consequently the elemental concentration  $W_i$ , described in the equation 1.

For the energy range of 1 to 5 keV, the absorption coefficient determination, however becomes very difficult, since for this energy range the sample is not transparent to the characteristic X-rays. Therefore, the transmission method can not be applied.

Therefore, another method was developed in order to obtain the total absorption coefficient for the elements of atomic number between 13 and 23 (Al to V), X-ray emitters in the 1 to 5 keV of energy range.

The total absorption coefficient for Fe-55 can be determined through equation 11, using the experimental measurement of the absorption coefficient for Cd-109, energy range of 5 to 20 keV, obtained by the transmission method. This expression was obtained from the equation 3, applied to excitation sources of Fe-55 and Cd-109 (HALLAK & SALEH, 1983).

$$\chi_{Fe}(E_i) = \chi_{Cd}(E_i) \frac{\operatorname{cosec} \phi_2'}{\operatorname{cosec} \phi_2} + \chi_{Cd}(6.0\text{keV}) \frac{\operatorname{cosec} \phi_1'}{\operatorname{cosec} \phi_1} - \chi_{Cd}(22.6\text{keV}) \frac{\operatorname{cosec} \phi_1}{\operatorname{cosec} \phi_2} \cdot \left[ \frac{\operatorname{cosec} \phi_1' + \operatorname{cosec} \phi_2'}{\operatorname{cosec} \phi_1 + \operatorname{cosec} \phi_2} \right] \quad (11)$$

where:  
 $\phi_1'$  and  $\phi_2'$  = incident and emergent angles for Fe-55 excitation and  
 $\phi_1$  and  $\phi_2$  = the same, for Cd-109 excitation.

As for Cd-109 excitation, the total absorption coefficient for Fe-55 excitation can be described by:

$$\chi_{Fe}(E_i) = \psi E_i^\delta \quad (12)$$

where  $\psi$  and  $\delta$  values are determined by the linear regression of  $\ln \chi_{Fe}(E_i)$  vs  $\ln E_i$ .

The elemental concentration determination for this energy range (1 to 5 keV) through Fe-55 excitation can be obtained by an iterative procedure, the total mass absorption coefficient values being associated to absorption jumps, taken into consideration.

The figure 1 shows a simplified scheme of iterative procedure steps, used to calculate the absorption jumps and the absorption correction factor, in order to determine the elemental concentration of the samples excited by Fe-55.

A summary of this procedure is:

1. the  $\chi_{Fe}(EK_{abs})$  value of the element i is determined by equation 12; this value corresponds to the upper edge of the absorption jump,  $\sigma_u$ ;
2. the  $\chi_i(E_i)$  value of the element i is determined by equation 12 and the  $A_i(E_i)$  value is calculated using equation 2;
3. the uncorrected concentration  $W_{oi}$  of the element i is calculated by equation 13 and the corrected concentration  $W_{li}$  determined by equation 14:

$$W_{oi} = \frac{I_i}{S_i (\rho_M D)} \quad (13)$$

$$W_{li} = \frac{W_{oi}}{A_i(E_i)} \quad (14)$$

4. the lower edge of the absorption jump  $\sigma_{Li}$  was determined using the equation:

$$\sigma_{Li} = \sigma_u \left[ 1 - W_{li} \left( 1 - \frac{1}{J_k} \right) \right] \quad (15)$$

5. an analogous relation to equation 12 was obtained, having the same inclination  $\delta$  and crossing by  $\sigma_{Li}$ ;

6. new values of  $\chi_2(E_i)$  and  $A_2(E_i)$  were determined as in step 2, and steps 3 and 4 were repeated to determine  $\sigma_{L2}$ ;

7. in the iterative process, steps 2 to 5 were repeated until the difference of two successive values of  $\sigma_L$  is smaller than 1%, and

8. at this stage  $A(E_i)$  and  $W_i$  values are calculated and the procedure is repeated for the next element i.

Two programs in Basic language were developed in order to facilitate the iterative procedures described above, for Cd-109 and Fe-55 excitations (SIMABUCO, 1993).

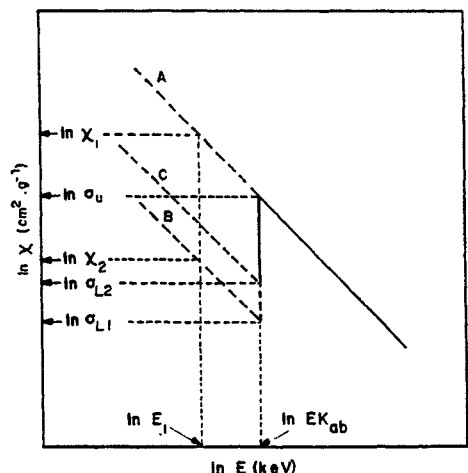


Figure 1. Schematic representation of the iterative procedure for Fe-55 excitation, used to calculate the edge absorption and the absorption correction factor.

TABLE 1. Experimental sensitivity  $S_1^{exp}$  ( $cm^2 \cdot g^{-1} \cdot s^{-1}$ ), detector efficiency  $\epsilon_1$  (adimensional), fundamental parameters constant  $K_1$  ( $cm^2 \cdot g^{-1}$ ) and calculated sensitivity  $S_1^{calc}$  ( $cm^2 \cdot g^{-1} \cdot s^{-1}$ ), for Fe-55 excitation.

Element	$S_1^{exp}$	$\epsilon_1$	$K_1$	$S_1^{calc}$
Al	$4.23 \times 10^4$	0.3977	2.8735	$5.47 \times 10^4$
Si	$9.74 \times 10^4$	0.5620	5.0453	$1.36 \times 10^5$
P	————	0.6496	7.7071	$2.40 \times 10^5$
S	$4.56 \times 10^5$	0.7243	11.4661	$3.98 \times 10^5$
Cl	————	0.7918	16.0842	$6.11 \times 10^5$
K	$1.18 \times 10^6$	0.8811	31.3367	$1.32 \times 10^6$
Ca	$2.32 \times 10^6$	0.9097	43.7827	$1.91 \times 10^6$
Sc	————	0.9317	54.0554	$2.41 \times 10^6$
Ti	$3.95 \times 10^6$	0.9476	70.0457	$3.18 \times 10^6$
V	$4.06 \times 10^6$	0.9595	86.7133	$3.99 \times 10^6$

## RESULTS AND DISCUSSION

In order to obtain the average geometry factor, the sensitivities (equation 1) were determined experimentally through the measurement of standards diluted in boric acid.

For the elements not contained in the standards the sensitivity was evaluated for the desired energy range, with Fe-55 and Cd-109 excitation, and the results are presented in TABLES 1 and 2, respectively.

The average geometry factor  $G$ , obtained with the average of the individual geometry factors  $G_i$ , was  $4.79 \times 10^4$  and  $1.14 \times 10^4 s^{-1}$ , for Fe-55 and Cd-109 excitations, respectively.

In the TABLES 1 and 2 it can be observed that the detector efficiency for the two excitation sources differ considerably. This difference occurs mainly because when Fe-55 excitation was used, the system was operated under vacuum condition, in order to reduce the absorption of the characteristic X-ray in the path length between the sample and the detector. The Cd-109 excitation, was not performed under vacuum. Figures 4 and 5 show the spectra of the certified standard sample Soil-5, using Fe-55 and Cd-109 excitations, respectively.

In Figure 2, the relationship of the detector efficiency and the atomic number, for Fe-55 and Cd-109 excitations is shown, presenting a good correlation. The same can be observed in

Figure 3, for the relationship of the calculated sensitivity and the atomic number.

TABLE 3 presents the results of average elemental concentrations, calculated with three replications, and their deviations, in comparison to certified values of the standard sample Soil-5 and their deviations, furnished by IAEA. The results for the certified standard samples SL-1 and SARM-4 are shown in TABLES 4 and 5, respectively.

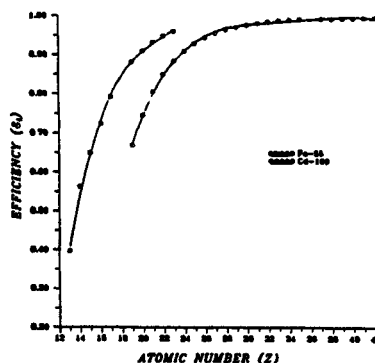


Figure 2. Relationship between atomic number  $Z$  and detector efficiency  $\epsilon_1$ , for Fe-55 and Cd-109 excitations.

The variation associated to the certified values are relative to the average standard deviation ( $s/\sqrt{N}$ ), while for the measured values are related to standard deviations ( $s$ ).

TABLE 2. Experimental sensitivity  $S_i^{exp}$  ( $cm^2 \cdot g^{-1} \cdot s^{-1}$ ), detector efficiency  $\epsilon_i$  (adimensional), fundamental parameters constant  $K_i$  ( $cm^2 \cdot g^{-1}$ ) and calculated sensitivity  $S_i^{calc}$  ( $cm^2 \cdot g^{-1} \cdot s^{-1}$ ), for Cd-109 excitation.

Element	$S_i^{exp}$	$\epsilon_i$	$K_i$	$S_i^{calc}$
K	$4.87 \times 10^3$	0.6686	0.7281	$5.55 \times 10^3$
Ca	$7.81 \times 10^3$	0.7450	1.0474	$8.90 \times 10^3$
Sc	-----	0.8044	1.3284	$1.22 \times 10^4$
Ti	$1.81 \times 10^4$	0.8492	1.7550	$1.70 \times 10^4$
V	$2.26 \times 10^4$	0.8832	2.2744	$2.29 \times 10^4$
Cr	-----	0.9089	2.9974	$3.11 \times 10^4$
Mn	$4.13 \times 10^4$	0.9285	3.7432	$3.96 \times 10^4$
Fe	-----	0.9434	4.7149	$5.07 \times 10^4$
Co	-----	0.9548	5.7247	$6.23 \times 10^4$
Ni	-----	0.9636	7.1731	$7.88 \times 10^4$
Cu	$9.30 \times 10^4$	0.9704	8.1905	$9.06 \times 10^4$
Zn	$1.23 \times 10^5$	0.9757	9.6512	$1.07 \times 10^5$
Ga	-----	0.9800	10.8332	$1.21 \times 10^5$
Ge	-----	0.9833	12.3112	$1.38 \times 10^5$
As	-----	0.9860	14.0603	$1.58 \times 10^5$
Se	-----	0.9882	15.3340	$1.73 \times 10^5$
Br	-----	0.9899	17.5654	$1.98 \times 10^5$
Rb	-----	0.9908	21.4358	$2.42 \times 10^5$
Sr	$2.72 \times 10^5$	0.9910	23.7378	$2.68 \times 10^5$
Y	-----	0.9917	26.0951	$2.95 \times 10^5$
Zr	$3.12 \times 10^5$	0.9927	28.2312	$3.19 \times 10^5$
Nb	-----	0.9935	31.0970	$3.52 \times 10^5$
Mo	-----	0.9942	38.1377	$4.32 \times 10^5$

With regard to accuracy of the proposed method, it was observed that Si was the element that showed the highest relative error. This is probably due to the non homogeneity of the sample

during its preparation, since this standard was simply mixed to boric acid and pressed to a pellet form, without receiving additional crushing and sieving.

TABLE 3. Elemental concentration of the standard sample Soil-5, obtained by the proposed method, using Fe-55 and Cd-109 excitations.

Element	Measured $\pm$ deviation	Certified $\pm$ deviation	Error (%)
Al	5.70 $\pm$ 0.58%	8.19 $\pm$ 0.28%	-30
Si	13.01 $\pm$ 0.49%	33.00%*	-60
K	1.56 $\pm$ 0.04%	1.86 $\pm$ 0.15%	-16
Ca	1.89 $\pm$ 0.05%	2.20%*	-14
Ti	0.41 $\pm$ 0.01%	0.47%*	-13
V	221 $\pm$ 45ppm	151ppm*	+46
Mn	1077 $\pm$ 13ppm	852 $\pm$ 37ppm	+26
Fe	4.78 $\pm$ 0.07%	4.45 $\pm$ 0.19%	+7
Cu	85 $\pm$ 8ppm	77.1 $\pm$ 4.7ppm	+10
Zn	376 $\pm$ 3ppm	368 $\pm$ 8.2ppm	+2
As	79 $\pm$ 3ppm	93.9 $\pm$ 7.5ppm	-16
Rb	185 $\pm$ 1ppm	138 $\pm$ 7.4ppm	+34
Sr	430 $\pm$ 10ppm	330ppm*	+31
Zr	363 $\pm$ 12ppm	221ppm*	+19

(\*) Not certified values

TABLE 4. Elemental concentration of the standard sample SL-1, obtained by proposed method, using Fe-55 and Cd-109 excitations.

Element	Measured value	Certified value	Error (%)
Al	8.79%	8.9%**	+1
Si	13.47%	---	---
S	0.074%	1.2%*	-38
K	0.980%	1.5%*	-35
Ca	0.350%	0.25%*	+40
Ti	0.424%	0.517%	-18
Mn	0.328%	0.346%	-5
Fe	5.770%	6.74%	-14
Zn	260ppm	223ppm	+16
Rb	188ppm	133ppm	+41
Sr	55ppm	80ppm*	-31
Zr	205ppm	241ppm*	-15

(\*) Not certified value

(\*\*) Only laboratory value



TABLE 5. Elemental concentration of the standard sample SARM-4, obtained for the proposed method, using Fe-55 and Cd-109 excitations.

Element	Measured value	Certified value	Error (%)
Si	29.60%	24.61%	+20
K	0.16%	0.21%	-24
Ca	9.89%	8.22%	+20
Ti	0.12%	0.12%	0
V	346ppm	220ppm	+57
Mn	0.19%	0.14%	+36
Fe	6.22%	6.27%	-1
Ni	97ppm	120ppm	-19
Zn	65ppm	68ppm	-4
Sr	275ppm	260ppm	+6
Zr	29ppm	23ppm*	+26

(\*) Not certified value

The sensitivity decreases exponentially with the reduction of the atomic number, for the range of superficial density obtained for the pellets. For elements with atomic number below 22 (Ti), the sample became too thick which explains the errors obtained for these lower atomic number elements.

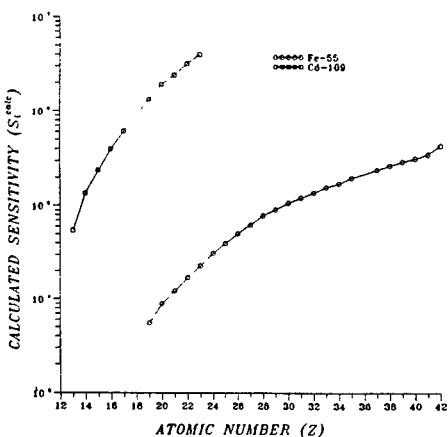


Figure 3. Relationship between atomic number Z and calculated sensitivity  $S_i^{calc}$ , for Fe-55 and Cd-109 excitations.

For the standard samples Soil-5 and SARM-4 the element presenting a significant error was V. This error could be assigned to the interference of the Ti  $K_{\beta}$  X-ray spectral line (present at % level) on V  $K_{\alpha}$  (present at ppm level), leading to an error in the estimate of the net areas of this element and consequently in its elemental concentration.

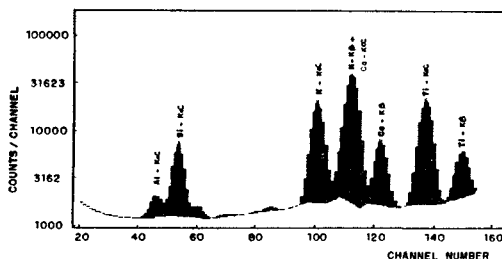


Figure 4. Characteristic X-ray pulse spectrum of the standard sample Soil-5, with Fe-55 excitation.

The method presents a relative error of the order of 20% for the other elements, values close to the errors cited in literature.

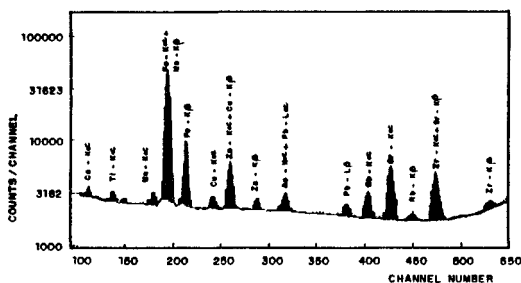


Figure 5. Characteristic X-ray pulse spectrum of the standard sample Soil-5, with Cd-109 excitation.

Elements present in the sample SL-1 were in higher discrepancy in relation to certified values were S, K and Ca.

### CONCLUSIONS

The determination of elemental sensitivity of the X-ray fluorescence system by dispersive energy and radioisotopic excitation, based on the fundamental parameters method, can be performed in a practical and inexpensive way, using standards prepared in the laboratory, from pure commercially available chemical compounds (salts, oxides, etc), diluted with boric acid.

The transmission method used for Cd-109 excitation, associated to the absorption jumps in the Fe-55 excitation, showed to be suitable for the absorption effect corrections.

It is possible to evaluate instrumentally and simultaneously the concentrations of Al, Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn, As, Rb, Sr and Zr in soil samples, using Fe-55 and Cd-109 radioactive sources.

This method can also be applied to geological samples, which present problems for conventional chemical analysis, due to the difficulties in sample digestion for further determination of some elements, e.g., Zr.

The accuracy is of the order of 20% for the elements with atomic number between 13 and 40 (Al to Zr), with exception to Si, S, K, Ca and V, depending on the type of the sample.

The precision of the proposed method, is inferior to 5% for the majority of the elements, what can be considered as good for the analysis of geological samples.

The great advantage of this technique consists in a simultaneous quantitative analysis of several elements in solid samples, without the need of pre-treatment or pre-concentration.

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