

**STUDY OF THE FUNDAMENTAL PARAMETERS OF X-RAY
FLUORESCENCE AND ITS IMPLICATIONS IN THE QUANTIFICATION OF
THIN AND THICK SAMPLES**

E. S. Galvão^a, C. A. R. Neto^a, R. C. Feroni^b.

^a*Departamento de Física, Universidade Federal do Espírito Santo, Vitória, Brazil.*

^b*Departamento de Engenharias e Tecnologia, Universidade Federal do Espírito Santo, São Mateus, Brazil.*

ABSTRACT

X-ray fluorescence (XRF) has been widely used in the analysis of the inorganic/metallic composition of samples in the most diverse areas of science. Among some aspects of the XRF principle, X-ray Fluorescence by Dispersive Energy (EDXRF) stands out, due to its low analytical cost, analytical simplicity and the almost non-existent need of preparation and manipulation of the samples previous the analysis. Several variables are related to the fundamental parameters, the method used to quantify the elemental composition of samples analyzed by XRF, as a way of correcting matrix effects that occur inside the samples. Since studied the variables influencing the matrix effect, an adequate form of quantification of the samples can be performed by means of the construction of calibration curves. In the present study, calibration curves were made for the quantification of samples analyzed by EDXRF, using calibration standards with elements deposited in Mylar® films, for 32 elements varying from Na ($Z = 11$) to Nd ($Z = 60$). All analyses were performed on a Shimadzu spectrophotometer, model EDX-720/800HS. The results show the quality of the curves obtained for elements separated by groups of atomic number, in which the curves presented coefficients R equal or superior to 0.89.

RESUMO

A fluorescência de raios X (XRF) tem sido amplamente utilizada em análises da composição inorgânica/metálica de amostras nas mais diversas áreas da ciência. Entre algumas vertentes do princípio da XRF, destaca-se a Fluorescência de Raios X por Energia Dispersiva (EDXRF), devido seu baixo custo analítico, simplicidade analítica e a quase inexistente necessidade de preparação e manipulação das amostras previamente as análises. Diversas são as variáveis relacionadas aos parâmetros fundamentais, método utilizado para a quantificação da composição elementar de amostras analisadas por XRF, como forma de corrigir efeitos de matriz que ocorrem no interior das amostras. Uma vez estudadas as variáveis que influenciam no efeito matriz, uma forma adequada de quantificação das amostras pode ser realizada por meio da construção de curvas de calibração. No presente estudo, foi realizada a construção de curvas de calibração para a quantificação de amostras analisadas por EDXRF, utilizando padrões de calibração com elementos depositados em filmes de Mylar®, para 32 elementos variando de Na ($Z=11$) ao Nd ($Z=60$). Todas as análises foram realizadas em um espectrofotômetro Shimadzu, modelo EDX-720/800HS. Os resultados mostram a qualidade das curvas obtidas para elementos separados por grupos de número atômico, nas quais as curvas apresentaram coeficientes R iguais ou superiores a 0,89.

INTRODUCTION

X-ray fluorescence (XRF) began in the 1950s, during studies of the chemical composition of conventional metallic alloys such as stainless steels and Ni alloys.^[1] Recently, XRF has been widely used in engineering, being applied to the studies of superconductors, metallic thin films, biomaterials, geology, environment, forensic and biomedical.^[2]

The XRF technique consists in inducing electronic transitions to occur the emission of characteristic X-rays, which are separated according to their energy, which is characteristic of each element and its atomic number, and then, are identified and quantified.^[3,4]

The identification of characteristic X-ray can be done by two main techniques: Wavelength Dispersive X-Ray Fluorescence (WDXRF) and Energy Dispersive X-Ray Fluorescence (EDXRF). The characteristic X-ray intensities (numbers of photons detected per unit time) are related to the concentrations of elements in the sample.^[5]

EDXRF technique can achieve detection limits comparable to other techniques, such as atomic absorption or emission spectrometry (AAS, ICP-OES), although its low analytical cost, minimum sample handling, and the dispensability of digestion of the samples make the EDXRF a better cost-effective technique.^[6,7]

As a way of solving the problem of detection limits, some parameters require great attention and control. Among the main parameters are the voltage and current of the excitation source, the X-ray tube and the absorption factor of the radiation by the sample.^[8]

Quantitative analyzes by XRF are based on the correlation of the fluorescent intensities of the elements in the sample with their respective concentrations. Each atom of a given element i has the same probability of being excited by a primary beam of photons and, therefore, a linear relation of the intensity of the characteristic X-rays is expected, according to Equation (1),^[9]

$$I_i = K_i \times W_i \quad (1)$$

where: I_i is the intensity of the fluorescent radiation of the element i ; W_i is the fraction of the element in the sample; and K_i is the proportionality constant.

The proportionality constant K_i depends on factors such as the intensity of the primary beam, the probability of the atom emitting characteristic radiation and the probability of the photons emitted by the atom being detected.^[9] Therefore, the concentration of the element i can be determined by measuring the intensity of the fluorescent X-rays from a sample containing only the element i . However, the samples may contain several elements and, therefore, the ratio of the characteristic X-ray intensity is not linear with the concentrations due to the matrix effects.^[9] All fluorescence techniques can present interferences influencing fluorescent intensity that is caused by matrix-effect that is associated with an attenuation of both primary and fluorescent radiation within the sample.^[10]

Considering a homogeneous sample with thickness D and neglecting enhancement effects, the intensity of the line K_α ($I_i E_i$) of an element produced in a layer dx at depth x (Figure 1) is a product of three probabilities: (i) probability of the incident radiation reaches a depth x of the sample (P_1), according to Equation (2); (ii) the probability of emission of X-ray photons characteristic of the K-line emitted by a sample (P_2), according to Equation (3); and (iii) the probability of the characteristic X-ray photons reaching the detector, not being absorbed by the sample (P_3), according to Equation (4).^[5]

$$P_1 = e^{\left(\frac{-\mu_0 \cdot x \cdot \rho_0}{\sin \theta_0}\right)} \quad (2)$$

Where: μ_0 is the mass absorption coefficient of the matrix ($\text{cm}^2 \cdot \text{g}^{-1}$); ρ_0 is the density of the matrix ($\text{g} \cdot \text{cm}^3$); and θ_0 is the angle of incidence between the direction of the incident beam and the surface of the sample.

$$P_2 = \tau \cdot \omega \cdot \left(1 - \frac{1}{j}\right) \cdot f \cdot \rho \cdot dx \quad (3)$$

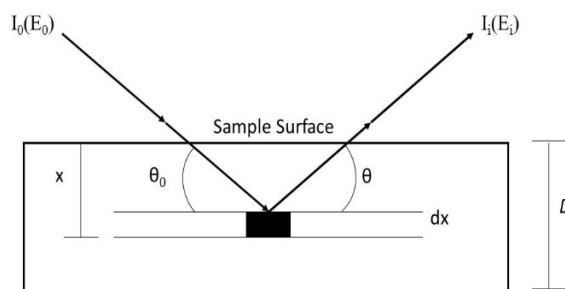


Figure 1. Excitation geometry for monoenergetic beam in ray fluorescence.

Source: Adapted from Nascimento, 1999.^[5]

Where: τ is the mass absorption coefficient ($\text{cm}^2 \text{g}^{-1}$) for the photoelectric effect of the element in the excitation energy; ω is the fluorescence yield of layer K ; j is the jump ratio between the layers ($L \rightarrow K$); f is the fraction of photons K emitted as K_α rays; ρ is the concentration of the element on a per unit volume basis of layer dx (g.cm^{-3}).

$$P_3 = \varepsilon \cdot e^{\left(\frac{-\mu_0 \cdot x \cdot \rho_0}{\sin \theta_0}\right)} \quad (4)$$

Where: ε is the detector efficiency.

The fluorescence intensity dl produced by an element contained in the depth layer dx can be written by Equation (5),

$$dl = G \cdot e^{\left(\frac{-\mu_0 \cdot x \cdot \rho_0}{\sin \theta_0}\right)} \cdot \tau \cdot \omega \cdot \left(1 - \frac{1}{j}\right) \cdot f \cdot \rho \cdot dx \cdot \varepsilon \cdot e^{\left(\frac{-\mu_0 \cdot x \cdot \rho_0}{\sin \theta_0}\right)} \quad (5)$$

where: G is the proportionality constant, dependent on the geometric arrangement of the excitation-detection system and the current of the X-ray tube.

The fluorescence intensity dl can also be written as a function of the coefficient of absorption of total mass χ and variable K , both related to the fundamental parameters,^[5] according to Equations (6), (7) and (8). Integrating Equation (8), as a function of the total thickness of sample D gives the fluorescence intensity I (counts.s^{-1}), according to Equation (9).

$$\chi = \frac{\mu_0}{\sin \theta_0} + \frac{\mu}{\sin \theta} \quad (6)$$

$$K = \tau \cdot \omega \cdot \left(1 - \frac{1}{j}\right) \cdot f \quad (7)$$

$$dl = G \cdot \varepsilon \cdot K \cdot e^{(-\chi \cdot \rho_0 \cdot x)} \cdot \rho \cdot dx \quad (8)$$

$$I = \frac{G \cdot \varepsilon \cdot K \cdot \rho}{\chi \cdot \rho_0} \cdot (1 - e^{(-\chi \cdot \rho_0 \cdot D)}) \quad (9)$$

The density of the element in relation to the density of the matrix (ρ/ρ_0) is the concentration C of the element of interest, so we can rewrite Equation (9), according to (10).

$$I = \frac{G \cdot \varepsilon \cdot K \cdot C}{\chi} \cdot (1 - e^{(-\chi \cdot \rho_0 \cdot D)}) \quad (10)$$

Considering Equation (11) related to the sensitivity (S) of the X-ray spectrometer, it is possible to rewrite Equation (10), according to (12).

$$S = G \cdot \varepsilon \cdot K \quad (11)$$

$$I = S \cdot C \cdot \frac{(1 - e^{(-\chi \cdot \rho_0 \cdot D)})}{\chi} \quad (12)$$

The last term on the right-hand side of Equation (12), $\frac{(1 - e^{(-\chi \cdot \rho_0 \cdot D)})}{\chi}$, represents the absorption factor (A), which can vary depending on the thickness of the sample, where $A = 1$ for thin samples, and $A = \frac{1}{\chi \cdot \rho_0 \cdot D}$ for thick samples. Thin samples are those with a thickness of less than 100 μm .^[11]

Given the context, it is imperative that previously the analysis of materials by XRF techniques, the user has notions of the physical characteristics of their samples, such as particle size and sample thickness. Thus, the present work aims to present a method of constructing calibration curves for analysis of fine samples using the EDXRF technique.

MATERIALS AND METHODS

Calibration curves for the analysis of thin samples were constructed using a set of XRF standards for 32 different elements ranging from sodium (Na; $Z=11$) to neodymium (Nd; $Z=60$). All standards have purity higher than 99.9% (Micromatter Technologies Inc., Canada).^[12] Standard elements are available deposited on Mylar film from 3.5 to 6.3 μm of thickness and 25 mm in diameter.

The analyzes were conducted on an EDXRF spectrometer, model EDX-720/800HS (SHIMADZU, Japan),^[11] (Figure 2). This model is equipped with a Rhodium (Rh) X-ray tube with a voltage of 50 kV, a tube current of 500 to 1000 μA , a collimator of 10 mm and an integration time of 1000 s per channel. Two channels of analysis are responsible for scanning from Na to U, one for scanning from Na to Sc and another one scanning from Ti to U. All analyzes were performed under vacuum.



Figure 2. EDX-720/800H (Shimadzu, Japan).

The limits of detection (LD) for each element were calculated according to Equation (13), as proposed by Bertin (1975).^[3]

$$LD = \frac{\sqrt[3]{\frac{BG}{t}}}{S} \quad (13)$$

Where: BG is the intensity (cps) of the continuum under the analyte peak; t the excitation/detection time (s); and S is the elementary sensitivity of the analyte ($\text{cps} \cdot \text{g}^{-1} \cdot \text{cm}^2$).

Thus, because they are fine samples, Equation (12) can be written as $S = \frac{I}{C}$. Given the sensitivities (S) of the equipment for each of the elements i of interest, it is possible to calculate the concentrations of the elements of interest (C), even in samples constituted by several elements.

RESULTS

For better mathematical adjustment of the calibration curves, the 32 standards were separated into 5 classes, ordered by their atomic number. The classes and their respective mathematical adjustments are shown in Table 1. For all calibration curves, the Pearson correlation coefficients (R) were equal to or greater than 0.89.

Table 1. Equation of the calibration curves as a function of the atomic number (Z).

Elements of Atomic Num. (Z)	Equação da Sensibilidade ($\text{cps} \cdot \mu\text{g}^{-1} \cdot \text{cm}^2$)	R
11 to 20	$-0.0069x^2 + 0.2217x - 1.6125$	0.89
21 to 30	$-0.012x^2 + 0.6376x - 7.9796$	0.89
31 to 40	$-0.0194x^3 + 2.0653x^2 - 73.135x + 861.99$	1.00
41 to 50	$-8\text{E-}05x^5 + 0.0164x^4 - 1.3904x^3 + 58.61x^2 - 1225.6x + 10157$	1.00
51 to 60	$-0.0012x^3 + 0.1953x^2 - 10.745x + 196.55$	0.99

Figures 3a to 3e show the sensitivity curves (S) as a function of the atomic number (Z) of the elements of interest.

The results show, through the correlation coefficients R , that the adjustments of the curves were satisfactory. Therefore, the 5 calibration curves made by the calculation of the sensitivities (S) for each standard can extrapolate this result for the quantification of other elements that do not have their own standards. It is worth mentioning that such curves only apply statistically to the range of Z greater or equal than 11 and less or equal than 60.

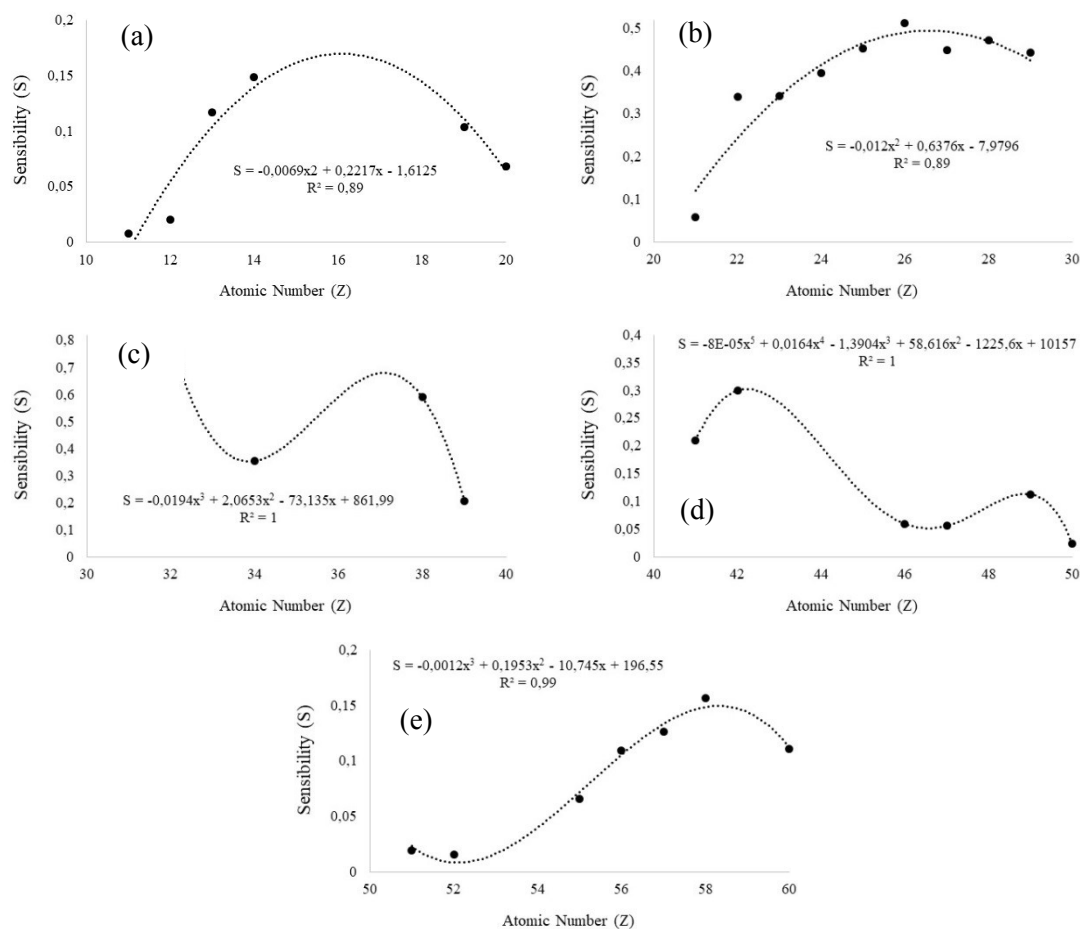


Figure 3. Sensitivity graphs for an element i in relation to the atomic number (Z): (a) $11 \leq Z \leq 20$; (b) $21 \leq Z \leq 30$; (c); $31 \leq Z \leq 40$; (d); $41 \leq Z \leq 50$; (e); $51 \leq Z \leq 60$.

CONCLUSION

X-Ray Fluorescence Spectrometry is a dynamic and useful tool for the quantitative and qualitative determination of the elements in a wide variety of samples. However, it demands the operator knows the physical aspects related to the technique, in order to minimize possible errors during the quantification of the elements due to matrix effects.

The identification of adequate absorption factors will provide correct sensitivity coefficients, minimizing possible quantification errors of the chemical composition of multielement samples.

The quantification of samples analyzed by XRF can be performed by constructing calibration curves, from standard materials, to be deposited in films (thin samples) or in bulk media (thick samples). However, the calculation method shall take into account the appropriate absorption factor.

According to the results presented in this work, the construction of calibration curves by the fluorescence technique, based on the grouping by atomic number, promotes a better mathematical adjustment of the curves, improving the statistical quality of the quantification of elements that possess or not their own calibration standards, within the range studied.

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