



Technical Note

Determination of X-ray excitation spectra in micro X-ray fluorescence spectrometry with capillary optics



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ABSTRACT

The quantitative X-ray fluorescence microanalysis by fundamental parameters requires the knowledge of the energy distribution of the excitation beam. When this beam is produced by capillary optics, its high intensity and anisotropy complicate a direct determination. An alternative is an indirect determination based on measurement of induced X-ray fluorescence in a set of targets. In this work the X-ray excitation spectrum is determined by an iterative deconvolution process of the fundamental parameter expression for the X-ray fluorescence intensities. The method has the advantage that it does not require any assumption about the energy distribution of the X-ray source or the energy dependence of the lens transmission. Numerous XRF targets of pure elements with emission lines covering the full energy range of the X-ray source are employed. The only requirement on the targets is a high homogeneity in its composition. In fact, it does not impose any condition on the sample thickness. The accuracy observed in the validation process implemented with reference materials is similar to that reported with alternative approaches: 5% for main components, 10% for minor elements and 15% for trace elements.

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1. Introduction

The X-ray fluorescence (XRF) from a bulk sample has a non-linear dependence with element concentrations because of the so called matrix effects which particularly affect the quantitative analysis by microanalysis of X-ray fluorescence (micro-XRF) [1,2]. A possibility to correct matrix effects consists in the comparison of the X-ray fluorescence emission with a set of standards of similar composition to that of the investigated object [3]. Another possibility consists in the application of the Fundamental Parameter model (FP) which requires few calibration standards for the quantification of a wide range of matrices [2,4]. This method was used in this work because of its versatility.

There exists a set of analytical equations in FP that describe the physical processes in the sample that lead to the emission of XRF. It requires a database of fundamental parameters, like photo ionization cross sections, fluorescence yields and transition probabilities; and also the spectral distribution of the excitation radiation. In case of polychromatic tube excitation combined with a capillary lens, the energy spectral distribution of the excitation radiation cannot be measured directly at the focal spot of the optical component because of the high flux in the output. One could increase the distance between the detector and the lens as to reduce the photon flux but since the photon flux is anisotropic, a partial determination of the excitation spectrum would be obtained. For all above, an indirect measurement of the energy spectral

distribution of the excitation radiation is preferable. The methods available can be classified into two groups according to the measurements required: one group employs X-ray scattering [5,6] and the other induced X-ray fluorescence in targets [7–10]. All of them have been validated by means of elemental quantification of certified reference materials. The accuracy of these approaches has been estimated by comparing the similarity in concentrations with certified values. Some approaches adopt assumptions for the energy profile of the excitation spectrum which require a previous deduction from experimental means [8–10]. In the Rossinger approach [10], this energy profile is approximated by a suitable model function with free parameters. Its type is suggested by the assumed behaviour known from a spectrum of scattered primaries. If this previous step is solved, then the Rossinger approach becomes a possible alternative to determine the excitation spectrum for spectrometers with capillary optics.

The method by X-ray scattering employs light matrices to characterize the excitation spectrum. A good precision for high energy photons can be obtained because in this regimen multiple scattering effects on the target can be neglected. The reported accuracy of the approach proposed by Padilla et al. [6] is better than 15% for major and minor elements in homogeneous samples (glasses, ceramics).

One of the earliest methods using X-ray fluorescence induced in targets was developed by Delgado et al. [7]. It consists in the measurement of the X-ray fluorescence intensity for several thick targets as to cover the emission energy interval of the X-ray source. The method has the advantage that it does not require any assumption about the emission

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spectrum of the X-ray source. The accuracy was tested in samples containing only two components and the reported accuracy was less than 10%. The accuracy can be improved by adding more XRF lines in the energy interval of the X-ray source. A drawback of this method is that the quantity obtained is the cumulative spectral distribution (which is the integral of the X-ray spectral distribution). It means that a reformulation of the quantification procedures is required in order to write the FP equations as a function of the cumulative spectral distribution.

A more recent methodology consists of the measurement of the $K\alpha$ X-ray fluorescence intensity of several thin targets as to cover the emission energy interval of the X-ray source [8]. It obtains the transmission of the lens assuming an energy dependence of the transmission function and applying the second mean value theorem. In addition, this method requires the input of the X-ray tube spectrum, but to obtain it requires dismounting the lens at least one time for an experimental determination or the employment of a theoretical model. The reported accuracy of this method for major and minor elements is less than 10%.

In the present work this last methodology was expanded to obtain the excitation spectrum for micro-XRF including the two main advantages of Delgado's approach *i.e.* the employment of robust thick targets and the lack of assumptions on the physical characteristics of the X-ray source. The proposed approach is described in detail and applied to characterize the X-ray source of our laboratory. Validation by means of quantitative analysis of several standard materials is also shown.

2. Theoretical background

2.1. Micro-XRF intensity

In this work the geometry 45° – 45° for micro-XRF was assumed for the theoretical descriptions since it was employed in the experimental measurements and is most usually implemented in micro-XRF spectrometers. Thus the incident beam and the detected beam form 90° between them and 45° with the sample. In addition the XRF targets were considered infinitely thick as to robustify the calibration approach. However the proposed approach is valid for any micro-XRF configuration, (e.g. other incident angles, emergent angles, or sample thickness). The fundamental parameter model applied to our micro-XRF setup gives rise to the following mathematical expression for the XRF photon flux of an element i :

$$N_i = \int_{E_{Bi}}^{E_{max}} \frac{dN_0}{dE}(E) K(E_{Fi}, E) dE \quad (1)$$

where dN_0/dE is the energy distribution of the excitation beam and K is the kernel of the equation given by:

$$K(E_{Fi}, E) = \frac{\Delta\Omega}{4\pi} \epsilon(E_{Fi}) e^{-\mu_{air}\rho_{air}t} \frac{\sqrt{2} C_i a_i(E)}{(\mu(E_{Fi}) + \mu(E))} (1 + H_i) \quad (2)$$

$$\text{with } a_i(E) = \sigma_i(E) \omega_i p_i \left(1 - \frac{1}{j_i}\right).$$

The nomenclature used in the above equations is summarized in Table 1. In the particular case in which an X-ray tube is employed as the photon source, the spectral energy distribution is composed of a continuous curve produced by the bremsstrahlung effect, and several discrete lines which are the characteristic radiation lines of the anode material. For the sake of simplicity both parts of the spectrum will be determined separately.

2.2. Characteristic radiation

The discrete lines of the characteristic radiation produced by an X-ray tube can be indirectly determined analyzing the dispersion in a thin light matrix. Each of them produces two new lines in the scatter

Table 1

Definition of the parameters employed in Section 2.

N_i	XRF photon flux emitted by element i .
E_{Bi}	Absorption edge for XRF emission of element i .
E_{max}	Maximum energy of the excitation spectrum.
E_{Fi}	Energy of the XRF emission of element i .
$dN_0/dE(E)$	Energy distribution at energy E of the excitation spectrum.
$\Delta\Omega$	Solid angle subtended by the detector.
$\epsilon(E)$	Detector efficiency at energy E .
μ_{air}	Mass attenuation coefficient for air at energy E_{Fi} .
ρ_{air}	Mass density of air.
t	Path length in air of the detected photon beam.
C_i	Mass fraction of element i in the sample.
$\sigma_i(E)$	Mass photoelectric coefficient of element i at energy E .
ω_i	Fluorescence yield for the excited shell of element i .
p_i	Line fraction of the element i .
j_i	Jump ratio for the excited shell of element i .
$\mu(E)$	Mass attenuation coefficient of the sample at energy E .
H_i	Contribution of the secondary excitation on the XRF emission of element i .

spectrum, one at the same energy by Rayleigh effect and other at slightly smaller energy by Compton effect. For a thin target of thickness d the FP model predicts similar descriptions for the intensity of both lines. If the photons of a characteristic line of energy E_L and intensity N_{0L} are scattered by one of the previous processes then the photon flux of the scattered beam can be written as:

$$N_{Ls} = S(E_{Ls}, E_L) N_{0L} \quad (3)$$

where E_{Ls} is the energy of the scattered line and S is a function similar than the kernel K given by:

$$S(E_{Ls}, E_L) = \frac{\Delta\Omega}{4\pi} \epsilon(E_{Ls}) e^{-\mu_{air}\rho_{air}t} \sqrt{2} \frac{d\sigma}{d\Omega}(E_L) \frac{[1 - \exp(-(\mu(E_{Ls}) + \mu(E_L))\sqrt{2} \varrho d)]}{(\mu(E_{Ls}) + \mu(E_L))}. \quad (4)$$

Here $d\sigma/d\Omega$ represents the differential cross section for coherent or incoherent scattering evaluated for a scattering angle of 90° according to the selected discrete line. In the particular case of the Rayleigh line the function S adopts a simpler form since $E_L = E_{Ls}$:

$$S(E_L, E_L) = \frac{\Delta\Omega}{4\pi} \epsilon(E_L) e^{-\mu_{air}\rho_{air}t} \sqrt{2} \frac{d\sigma}{d\Omega}(E_L) \frac{[1 - \exp(-2\sqrt{2}\mu(E_L) \varrho d)]}{2\mu(E_L)}. \quad (5)$$

Previous equations were derived assuming single scattering in the sample which means that the thickness d of the sample is small enough to neglect higher order interactions. Mathematically,

$$d \ll \frac{1}{\mu(E_L)}. \quad (6)$$

This means that the thickness d is much smaller than the mean free path of the radiation. From the Eq. (3), it is possible to calculate the photon flux for every characteristic line fitting the coherent and/or incoherent scattering lines and evaluating the S function. A specific Monte Carlo simulation program developed in FORTRAN language was employed for a precise evaluation of the S function. It requires the input of the excitation beam cross section, the thickness of the sample, its composition, the distance sample-detector, and the dimensions of the detector collimator.

2.3. Continuous spectrum

The FP model allows calculating the contribution N_{ci} of the continuous part of the excitation spectrum to the XRF photon flux of an element

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