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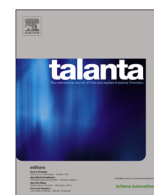

Direct deconvolution approach for depth profiling of element concentrations in multi-layered materials by confocal micro-beam X-ray fluorescence spectrometry

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ABSTRACT

A new approach for the determination of element concentration profiles in stratified materials by confocal X-ray fluorescence spectrometry was elaborated. The method was based on a direct deconvolution of the measured depth-dependent X-ray fluorescence intensity signal with the established response function of the spectrometer. Since the approach neglects the absorption of primary and secondary radiation within the probing volume, it is applicable only to low absorbing samples and small probing volumes. In the proposed approach the deconvolution is performed separately for all detectable elements and it is followed by the correction of absorption effects. The proposed approach was validated by using stratified standard samples. The determined elemental profiles were compared with the results obtained by using existing analytical approaches.

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1. Introduction

The confocal micro-beam X-ray fluorescence (confocal μ-XRF) technique is an analytical tool that enables examination of spatial distributions of elements within a sample with a resolution ranging from several up to tens of micrometers. The method was proposed in 1993 by Gibson and Kumakov [1] and since then many authors proved its capability for analyzing samples of different origin, such as pigment layers in art objects or elemental distributions in biological and environmental samples [2–5]. The technique has been used with spectrometers operated either with synchrotron radiation or the radiation generated by X-ray tubes [6–8]. The main advantage of the technique is its capability for collecting depth resolved elemental information with extremely high signal to background ratio arising due to the inherently limited probing volume. The disadvantages include limited sensitivity for high-Z elements and element-dependent spatial resolution, both effects linked to the way in which X-rays are transmitted and reflected in the focusing/collimating optics of the spectrometer. Nevertheless, for certain applications, the technique was found very useful as the only one the technique capable of non-invasive probing the sequence and chemical composition of sample layers. The comparison of the detection limits and elemental sensitivities of conventional μ-XRF versus confocal μ-XRF techniques can be found in [9].

The elaboration of any quantification procedure for confocal μ-XRF technique is a demanding task since the spatial description of the matrix effects inside heterogeneous sample is much more difficult than in the case of conventional XRF. So far a few method were developed. The first quantification procedure for confocal μ-XRF was presented in 2004 by Smit et al. [10]. In this work the fundamental parameter approach assuming a spherical probing volume was proposed for the investigation of paint layers. A more detailed model of confocal volume was proposed by Malzer and Kanngießer in 2005 [11]. The authors also derived a general equation for the depth-dependent intensity of X-ray fluorescence radiation in confocal geometry as well as a calibration procedure. Mantouvalou et al. [12] used this approach to derive the equations describing the intensity of X-ray fluorescence radiation versus the probing depth in multi-layered samples. A Monte Carlo (MC) based quantification approach was presented and compared with the existing analytical methodologies by Czyzycki et al. in two articles [13–14]. Perez et al. [2] applied the model of Malzer and Kanngießer [11], neglecting the self-absorption effects, for the analysis of metals in thin biological samples. Both the analytical and MC approaches used the parallel beam approximation [15]. Schoonjans et al. [16] elaborated a fundamental parameter method for nano-X-ray fluorescence analysis of cometary dust particles trapped in silica-based aerogel returned by NASA's Stardust mission. The analytical approach

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used in our work was based on the initial equation proposed originally by Malzer and Kanngieβer in [11].

2. Theory

In the model derived by Malzer and Kanngieβer [11] the spectrometer sensitivity function $\eta_j(x)$ was introduced. In this model, depth-dependent intensity of X-ray fluorescence radiation of given element j recorded in confocal geometry, assuming monochromatic excitation, paraxial X-ray optics, and neglecting enhancement effects, is given by:

$$\Phi_j(x) = \int_0^D \eta_j'(\zeta - x)\rho_j(\zeta)\exp\left(-\int_0^\zeta \overline{\mu}_{lin,j}(\xi)d\xi\right)d\zeta, \tag{1}$$

$$\eta_j'(x) = \Phi_0\tau_{F,j}\eta_j(x) = \Phi_0\tau_{F,j}\frac{\tilde{\eta}_j}{\sqrt{2\pi}\sigma_{x,j}}\exp\left(\frac{-x^2}{2\sigma_{x,j}^2}\right), \tag{2}$$

$$\overline{\mu}_{lin,j}(x) = \sum_i \rho_i(x)\left(\frac{\mu_{0,i}}{\cos\varphi} + \frac{\mu_{j,i}}{\cos\psi}\right), \tag{3}$$

where $\tilde{\eta}_j$ takes into account the geometry of the confocal volume and the transmission factors of the excitation/detection X-ray optics and the detection efficiency, $\sigma_{x,j}$ is the width of the sensitivity profile, Φ_0 is the flux of the impinging beam, $\tau_{F,j}$ is the X-ray peak production cross section, φ and ψ are the incidence and take off angles measured to the sample normal, $\mu_{0,i}$ and $\mu_{j,i}$ are the mass absorption coefficients for the primary and secondary radiation. The function $\rho_j(x)$ describes the local density profile of the analyzed element. For thin samples, when the absorption effects can be omitted

$$\Phi_j(x) = \eta_j'(x)Q_j, \tag{4}$$

where Q_j is the mass deposit per unit area of the analyzed element. In the approach proposed in this work the absorption term in Eq. (1) is split in two separate terms:

$$\exp\left(-\int_0^\zeta \overline{\mu}_{lin,j}(\xi)d\xi\right) = \exp\left(\int_\zeta^x \overline{\mu}_{lin,j}(\xi)d\xi\right)\exp\left(-\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right). \tag{5}$$

The first term in the right side of Eq. (5) corrects for the absorption effects within the confocal volume. The second term corrects for the attenuation of the primary and secondary radiation on the path from the sample surface to the probing position x. This term does not depend on ζ and therefore it can be excluded from the main integral

$$\Phi_j(x) = \exp\left(-\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right)\int_0^D G_j(\zeta, x)\rho_j(\zeta)d\zeta, \tag{6}$$

$$G_j(\zeta, x) = \eta_j'(\zeta - x)\exp\left(\int_\zeta^x \overline{\mu}_{lin,j}(\xi)d\xi\right). \tag{7}$$

Function $G_j(\zeta, x)$ takes into account the absorption effects within the probing volume. It can be considered as an expanded version of the original sensitivity function $\eta_j'(x)$. As shown in Eq. (7) the absorption of primary and secondary radiations inside the confocal volume modifies the original sensitivity function $\eta_j'(x)$ in a way that for $\zeta < x$ the sensitivity profile is enhanced by the exponent term which becomes > 1, whereas for $\zeta > x$ the exponent term becomes < 1 and the sensitivity profile is attenuated. The distortion of the original sensitivity function depends on the effective linear absorption coefficient as well as on the size of the confocal volume. In the case of weakly absorbing matrices and small probing volumes

$$\exp\left(\int_\zeta^x \overline{\mu}_{lin,j}(\xi)d\xi\right) \approx 1 \Rightarrow G_j(\zeta, x) \approx \eta_j'(\zeta - x). \tag{8}$$

In such a case Eq. (6) can be simplified to

$$\begin{aligned}\Phi_j(x) &= \exp\left(-\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right)\int_0^D \eta_j'(\zeta - x)\rho_j(\zeta)d\zeta \\ &= \exp\left(-\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right)(\eta_j' * \rho_j)(x).\end{aligned} \tag{9}$$

where operators * and × are convolution and multiplication, respectively. The derived Eq. (9) opens up a possibility for determining the local density depth profile of the j-th element by a direct deconvolution of the observed X-ray fluorescence signal $\Phi_j(x)$ with known sensitivity function $\eta_j'(x)$ followed by the absorption correction of the deconvolved profile $\Phi_{j,deconvolved}(x)$

$$\Phi_j(x); \eta_j'(x) \overset{deconvolution}{\rightarrow} \Phi_{j,deconvolved}(x) = \exp\left(-\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right)\rho_j(x), \tag{10}$$

$$\rho_j(x) = \Phi_{j,deconvolved}(x)\exp\left(\int_0^x \overline{\mu}_{lin,j}(\xi)d\xi\right) \tag{11}$$

$\Phi_{j,deconvolved}(x)$ is a dimension of density. The function $\eta_j'(x)$ must be known in advance, it can be determined by fitting Eq. (4) to the measured depth profile of a thin film standard sample. As shown in Eq. (11) the local density profile of the analyzed element is calculated by multiplying the deconvolved intensity profile by the exponential term determined at each probing position. This term is responsible for correcting the absorption effects due to the presence of absorbing layers of the sample between the current position of the probing volume and the sample surface. To convert the local density profiles $\rho_j(x)$ into profiles of the concentration we assume a known density of the matrix and known densities of the elements (or chemical compounds containing given element) mixed with the matrix. Assuming that the elements (compounds) are not diluted but mixed with the matrix one can calculate the overall sample density at given depth and use it to obtain concentration depth profiles.

The deconvolution with regularization procedure [17,18] was used to deconvolve the intensity profiles. In this procedure the analyzed signal h (the measured characteristic peak intensity profile) is a convolution of the known point spread function (PSF) g (the spectrometer sensitivity function) and the real signal f (the absorption modified element density profile) with superimposed noise n (statistical fluctuations of the measured intensity profile). The relation between these functions can be written in the following form:

$$h = f * g + n \tag{12}$$

where $*$ is a convolution operator. Function f is approximated by $\hat{f}$ which minimizes the following expression:

$$\sum_x \frac{((\hat{f} * g)(x) - h(x))^2}{n^2(x)} + \lambda\sum_x\left|\frac{\Delta\hat{f}(x)}{\Delta x}\right|. \tag{13}$$

The dimensionless λ parameter controls the strength of the regularization (smoothing). For given problem the value of this parameter has to be chosen empirically to get the best compromise between the smoothing and the maximization of goodness of fit. The first term in this sum governs how accurately the convolution of the approximated function $\hat{f}$ and the sensitivity function g fits to the signal h. The second term avoids solutions affected with high noise.

In the numerical implementation used in this work the measured and deconvolved signals were discrete functions of probing positions. The sample was divided into a stack of layers

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