Nuclear Instruments and Methods in Physics Research B 268 (2010) 3568–3575

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

X-ray scattering in X-ray fluorescence spectra with X-ray tube excitation – Modelling, experiment, and Monte-Carlo simulation

V.-D. Hodoroaba [a,*], M. Radtke [b], L. Vincze [c], V. Rackwitz [a], D. Reuter [a]

[a] BAM Federal Institute for Materials Research and Testing, Division VI.4 Surface Technologies, D-12200 Berlin, Germany
[b] BAM Federal Institute for Materials Research and Testing, Division I.3 Structure Analysis; Polymer Analysis, D-12200 Berlin, Germany
[c] Ghent University, Department of Analytical Chemistry, B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 31 August 2010
Received in revised form 23 September 2010
Available online 1 October 2010

Keywords:
X-ray scattering
X-ray fluorescence
Spectral background
Modelling
Monte-Carlo simulation

ABSTRACT

X-ray scattering may contribute significantly to the spectral background of X-ray fluorescence (XRF) spectra. Based on metrological measurements carried out with a scanning electron microscope (SEM) having attached a well characterised X-ray source (polychromatic X-ray tube) and a calibrated energy dispersive X-ray spectrometer (EDS) the accuracy of a physical model for X-ray scattering is systematically evaluated for representative samples. The knowledge of the X-ray spectrometer efficiency, but also of the spectrometer response functions makes it possible to define a physical spectral background of XRF spectra. Background subtraction relying on purely mathematical procedures is state-of-the-art. The results produced by the analytical model are at least as reliable as those obtained by Monte-Carlo simulations, even without considering the very challenging contribution of multiple scattering. Special attention has been paid to Compton broadening. Relevant applications of the implementation of the analytical model presented in this paper are the prediction of the limits of detection for particular cases or the determination of the transmission of X-ray polycapillary lenses.

1. Introduction

X-ray fluorescence (XRF) is a well established analytical method for determining element concentrations in solid samples for main, secondary and trace elements. Sustained by the ongoing development of personal computers processing speed and memory capacity, the new evaluation of relatively old physical models describing the interaction of X-ray photons with matter seems to be worthwhile for a systematic reconsideration. In addition to this, metrological measurements performed with modern calibrated instrumentation can be related to. Reference-free XRF quantification – obviously very attractive for most XRF users – contains many sources of uncertainties, which are unfortunately known by the fewest users. One of the main information which enters the quantification routines is the net areas of the fluorescence peaks. They result after appropriate subtraction of the spectral background, which is determined by both the X-ray spectrometer and X-ray scattering in the sample. Extensive work has been invested in the last decade in the calibration of energy-dispersive spectrometers (EDS). Calibration procedures are nowadays available at synchrotron facilities and even in a conventional laboratory for X-ray spectrometry.

The aim of the present paper is to implement the physical models and data existing in the literature on X-ray scattering and, based on a calibrated X-ray spectrometer, to calculate a physical background of the XRF spectra. It must be noted that the excitation related to in this paper is a polychromatic, unpolarised one coming from a commercial side-window X-ray tube. The conventional way of background subtraction in XRF spectra is purely mathematical and for many applications not realistic. Even the consideration of empirical backgrounds, based on measurements on similar matrices, has not become prevalent for the community.

The alternative to the possibilities described above is offered by the Monte-Carlo simulations. In spite of the fact that they describe rather realistically the scattering processes taking place in the sample, the existing Monte-Carlo software packages cannot be appropriately used by most users (portability, installation, help/guidance etc.).

We compare XRF spectra calculated by physically modelling the X-ray scattering background to metrological measurements performed in our laboratory on representative sample matrices, and relate these to Monte-Carlo simulations as well.

2. Experimental

In order to check the accuracy of the X-ray scattering model implemented as described later in this work metrological

* Corresponding author. Tel.: +49 030 81043144; fax: +49 030 81041827.
E-mail address: Dan.Hodoroaba@bam.de (V.-D. Hodoroaba).

0168-583X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2010.09.017

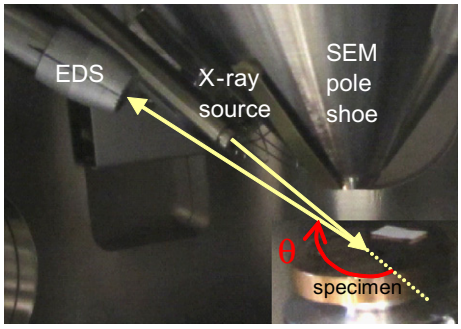

Fig. 1a. Photograph of the experimental setup, highlighting the scattering geometry. The geometry arises from the port configuration of the SEM, yielding the scattering angle $\theta = 155°$.

measurements based on calibrated instrumentation have been performed. The base instrument is a scanning electron microscope (SEM) *Zeiss Supra™40* having attached an EDS system *NSS* with a Si(Li) detector (*Thermo Fisher Scientific*) and a low-power micro-focus X-ray source of type *iMOXS* (*IFG – Institute for Scientific Instruments*), so that micro-focus XRF can be performed with a SEM [1,2], see Fig. 1a. The EDS is calibrated up to 60 keV by using synchrotron radiation from the electron storage ring BESSY II. Both detector efficiency and spectrometer response functions are hence well-known [3–6]. The solid angle encompassed by the ED detector was also carefully measured by calibrated apertures [7] and the references therein.

Polychromatic excitation with a micro-focus X-ray source in conjunction with a SEM has been possible since just a few years. By accurate knowledge of the X-ray tube and of the polycapillary X-ray optic, the excitation spectrum being emitted from the X-ray source can be calculated [2]. The X-ray tube anode used was Rhodium with a 25° inclination and an 8 μm Beryllium side-window at 0° elevation angle relative to the Rh target surface. For all the measurements performed in this work, excitations at 40 kV and 700 μA, and 20 kV and 400 μA have been applied. Measurements with a calibrated double collimator, but also with the X-ray polycapillary optic have been carried out. The polycapillary optic has been taken into account into the excitation spectrum by its transmission, which was carefully determined by means of a procedure described elsewhere [8]. The thickness of the Beryllium window placed in the front of the X-ray polycapillary optic was 12.5 μm.

It must be noted that the overall scattering geometry resulting from using the micro-focus X-ray source and the EDS at the ports available at the SEM has yielded a high scatter angle (θ) of 155° (see Fig. 1a). Since the scattering effects corresponding to this geometry are quite pronounced in the X-ray scatter spectra, this was rather beneficial for the purpose of testing and validation the model and simulations discussed here.

The materials selected as scattering body have been pure reference materials such as PMMA, glassy carbon and SiO_2 of low atomic number, and pure aluminium and copper as representative for materials of mid atomic number. Materials of higher atomic number have not been considered in this study, since X-ray scattering, even for our selected extreme conditions, becomes analytically insignificant.

3. Theory

Scattering of X-rays by electrons can occur without energy loss, i.e. elastically, or with energy loss, i.e. inelastically. Similar to fluorescence, the intensities of the elastic (Rayleigh), I_{Ra}, and inelastic (Compton), I_{Co}, X-rays scattered by a scattering body (of density ρ and thickness d) when irradiated with incident X-rays of intensity $I_0(E)$ can be calculated according to equations [9]:

$$I_{Ra}(E) = \frac{\Omega}{4\pi}\frac{MSC_{Ra}(E)}{\left(1+\frac{\sin\Psi_1}{\sin\Psi_2}\right)MAC(E)} \times\left\{1-\exp\left[-\rho d\left(1+\frac{\sin\Psi_1}{\sin\Psi_2}\right)\frac{MAC(E)}{\sin\Psi_1}\right]\right\}I_0(E), \quad (1)$$

$$I_{Co}(E') = \frac{\Omega}{4\pi}\frac{MSC_{Co}(E)}{MAC(E)+\frac{\sin\Psi_1}{\sin\Psi_2}MAC(E')} \times\left\{1-\exp\left[-\rho d\left(\frac{MAC(E)}{\sin\Psi_1}+\frac{MAC(E')}{\sin\Psi_2}\right)\right]\right\}I_0(E), \quad (2)$$

$\Omega/4\pi$ is the solid angle subtended by the detector; MAC is the mass attenuation coefficient (in cm^2/g) and $MSC_{Ra,Co} = \sigma_{Ra,Co}\cdot N_A/A$ is the mass scattering coefficient (in cm^2/g, taken from [10]); $\sigma_{Ra,Co}$ are the atomic Rayleigh and Compton scatter cross sections (in cm^2/atom), N_A is the Avogadro number and A is the atomic weight; Ψ_1 and Ψ_2 are the incidence and the emergence angles (relative to the sample surface), see Fig. 1b. The excitation X-ray spectrum $I_0(E)$ dealt with in this paper is the X-ray spectrum emitted by an X-ray tube, which is calculated in [photons·nA^{-1} s^{-1}·msr^{-1}·eV^{-1}] according to [2].

In the case of semi-infinite specimen thickness, the term in the curly brackets reduces to one. The energy loss accompanying the Compton scattering, i.e. the so-called *Compton shift*, can be calculated from the energy and momentum conservation laws and results in a shift of the Compton scatter spectrum to lower energies:

$$E' = \frac{E}{1+\frac{E}{m_e c^2}(1-\cos\theta)}, \quad (3)$$

where θ is the scattering angle. The nonlinearity of the Compton shift with the energy for two representative scatter angles is visualised in Fig. 2.

Note that Eqs. 1 and 2 describe a single scattering event in the scattering body, attenuation of the incident radiation and attenuation of the scattered radiation in the scattering body on its way toward the detector. As a consequence of this formulation of the problem, multiple scattering events are not considered in this model. The implications of this will be discussed in Section 6.

Because X-ray scattering takes place anisotropically, differential cross sections for Rayleigh and Compton scattering must be considered for a realistic model [11]:

$$\frac{d\sigma_{Ra}(\theta,E)}{d\Omega} = \frac{d\sigma_{Th}(\theta,E)}{d\Omega}[F(x,Z)]^2, \quad (4)$$

$$\frac{d\sigma_{Co}(\theta,E)}{d\Omega} = \frac{d\sigma_{KN}(\theta,E)}{d\Omega}S(x,Z), \quad (5)$$

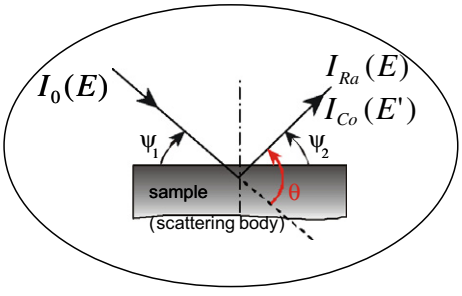

Fig. 1b. Schematic detailing the angles ψ_1, ψ_2 and θ as geometrical determinants for the calculation of the scattered intensities I_{Ra} and I_{Co} in Eqs. 1 and 2.