

# Influence of X-ray tube spectral distribution on uncertainty of calculated fluorescent radiation intensity

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Received 11 December 2006; accepted 5 June 2007

Available online 13 June 2007

## Abstract

The relative radiation intensity ( $R_i$ ) defined as fluorescent radiation intensity of analyte in specimen to fluorescent radiation intensity of pure element or compound, e.g., oxide is used in calculation in both fundamental parameter methods and in theoretical influence coefficient algorithms. Accuracy of calculated  $R_i$  is determined by uncertainties of atomic parameters, spectrometer geometry and also by X-ray tube spectral distribution. This paper presents the differences between  $R_i$  calculated using experimental and theoretical X-ray tube spectra evaluated by three different algorithms proposed by Pella et al., Ebel, and Finkelshtein–Pavlova. The calculations are performed for the most common targets, i.e., Cr, Mo, Rh and W. In this study,  $R_i$  is calculated for V, Cr, Mn, Fe, Co, Ni, Cu and Mo in steels as an example. The differences between  $R_i$  calculated using different X-ray tube spectrum algorithms are presented when pure element standard, multielement standard similar to the analyzed material and one pure element standard for all analytes is used in X-ray fluorescence analysis. The differences between  $R_i$  for intermediate-thickness samples (and also for thin films) and for X-ray tube, which ran for many hours, are also evaluated.

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*Keywords:* X-ray tube spectrum; X-ray fluorescence spectrometry; XRF; Matrix effects; Matrix correction

## 1. Introduction

The equation used for the calculation of the fluorescent radiation intensity as a function of the total sample composition was derived by Sherman in 1955 [1]. This equation, later corrected in enhancement term by Shiraiwa and Fujino [2], is the base of fundamental parameters methods and theoretical influence algorithms. The calculation of fluorescent radiation intensity requires knowledge of the atomic parameters, measurement geometry and also X-ray tube spectrum (the equation is integrated from the short-wavelength limit  $\lambda_0$  to

wavelength of analyte absorption edge  $\lambda_{\text{edge}}$ ). The Sherman equation for thick sample can be expressed as follows:

$$I_i = Q_i q_i W_i \int_{\lambda_0}^{\lambda_{\text{edge}}} \frac{\tau_i(\lambda)}{\mu(\lambda) \csc \phi_1 + \mu(\lambda_i) \csc \phi_2} \left( 1 + \sum_{jm} S_{ijm} W_j \right) I(\lambda) d\lambda \quad (1)$$

where  $Q_i$  is the spectrometer sensitivity for analyte fluorescent X-ray radiation depending on instrumental configuration and measurement condition;  $q_i$  is sensitivity of the analyte element  $i$ , if  $K_\alpha$  line is used then  $q_i = \omega_{K,i} f_{K\alpha} (1 - 1/J_{K,i})$ , where  $\omega_{K,i}$  is fluorescence yield of  $K$  radiation,  $f_{K\alpha}$  is weight of  $K_\alpha$  line within  $K$ -series,  $J_{K,i}$  is the absorption edge jump ratio. If the  $L_{\alpha 1}$  or  $L_{\beta 1}$  is chosen as the analytical line, then Coster–Kronig transition probabilities have to be additionally taken into consideration;  $I(\lambda)$  is intensity of the primary radiation;  $W_i$ ,  $W_j$  are weight fractions of the analyte element  $i$  and matrix elements  $j$ , respectively;  $m$  is the subscript for the matrix element line;  $\tau_i(\lambda)$

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is photoelectric absorption coefficient,  $\mu(\lambda)$ ,  $\mu(\lambda_i)$  are total mass attenuation coefficients for the incident  $\lambda$  and fluorescent radiation  $\lambda_i$ , respectively;  $\phi_1$ ,  $\phi_2$  are angles of incidence and exit of primary and fluorescent radiation, respectively;  $S_{ijm}$  is the enhancement term for each line  $m$  of the matrix element  $j$ , which enhances the analyte element  $i$ . The enhancement term  $S_{ijm}$  is calculated from Eq. (1a).

$$S_{ijm} = 0.5 \frac{\tau_j(\lambda)}{\tau_i(\lambda)} \tau_i(\lambda_{jm}) q_j \left[ \ln \left( 1 + \frac{\mu(\lambda)}{\mu(\lambda_{jm}) \sin \phi_1} \right) \frac{\sin \phi_1}{\mu(\lambda)} + \ln \left( 1 + \frac{\mu(\lambda_i)}{\mu(\lambda_{jm}) \sin \phi_2} \right) \frac{\sin \phi_2}{\mu(\lambda_i)} \right] \quad (1a)$$

The spectrometer sensitivity  $Q_i$  is usually eliminated for calculation in fundamental parameter methods and in theoretical influence coefficient algorithms by replacing the absolute intensity  $I_i$  with the relative intensity  $R_i$ . The relative intensity is defined as fluorescent radiation intensity of analyte in binary, ternary or in multielement specimen to fluorescent radiation intensity of pure element or compound, e.g., oxide.  $R_i$  is calculated for given measurement conditions (spectrometer geometry, X-ray tube target, voltage, etc.), standard composition and specimen preparation: alloys, fused samples etc. Accuracy of calculated  $R_i$  is determined by uncertainties of atomic parameters (i.e., fluorescent yields, mass absorption coefficients, transition probabilities), spectrometer geometry, and X-ray tube spectral distribution. Many experimental spectral distributions of the X-ray tubes of various targets are published [3–9]. Nevertheless, the measurements are performed only for selected voltage and type of X-ray tube (take-off angle and thickness of the Be window but absorption in Be window can be easily corrected). Therefore, the theoretical algorithms to the calculation of X-ray tube spectral distribution (both characteristic line intensities and continuum intensity) are still developed to obtain high quality of the quantitative XRF analysis. Algorithms are usually compared on the basis of calculated characteristic line intensities and continuum intensity. The effect of different X-ray tube distribution on uncertainty of calculation of  $R_i$  is rather rarely investigated and usually only for selected targets. Tao et al. [10] examined the influence of spectrometer geometry, mass absorption coefficients and spectral distribution of X-ray tube on calculated  $R_i$ . The investigations were performed using synthetic standards prepared by fusion and three various spectral distributions of Cr target X-ray tube operated at 40 kV. Pella et al. [11] compared their algorithm for the evaluation of X-ray tube spectrum with measured primary spectrum in analysis of Fe–Ni–Cr alloys. The analysis was performed using both fundamental parameters method (pure element standards) and theoretical Lachance  $\alpha$ -coefficients (six ternary standards) and W target X-ray tube.

The aim of this work is to show how big differences between relative radiation intensities  $R_i$  calculated using experimental and theoretical X-ray tube spectra can be expected. The calculations are performed using experimental data and three various algorithms: Pella et al. algorithm [11], Ebel algorithm [12] and Finkelshtein–Pavlova algorithm [13]. The most popular targets, i.e., Cr, Mo, Rh and W are selected in this work and  $R_i$  is calculated for V, Cr, Mn, Fe, Co, Ni, Cu and Mo in steels as

an example. The differences between  $R_i$  calculated using different algorithms when various methods of calibration are applied (pure element standard, multielement standard similar to the analyzed material and one pure element standard for all analytes) are presented. What is also presented is how accurate results can be expected when intermediate-thickness samples are analyzed and tube runs for many hours.

## 2. Algorithms to be compared

### 2.1. Pella et al. algorithm

The first algorithm compared in this study was developed by Pella et al. [11] (so-called NIST algorithm). This semi-empirical algorithm was derived using experimental data for the evaluation of target absorption correction factor and for calculation of characteristic X-ray line intensities. The algorithm is based on uncorrected Kramers law and is derived for electron incidence angles of 90°. The formula for calculation of the continuum spectral distribution is expressed as follows:

$$I(\lambda) = 2.72 \times 10^{-6} Z \left( \frac{\lambda}{\lambda_0} - 1 \right) \frac{1}{\lambda^2} f F_{\text{Be}} \quad (2)$$

$I(\lambda)$  is radiation intensity at wavelength  $\lambda$  in units of photons  $\text{\AA}^{-1} \text{sr}^{-1} \text{elektron}^{-1}$ ;  $Z$  is target atomic number;  $\lambda$  and  $\lambda_0$  are wavelength and short-wavelength limit in  $\text{\AA}$  ( $\lambda_0 = 12.398/\text{kV}$ );  $F_{\text{Be}}$  is the Be window absorption correction term calculated from  $F_{\text{Be}} = \exp(-0.35 \lambda^{2.86} t_{\text{Be}})$ ,  $t_{\text{Be}}$  is the thickness of the Be window;  $f$  is the target absorption correction factor. In this algorithm it is based on Heinrich formula [14,15].

$$f = (1 + C\xi)^{-2} \quad (2a)$$

$$\xi = \left( \frac{1}{\lambda_0^{1.65}} - \frac{1}{\lambda^{1.65}} \right) \frac{\mu(\lambda)}{\sin(\psi)}$$

where  $\mu(\lambda)$  is the mass absorption coefficient for the target,  $\psi$  is the target take-off angle,  $C$  is the proportionality factor derived by least-squares fits of experimental obtained for various targets and voltages. The authors obtained following relationship between  $C$  and target atomic number  $Z$  and voltage:

$$C = \frac{1 + (1 + 2.56 \times 10^{-3} Z^2)^{-1}}{(1 + 2.56 \times 10^3 \lambda_0 Z^{-2})(0.25 \xi + 1 \times 10^4)}$$

The authors expressed characteristic radiation as the ratio of the characteristic line to the underlying continuum intensity at the wavelength of this line.

$$\frac{N_{\text{chr}}}{N_{\text{con}}} = \left( \frac{a}{b + Z^4} + d \right) \exp \left[ -0.5 \left( \frac{U - 1}{1.17U + 3.2} \right)^2 \right] [U \ln U / (U - 1) - 1] \quad (2b)$$

where  $U_0$  is the over voltage ( $U = E/E_q$  where  $E_q$  is the energy of absorption edge of the corresponding X-ray line);  $a$ ,  $b$ , and  $d$

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