An overview of quantification methods in energy-dispersive X-ray fluorescence analysis

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Abstract. This paper reviews the major factors influencing the accuracy of the energy-dispersive X-ray fluorescence (EDXRF) analysis including physical and chemical matrix effects (resulting from particle size, surface irregularity, mineralogy, moisture, absorption and enhancement) as well as the correction procedures with emphasis on the analysis of unprepared samples. Quantification methods for thin samples, samples with intermediate thickness and thick samples are presented including fundamental parameter methods, influence coefficient algorithms, empirical coefficient algorithms and quantification methods based on scattered primary radiation. Quality control procedures are also reviewed.

Keywords. X-ray fluorescence; X-ray spectrometry; quantitative XRF analysis; in situ XRF measurements.

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1. Introduction

Quantitative X-ray fluorescence (XRF) analysis requires the conversion of measured intensities of the characteristic radiation to the concentrations of the elements to be determined (analytes). This process is based on the relationship between the measured characteristic X-rays and the excitation source intensity, concentration of the analyte, overall composition and absorption properties of the sample. In many cases, a meaningful conversion of the intensities to the concentrations requires careful consideration of the interfering effects. A wide range of literature relevant to this topic is available, e.g. [1–3], which provides valuable information on numerous quantification methods including their fundamentals, advantages and limitations. Because of the availability of portable XRF spectrometers one can observe a growing interest in the applications of EDXRF technique for in situ characterization of materials such as contaminated soil, archaeological and cultural heritage objects etc. The analysis of unprepared samples, especially
when quantification is required, presents a real challenge [4] because of the presence of a number of interfering effects which are often eliminated (or considerably reduced) in the laboratory analysis where adequate sample preparation techniques are applied. Moreover, major parameters of the in situ EDXRF measurements should be carefully reviewed and reassessed.

2. Parameters of in situ EDXRF measurements

In this section, the following parameters of EDXRF analysis are presented: critical penetration depth, detection limit and total uncertainty. Knowledge of these parameters is essential in all modes of XRF techniques but the analysis of unprepared samples (in situ measurements) requires special attention.

2.1 Critical penetration depth

The measured intensity of the characteristic X-rays of the analyte element originates from a well-defined layer of the sample called critical penetration depth $t_{\text{crit}}$ which can be calculated from

$$t_{\text{crit}} = 4.61 / (\rho \mu_{\text{tot}}) ,$$  \hspace{1cm} (1)

where $\rho$ is the density of the sample material, $\mu_{\text{tot}}$ is the sum of the mass attenuation coefficients of the primary and characteristic radiations in the analysed sample multiplied by the cosec of the incident and take-off angles, respectively [4]. The critical penetration depth is the sample thickness from which 99% of the characteristic X-rays originate. In principle, calculation of $t_{\text{crit}}$ requires knowledge of the sample composition. In practice, the absorption properties of the sample material ($\mu_{\text{tot}}$) can be assessed with sufficient accuracy by assuming the average atomic number of the material based on the major constituents of the sample. Typical values of $t_{\text{crit}}$ are in the range of 10–1000 $\mu$m depending on the atomic number of the analyte element and composition of the sample.

One has to remember that the contribution to the measured X-rays is not uniform across $t_{\text{crit}}$. A major contribution comes from the surface layer (90% of the characteristic X-rays originate from the surface layer of $0.5t_{\text{crit}}$ thickness). The existence of $t_{\text{crit}}$ is of great importance in the analysis of heterogeneous and/or near-surface contaminated samples, and should always be considered during interpretation of the analytical data obtained for the unprepared samples, e.g. archaeological or cultural heritage materials.

2.2 Detection limits

Detection limit (DL) is the lowest concentration level that can be determined as statistically significant from the blank signal [5]. According to a simple definition applied in the laboratory measurements, the so-called interference-free DL (DL$_{\text{intfree}}$) is the concentration or amount of the analyte element that generates a measured signal equal to three times the standard deviation of background in the relevant energy interval. Although the DL$_{\text{intfree}}$ is a good assessment of the detection ability of the EDXRF spectrometers, its application for in situ measurements can provide overoptimistic expectation, and therefore two different approaches are recommended [4,5]: