

## 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

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

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  $\mu\text{m}$  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 ( $\text{DL}_{\text{intfree}}$ ) 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  $\text{DL}_{\text{intfree}}$  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]:

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- Precision-based DL calculated as three times the standard deviation of the results obtained for replicate analyses of low-concentration samples (either appropriate RMs or spiked samples).
- Field or performance-based DL based on the analysis of the low concentration outliers on data cross plots for the  $\log_{10}$  transformed portable EDXRF results vs.  $\log_{10}$  transformed results obtained by a confirmatory (reference) method.

Both the approaches give more realistic assessment of the ‘effective’ detection limits, and the values obtained should be used whenever EDXRF is applied for the *in situ* determination of the elements at low concentration level.

### 2.3 *Total uncertainty*

Calculation of the total uncertainty requires identification of the individual sources of uncertainty and quantification of their contributions. It is rather a complex process based on the solid knowledge of the methodology of the EDXRF technique. A carefully performed uncertainty budget allows identifying major source(s) of uncertainty and selecting the most effective analytical strategy to improve the quality of the analytical data. Since EDXRF analysis includes several steps (sampling, sample handling and sample preparation, measurement, quantification), the uncertainties associated with these steps should be assessed (quantified) and included in the calculation of the total uncertainty. The last two components of uncertainties (measurement and quantification) can be assessed based on contribution from counting statistics, calibration and quantification method applied [6]. Assessment of the contribution of the uncertainties of sampling, sample handling and sample preparation is often time-consuming and requires preparation of a number of replicate samples. In *in situ* measurements, calculation of the total uncertainty is even more complicated (although there is no need for sample preparation) because the interfering effects are more pronounced and the quantitative analysis requires the correction methods which can effectively be used only when the parameters describing the materials under study (heterogeneity, mineralogy, particle size, surface irregularity, moisture content) are well defined [4]. In the result, the *in situ* EDXRF analysis is often only semi-quantitative.

### 3. **Remarks on *in situ* EDXRF analysis**

*In situ* EDXRF analysis is often done for unprepared samples (contrary to the laboratory measurements where an ‘ideal’ sample is prepared for the XRF measurements). To generate meaningful analytical data for *in situ* measurements, the following physical matrix effects should be considered: particle size effects, heterogeneity, surface irregularity effects, mineralogy effects and moisture effects [4].

*The particle size effects* manifest in the dependence of the intensity of the characteristic X-rays on the particle size (or particle size distribution) of the fluorescent and nonfluorescent particles as well as on their composition [7–9]. These effects exist in the EDXRF analysis of any granular materials (when traditional methods of fusing or grinding cannot be used) irrespective of the sample thickness, and may contribute substantially to the total uncertainty of the analytical results. The influence of the particle size effects can

be assessed theoretically or experimentally [10]. Heterogeneity effects are difficult to eliminate, but can be reduced using a preliminary procedure for homogenization of the materials (e.g. contaminated soil) or by collecting the integrated X-ray fluorescence signal from a large area of the sample material.

*The surface irregularity effects* appear in the analysis of unprepared geological and archaeological materials. Quantification presents a problem because the EDXRF spectrometers are calibrated using flat calibration samples which do not match the irregularly shaped surfaces of the unknown samples. The detected X-ray fluorescence intensities are systematically lower than those detected for flat samples [11,12]. An effective correction for the surface irregularity effects can be done using the Compton and Rayleigh scattered primary radiation within a limited surface irregularity range ( $\sim$  a few mm). Another correction method is based on relative calibration factors using a reference element present in the sample (assuming that the intensities of the characteristic X-rays for the analyte and reference element undergo similar variations with surface irregularity).

*Mineralogy effects* can be expected in the analysis of unprepared rocks and archaeological samples. They manifest in the dependence of the characteristic X-ray intensities on the mineral assemblage (size, distribution and position of minerals) present in the excited volume. The mineralogy effects can be assessed experimentally by repetitive analysis of nonoverlapping spots of the ideally flat representative samples. Based on the experimental results, one can derive the number of individual measurements required for a given sampling precision [13].

*Moisture* content may influence the quantitative EDXRF analysis of the soil and sediment samples saturated with water [14]. To correct this effect (and generate results on the so-called dry sample basis) drying of samples before the analysis is often required. Alternatively, one can use moisture gauge to determine moisture content and apply a simple correction. Another problem exists during EDXRF logging applied for determining the mineral concentrations in wet boreholes. In this case a layer of drilling fluid (water) is formed between a detector window and the wall which results in additional absorption and scattering effects. Here, a simple correction method based on measurement of the intensities of the two scattered peaks of primary radiation to assess the thickness of the water layer is used and finally a proper correction will be introduced [15].

#### **4. Quantification in EDXRF analysis of thin samples**

For thin samples both the absorption and enhancement effects can be neglected and the mass per unit area (or concentration) of the analyte is a linear function of the intensity of its characteristic X-rays. The calibration of an EDXRF spectrometer is straightforward and can be done either theoretically or experimentally based on the measurements of thin homogeneous (single or multielement) calibration samples. This simple approach is not applicable for the analysis of heterogeneous thin samples, so that an additional correction for the heterogeneous sample loading combined with the distribution of the excitation-detection factor can be used as a solution [16]. Thin samples are often applied in total-reflection XRF. But, to correct the inhomogeneous excitation and geometric effects, an internal standard method is applied in the experimental calibration procedure [17].

## **5. Quantification of intermediate thickness samples**

The intermediate thickness samples are characterized by the thickness in the range between the thin and thick samples (for definition, see §4 and 6). This type of sample is sometimes preferable and provides advantageous detection limit and accuracy as well as flexibility in sample preparation. The oldest correction method for quantification of the intermediate thickness samples is the emission-transmission (E-T) method in which the absorption properties of the sample are determined experimentally using a multielement target and then applied to calculate the absorption correction factors [18]. Some problems exist in the analysis of heterogeneous samples [19] and samples containing minor and major elements [20,21]. Another group of correction methods are based on scattered primary radiation. The scattered peaks of the primary radiation undergo matrix absorption and geometrical/instrumental variations similar to that of the fluorescent peaks which can be treated as a sort of fluorescent peaks from internal standards [18]. In a more sophisticated version of the correction procedure for intermediate thickness samples, the additional correction for the enhancement effect is also included [22]. An alternative approach for the assessment of the enhancement effect is based on the enhancement factor for thick sample (described by a relatively simple equation) and thickness of the sample [23]. This simple method appears to be very convenient to define the region of sample thickness where the enhancement effect is negligible and/or to determine the minimum sample thickness for which the bulk enhancement correction can safely be used [24]. A more versatile quantification method is based on a backscatter fundamental parameter (BFP) model which can also be applied for samples containing low-*Z* elements (dark matrix) which are not detected in characteristic X-rays [25]. In this case, two additional light elements are defined to represent the dark matrix of the analysed sample and to perform a full correction for the matrix absorption and enhancement effects. To improve the quality of the analytical data, other modifications of the BFP method such as applying differential mass scattering cross-sections integrated over the average scattering angle, instead of the total scattering cross-sections (to improve calibration), experimentally determining effective incident and take-off angles (to take into account a broad geometry experimental set-up) and taking thin (or intermediate thickness) samples for calibration (to minimize the influence of the uncertainties of the fundamental parameters on the accuracy of the calibration factors) were proposed [25].

## **6. Quantification of thick samples**

Thick sample means its thickness is greater than a limiting value (called saturation thickness) above which practically no further increase in the intensity of the characteristic radiation is observed even when the sample thickness is increased. In this case a simplified equation for the intensity of the characteristic radiation can be applied where dependence on the sample thickness disappears [26]. Since majority of the samples analysed by EDXRF technique are thick, various quantification methods were developed and are currently applied in commercial XRF spectrometers and research institutions. They include relatively simple methods based on scattered radiation (Compton alone or Compton

combined with Rayleigh scattered radiation), fundamental parameter methods and empirical and theoretical influence coefficients methods [2,27].

### 6.1 *Methods based on scattered primary radiation*

Since the intensities of the characteristic X-rays of the analyte element and the Compton scattered radiation depend in a similar way on the composition of the sample material, their ratio becomes less sensitive to the variation in the composition of the analysed material and can be used for the correction of the matrix absorption effects. This simple version of the 'fluorescent-to-Compton' correction method can advantageously be applied if the matrix variations are limited and no significant absorption edges occur between the Compton line and the fluorescent line of the analyte [28]. To extend the applicability range and to increase effectiveness of the 'fluorescent-to-Compton' correction method some modifications were suggested [29,30]. Scattered primary radiation can also be applied for characterizing low-Z elements in the analysed sample (dark matrix) in the backscatter fundamental parameter methods [25,31].

### 6.2 *Fundamental parameter methods*

The fundamental parameter (FP) methods are based on a fully theoretical approach to calculate the theoretical intensities of the characteristic radiation of the analytes from a composite sample of known composition [32,33]. Applications of these methods involve two steps: calibration and analysis. The first step is based on the measurements of pure element samples to calculate the relative intensities for each analyte. By using iterative calculation in the second step which involves comparison of the theoretical results with the experimental data, the concentrations of the elements are found. Major problems in applying the FP methods are evaluation of the first estimate of the composition and necessity to normalize the concentrations to 100% (which is obviously impossible when very light elements like C, N, O are present in a sample). To extend the applicability of the FP methods for the analysis of samples with low-Z elements (dark matrix), a backscatter FP (BFP) method was developed [22,25,31] (see also §5).

### 6.3 *Influence coefficient methods*

Influence coefficient methods are based on numerical coefficients that correct the effect of each matrix element on the element to be determined (analyte) in a given sample. The influence coefficients can be classified into two categories: empirical and theoretical [34]. Each category can be calculated from binary or multielement standards. The binary coefficient approach is based on the assumption that the total matrix effect on the analyte is equal to the sum of the effects of each element of the matrix calculated independently of each other (in this case a sample is considered as a sum of binary mixtures). In the multielement approach the empirical coefficients are obtained from linear multiple regression analysis using measured intensities and compositions of multielement reference materials. Some limitations of the empirical coefficients methods are; necessity to prepare a substantial number, at least  $2 \times (\text{number of analytes} + 1)$  multielement reference samples of compositions similar to the compositions of unknown samples, no physical meaning and limited application range. On the other hand, the empirical coefficients are

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calculated once for a given set of reference materials and can correct for other interfering effects like particle size effects, mineralogical effects and surface roughness effects as well as for poor knowledge of the composition of the reference materials and poor sample preparation. Therefore, the empirical coefficient methods are particularly suitable for the EDXRF analysis of nonhomogeneous samples and also when some elements present in the sample are not detected (no need for normalization to 100%).

Some unique advantages are offered by the theoretical multielement influence coefficient methods. They require only a limited number of reference materials for calibration procedure which is necessary to adapt the experimental data obtained by an EDXRF spectrometer to account for the instrumental parameters not considered by theory as well as to reduce the influence of uncertainties in the fundamental parameters. The methods can cover wide concentration ranges with good accuracy and allow the absorption and enhancement effects to be corrected effectively. A useful feature of the theoretical multielement coefficient methods is that they allow to predict potential matrix effect problems and to select optimum analytical strategy. Since the methods consider only the chemical matrix effects, they do not correct any physical interfering effects associated with particle size, mineralogy and surface roughness.

## **7. Quality control**

Generation of high-quality (reliable) analytical data using EDXRF technique requires maximum care during every step of the analytical procedure including sample collection, sample handling, sample preparation, measurement and quantification. In order to verify the repeatability over extended periods of time, the quality control samples should be analysed periodically. The samples have known composition, typical for the unknown samples, and are not used for calibration. If the results for the quality control samples fall outside a predetermined range, the reasons for the deviation should be identified to take adequate corrective measures [27]. To check a long drift of the equipment, drift-correction monitors are applied. These samples are measured periodically for each of the analyte and the ratios of the observed intensities of the characteristic X-rays to those obtained during calibration are calculated. The ratios can be used as a correction to the slope of the calibration curves or to correct the measured intensities before conversion to concentrations. When a reconstruction of the calibration curves is required (e.g. after maintenance of the EDXRF spectrometer) there is no need to repeat measurements of all standards. Instead, a few original standard samples (called the recalibration standards) can be selected and used to determine the parameters of the calibration graph such as new slope and intercept.

Other aspects related to the quality in EDXRF analysis include calculation of the total uncertainty [6], quality management, traceability of the results and method validation [35].

## **8. Conclusions**

Currently a variety of quantification methods are available for specific types of samples. The choice of the optimum (adequate) quantification method is not a trivial task which

often requires substantial knowledge and experience. A particular challenge exists in EDXRF analysis applied for *in situ* measurements where most of the interfering effects cannot be eliminated (or even reduced) by proper sample handling and sample preparation. Consequently, interpretation and quantification of the results require maximum care and a good background in X-ray physics. Taking full advantage of the EDXRF and nondestructive analytical capability in particular, makes the whole analytical procedure (especially its quantification part) more complex and creates a potential risk to generate less reliable analytical data. To cope properly with the problems, a professional advanced training in the methodology of EDXRF is becoming more essential than ever before. It is also advisable for the EDXRF laboratories to consider establishing a formal quality management system and to apply quality control/quality assurance procedures in a systematic way.

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