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Review

Standardless quantification methods in electron probe microanalysis

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ABSTRACT

The elemental composition of a solid sample can be determined by electron probe microanalysis with or without the use of standards. The standardless algorithms are quite faster than the methods that require standards; they are useful when a suitable set of standards is not available or for rough samples, and also they help to solve the problem of current variation, for example, in equipments with cold field emission gun. Due to significant advances in the accuracy achieved during the last years, product of the successive efforts made to improve the description of generation, absorption and detection of X-rays, the standardless methods have increasingly become an interesting option for the user. Nevertheless, up to now, algorithms that use standards are still more precise than standardless methods. It is important to remark, that care must be taken with results provided by standardless methods that normalize the calculated concentration values to 100%, unless an estimate of the errors is reported. In this work, a comprehensive discussion of the key features of the main standardless quantification methods, as well as the level of accuracy achieved by them is presented.

Contents

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1. Introduction

The technique known in our days as electron probe microanalysis (EPMA) was developed by Raymond Castaing in the middle of the last century [1,2]. This non-destructive technique for chemical characterization is based on the analysis of the X-ray spectrum emitted when a sample is irradiated by an electron beam. In its original version, a wavelength dispersive spectrometer (WDS) was used for the detection of X-rays. An important change was introduced in 1968 with the Si(Li) X-ray detectors [3], which gave rise to the energy dispersive spectrometers (EDS). They are faster, more stable and more efficient than the crystal spectrometer, although an important loss in resolution has to be paid.

To obtain the mass concentrations C_j, conventional EPMA involves the use of standards. In this case, the intensity $P_{j,q}$ of the characteristic line q emitted by each element j of an unknown sample is compared with the corresponding intensity $P_{j,q,0}$ emitted from a standard with concentrations $C_{j,0}$.

$$\frac{C_j}{C_{j,0}} = \frac{P_{j,q}}{P_{j,q,0}} \cdot \mathbf{ZAF} \tag{1}$$

Thus, to obtain the unknown concentrations, the intensity ratios $k_j = P_{j,q}/P_{j,q,0}$ must be corrected by matrix effects, denoted as **ZAF** correction factors, i.e., effects related to all the elements present in the sample and in the standard. Thus, production (**Z**), absorption (**A**) and enhancement of the characteristic radiation (**F**) must be taken into account. Two groups of methods have been extensively used to carry out these corrections: the models based on the **ZAF** factors and the ones which use the ionization distribution function $\varphi(\rho z)$ [4,5]. According to the last formulation,

$$\mathbf{ZA} = \frac{\int_0^\infty \varphi(\rho z) e^{-\mu \csc\psi \rho z} d\rho z}{\int_0^\infty \varphi_0(\rho z) e^{-\mu_0 \csc\psi \rho z} d\rho z}$$

where μ is the mass absorption coefficient for the analyzed energy and ψ is the take-off angle formed between the direction of the X-rays in their way to the detector and the sample surface. The subindex 0 refers to the standard.

These models have been proposed for different types of samples, leading to a progressive improvement in EPMA precision. The relative uncertainties are about 5% for major and minor elements, i.e., with concentrations greater than 10% and between 1 and 10%, respectively, and somewhat greater for trace elements (concentrations lower than 1%) [6]. Mineral samples constitute a special case for which, provided the adequate standards are available, the relative errors of the elemental concentrations are lower than 2% in most of the typical situations [7].

The main inconvenience of the methods described is that they require the measurement of a proper set of standards, which must be suitable for the particular sample studied. This requirement comprises two obvious conditions: first, an adequate set of standards must be available, and second, whole spectra or at least, some values at specific energies, must be measured for each standard to determine the net characteristic peak intensities. Usually, the unknown and standards must be measured in the same conditions, which imply that all measurements should be performed close in time. Otherwise, changes in detector efficiency and filament emission rate, among other possible parameters, could become significant sources of error. On the other hand, an important advantage related to the use of standards is that several atomic and experimental parameters cancel out in the k ratio, which reduces the uncertainty of the concentrations obtained.

According to Gauvin [8] and to our own experience, despite its good precision, quantitative X-ray microanalysis with standards is not used by most of the microscopists who acquire EDS spectra in electron microscopes. In fact, most of the samples of interest are not perfectly homogeneous and flat, as required by the current models. In addition, a proper set of standards is not always available. For these reasons, a compromise must be done between an ideal accurate quantification with standards, and a standardless method actually applicable to the particular situation. To optimize this compromise, a great effort has been done to improve [9–15] and develop [6,16–24] standardless algorithms in the last thirty years. Summarizing the advantages of standardless analysis, the main and obvious one is that they are not constrained to the samples for which a proper set of standards is available, besides, they are less time-consuming and some of the methods can be used for irregular samples.

The main disadvantage of the standardless methods of analysis in EPMA, as compared to the conventional ones, is that several fundamental and instrumental parameters must be known to obtain results with reasonable precision, particularly for the methods based on first principles (see below). Thus, the physics underlying generation, propagation and detection of X-rays must be properly known. Therefore, adequate descriptions of characteristic radiation, bremsstrahlung, and detection artifacts are required.

2. Advances in the description of generation, attenuation and detection of X-rays

The improvement of the accuracy and precision of standardless quantification methods in EPMA is related to the advances performed to improve the description of generation, propagation and detection of X-rays. In addition, the development of silicon drift X-ray detectors contributed to the quality of both conventional and standardless EPMA analysis. The main achievements in those fields are shortly described in this section.

2.1. X-ray generation

2.1.1. Bremsstrahlung

In the last two decades, several advances were produced in the description of the continuous X-ray spectrum generated by 1–40 keV electrons. Three different kinds of approaches have been faced to study the bremsstrahlung behavior as a function of the atomic number and the incident energy: theoretical calculations, Monte Carlo simulations and empirical fitting. Theoretical models are based in the assessment of a numerical integration involving the bremsstrahlung differential cross section [25,26] as a function of the photon energy. In this sense, Ambrose et al. [27] developed a model for the thick target bremsstrahlung that was later applied by Semaan and Quarles [28] to describe the continuum spectrum obtained with a scanning electron microscope. On the other