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Accuracy and precision in model based EELS quantification

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Abstract

We present results on model based quantification of electron energy loss spectra (EELS), focusing on the factors that influence accuracy and precision in determining chemical concentrations. Several sources of systematical errors are investigated. The spectrometer entrance aperture determines the collection angle, and the effects of its position with respect to the transmitted beam are investigated, taking into account the diffraction by the crystal structure. The effect of the orientation of the sample is tested experimentally and theoretically on $SrTiO_3$, and finally, a simulated experiment on c-BN at different thicknesses confirms the superior results of the model based method with respect to the conventional method. A test on a set of experimental reference compounds is presented, showing that remarkably good accuracy can be obtained. Recommendations are given to achieve high accuracy and precision in practice.

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Keywords: Electron energy loss; EELS; Model based quantification; Accuracy; Precision

1. Introduction: accuracy and precision

In previous papers [1,2] we have discussed the theory of model based quantification technique, as an alternative method to electron energy loss (EELS) conventional quantification based on background subtraction and integration of spectra from core excitations [3]. We showed that a correct description of the experimental noise is important to obtain statistically valid estimates of the parameters in the fitting procedure [4]. We demonstrated that the noise in a spectrum can be approximately treated as Poisson distributed, if the signal is scaled by a gain factor, and correlation effects are taken into account. These factors depend on the detector used in the measurements, and can be easily measured with an automated procedure [4]. In this way the *precision* of the estimated fitting parameters can be correctly estimated. The precision is the standard deviation in a set of repeated measurements and it is often confused with *accuracy*, which is the deviation of the mean value of a parameter in a set of repeated experiments with respect to the true value. Systematic errors can influence the accuracy of the parameter estimations if they are not properly taken into account in the model. These can originate, among others, from:

- finite convergence angle α,
- displacement of the collection aperture d,
- sample orientation τ,
- sample thickness t,
- approximations in the model for the cross-sections of the ionization edges (e.g., hydrogenic, Hartree-Slater, etc.),
- instrument (background in the spectrum, noise, artifacts, etc.).

In the next sections we examine the influence of these factors on the EELS spectra in more detail.

For testing the effects of the *convergence angle* and *collection aperture*, we approximate the angular dependence of inelastic scattering with a Lorentzian function

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with half width at half maximum (HWHM) given by θ_E,

$$\frac{\mathrm{d}\sigma_k}{\mathrm{d}E\,\mathrm{d}\Omega} \propto \frac{1}{\theta^2 + \theta_E^2}, \tag{1}$$

where $\theta_E = E/\gamma m v^2 \simeq E_k/\gamma m v^2$, and E_k is the energy onset for the edge of interest. For simplicity, the cross-section intensity I_k is evaluated as the differential cross-section at the edge onset E_k by integrating Eq. (1) in the detector solid angle.

The influence of *sample orientation* is verified in an experiment and a simulation on a crystalline $SrTiO_3$ film, measuring the Ti/O ratio as a function of the tilt angle with respect to a low index zone axis.

The effect of *sample thickness* is considered in a virtual experiment on c-BN, where the ratio B/N is estimated from simulated EELS spectra, making use of the FEFF code [5]. The ratios estimated at different thicknesses using both model based and conventional quantification are compared.

We will see that the *instrument* has an effect on the spectra, introducing correlation in the noise, and influencing the background of the EELS spectrum. In the last section we present a set of experimental measurements on different samples of known compositions to verify accuracy and precision obtainable in practical model based quantification.

2. Finite convergence angle

The incident beam traversing the sample is seldom perfectly parallel. This effect is larger in a scanning electron microscopy (STEM) experiment, where a highly condensed probe is formed [6,3]. The effect of convergence can be taken into account by means of a convolution of the incident intensity with the inelastic scattering (described by Eq. (1)). Using the results of Scheinfein and Isaacson [7], we can calculate a correction factor F_k [3] with respect to the differential cross-section $I_k(\beta, E)$ at parallel illumination (with β the collection aperture), assuming the incident intensity constant up to a cutoff angle α (defined as the convergence angle),

$$\begin{aligned} F_k &= \frac{I_k(\alpha,\beta,E)}{I_k(\beta,E)} \\ &= \Bigg[\sqrt{(\alpha^2+\beta^2+\theta_E^2)^2 - 4\alpha^2\beta^2} - \alpha^2 - \beta^2 - \theta_E^2 \\ &\quad + 2\beta^2 \ln\left(0.5\Big/\theta_E^2\left(\sqrt{(\alpha^2+\theta_E^2-\beta^2)^2 + 4\beta^2\theta_E^2} \right.\right. \\ &\quad \left.\left. +\alpha^2+\theta_E^2-\beta^2\right)\right) \\ &\quad + 2\alpha^2 \ln\left(0.5\Big/\theta_E^2\left(\sqrt{(\beta^2+\theta_E^2-\alpha^2)^2 + 4\alpha^2\theta_E^2} \right.\right. \\ &\quad \left.\left. +\beta^2+\theta_E^2-\alpha^2\right)\right)\Bigg] \\ &\quad \times \frac{1}{2\alpha^2 \ln(1+\beta^2/\theta_E^2)}. \end{aligned} \tag{2}$$

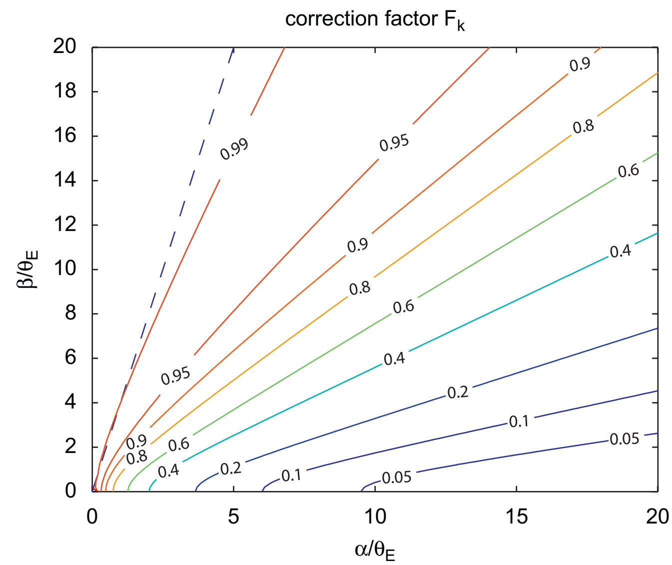

Fig. 1. (Color online) Plot of the correction factor F_k according to Eq. (2), as a function of convergence angle α and collection aperture β. θ_E is the characteristic angle of scattering (from Eq. (1)). The dashed line corresponds to $\beta = 4\alpha$.

Fig. 1 shows the results for F_k from Eq. (2), with α and β in units of θ_E. It is clear that the best condition to give a constant value for F_k is $\beta \gg \alpha$. For instance, the condition $\beta \geqslant 4\alpha$ is sufficient to achieve $\Delta F_k < 0.01$ for every θ_E (i.e., every E). Alternatively, or when this condition is not achievable (e.g., in some STEM cases), Eq. (2) permits to calculate the expected value F_1/F_2 of the chemical ratio between two elements (with corresponding edges at E_1 and E_2, respectively), according to the values of α and β in the experiment.

3. Displacement of the collection aperture

The models currently used for quantification consider the transmitted beam exactly on the optical axis, and the collection angle exactly centered around the optical axis. A source of systematic error comes in this case from the alignment of the diffraction pattern with respect to the entrance aperture of the spectrometer, usually manually operated by the user, and to electronic instabilities and hysteresis in the objective lens. Furthermore, some Bragg reflections can enter the spectrometer. We simulated this effect in the case of crystalline $SrTiO_3$ as depicted in Fig. 2a. A diffraction pattern consisting of the central beam plus the first Bragg spots (with 110 symmetry in the case of a [0 0 1] oriented $SrTiO_3$ sample) for a 70 nm thick film was created. Inelastic scattering was added at each Bragg reflection by convolution with a Lorentzian function from Eq. (1). The differential cross-section is calculated by numerical integration in a circular entrance aperture of radius β. The effect of displacement is taken into account by moving the center of the aperture over a distance d before performing the integration. The result of such simulation, as a function of collection aperture β and