doi:10.1017/S1431927614005261
Microsc. Microanal. 20 (Suppl 3), 2014

Application of Monte Carlo Calculations to Improve Quantitative Electron Probe Microanalysis

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The generation of x rays from solid samples under electron bombardment is the basis of electron probe microanalysis (EPMA), a widely used technique for materials analysis. The problem of quantitative analysis, i.e. the transformation of the measured x-ray intensities into element concentrations, is generally solved by means of approximate, semi-empirical algorithms. These algorithms provide reliable results for samples that are homogeneous at the micron scale, and, with suitable modifications, they can also be used for thin films. However, when the sample volume from which x-rays are generated is not homogeneous (e.g. small particles, multilayer films, lamellae structures...) or under unconventional measurement conditions (e.g. low voltage, low overvoltage, oblique incidence, standardless analysis...) the legitimacy of the simplifications underlying conventional quantification algorithms is not firmly established and there is a need for more realistic procedures. This need has lead to the use of the Monte Carlo simulation (MC) method.

One of the advantages of the MC method is that it can handle geometrical situations that would be difficult by other means. In addition, the increasing availability of fast computers has enhanced the attractiveness of the method. There are some disadvantages of the MC method but in recent years progress has been made in overcoming them. One drawback is that simulation results are affected by statistical uncertainties, which can be reduced to acceptable limits at the expense of increasing the simulation time and/or by using variance reduction techniques. On the other hand, the accuracy of MC simulation relies mostly on that of the cross sections and fundamental parameters adopted for the various interaction mechanisms. Early MC calculations of electron transport used approximate analytical interaction models, but today we can employ much more reliable physical models which are often described by means of extensive numerical databases. One such database is the new NIST Standard Reference Database 164 [1], which contains tables of cross sections for ionization of inner-shells required in EPMA simulations. These tables were calculated using state-of-the-art theories and numerical algorithms [2] and have been evaluated by extensive comparison with experimental data [3]. These developments are crucial to allow MC simulation to be used as the basis of quantification procedures.

In this communication, we discuss the availability and accuracy of interaction models and fundamental parameters needed for the simulation of EPMA measurements. We illustrate the possibilities of PENEPMA [4] as a valuable tool to improve quantitative EPMA, namely to assess the reliability of practical quantification methods, to guide the development of improved algorithms and to select the instrument parameters for optimal EPMA measurements. PENEPMA is a dedicated program for the simulation of x-ray spectra based on the general-purpose code PENELOPE [5]. Some recent

applications of PENEPMA include the evaluation of predictive formulas for the calculation of the surface ionization at low voltage [6] and the development and validation of a semi-analytical method for the calculation of secondary fluorescence across phase boundaries [7]. In the latter method, secondary fluorescence intensities are calculated numerically by integrating the equations that describe the emission of x-ray fluorescence from adjacent media. The calculation makes use of the intensities of primary photons, which are generated from short PENEPMA runs as they are not readily available and do not allow analytical calculation. Other examples include the accurate determination of the spatial resolution of EPMA measurements at low voltage and the calculation of k-ratios for unconventional x-ray lines such as the Ll or Lη lines. The latter lines have proven to be valuable for the analysis of transition elements at low voltage [8], but they are not generally available in conventional quantification algorithms. In all the presented cases, simulation results are compared with experimental measurements to further assess the reliability of PENEPMA.

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https://doi.org/10.1017/S1431927614005261 Published online by Cambridge University Press