# Accuracy of Quantitative EPMA Models at Low Voltages

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Castaing [1] in 1951 established the basis of quantitative electron probe microanalysis (EPMA) by showing the existence of a relationship between element concentration and characteristic x-ray intensity. Since then, many improvements in instrumentation as well as in the data-reduction procedures have been performed. One of the most important theoretical development has been the emergence of models that allow realistic calculations of the depth-distribution of generated x-rays, the $\phi(\rho z)$ distribution. This distribution is the key parameter for the calculation of the emitted x-ray intensity and has the advantage that it can be measured experimentally by the tracer method [2]. Indeed, in the past decades, a number of analytical models have been proposed to parameterize the $\phi(\rho z)$ function, which make it possible to estimate the element concentrations from the measured x-ray intensities by means of relatively simple, analytical algorithms. These models are generally defined by a few parameters which are computed from physical quantities (e.g. backscattering coefficient, stopping power, etc..) and/or fits to experimental or Monte Carlo simulation data. Thus, improvements in the description of the interaction properties of electrons with matter (due to the advent of fast computers), and the availability of new and more accurate experimental data, have allowed realistic $\phi(\rho z)$ distributions to be obtained. As a result, the accuracy of the EPMA analysis of ultra-light elements (from beryllium to oxygen) and the analysis of thin films and multilayers has improved significantly [3, 4, 5]. The use of $\phi(\rho z)$ models in simulation procedures has also proven to be a valuable tool to optimise experimental parameters (e.g. accelerating voltage, measured lines, etc..).

More recently, with the employment of field-emission sources in electron microprobe instruments, EPMA at low accelerating voltages has become feasible and the spatial resolution of the technique has improved significantly, reaching the sub-micrometer level [6]. The incorporation of field-emission guns, along with the use of new synthetic multilayer crystals in wavelength-dispersive spectrometers, opens a wide range of new possibilities for the characterization of materials that are heterogeneous on a sub-micrometer scale. However, the reliability of EPMA analysis at low voltages is not yet firmly established. On one hand, at low accelerating voltages, the less intense, unfamiliar low-energy x-ray lines (mostly L- and M-lines) have to be used, which are often affected by spectroscopic problems (peak shifts, peak overlapping) and larger uncertainties in the associated mass-attenuation coefficients or fluorescence yields. One the other hand, at low energies, most x-ray lines are measured at low overvoltage ratios, and in such energy range, the realiability of existing $\phi(\rho z)$ models is questionable. Moreover, low-energy x-ray lines have generally low peak-to-background ratios and consequently lower detection limits, as the corresponding electron shells are subject to low fluorescence yields. EPMA at low energies may also be affected by experimental problems, such as carbon contamination, surface oxidation, or surface roughness, which may affect the accuracy of results. At such energies, samples are often not bulk anymore and have to be

considered as layered structures, thus requiring the use of $\phi(\rho z)$ models suitable for thin films and multilayers [7].

In this communication, we review the basic features of quantitative EPMA models, placing special emphasis in their fundamental limitations at low accelerating voltages. For instance, the simple analytical expressions adopted in most $\phi(\rho z)$ models for the calculation of the ionization cross section or the stopping power largely affect the reliability of results at low accelerating voltages (and low overvoltages). As a example, we show how most of the currently available analytical parameterizations of the surface ionization, $\phi(0)$, fail to consistently reproduce new measurements of this quantity recently performed for L- and M x-ray lines [8]. Conversely, calculations of $\phi(0)$ with the MC simulation code PENELOPE [9], which adopts more elaborate models for the ionization cross section [10] and for the stopping power, reproduce the measured $\phi(0)$ values reasonably well. We conclude that improved EPMA models for the analysis at low accelerating voltages, low overvoltages and using low-energy L and M x-ray lines are still required.

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