

High Speed Matrix and Secondary Fluorescence Effects From Fundamental Parameter Monte Carlo Calculations

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Monte-carlo simulations of electron solid interactions can provide quantitative information on the production of characteristic x-ray intensities based on fundamental physical parameters. Such calculations, if performed long enough to attain sufficient levels of precision, can allow the analyst to predict the emitted x-ray intensities for arbitrary materials and geometries including bulk matrix corrections and boundary effects from secondary fluorescence. However the computational time required for such calculations, especially for those without simplifying approximations are generally extremely time consuming and impractical for routine use in the lab.

Calculations for the specimen and standard material using Penepma (version of Penelope optimized for EPMA), is often a matter of days or even weeks of computation, particularly when attempting to characterize the degree of secondary fluorescence from multiple discrete distances from a phase boundary. Similarly, iterative calculations involving bulk matrix calculations are equally prohibitive time-wise.

Work on deriving a general analytical/numerical method based on fundamental parameters for such matrix and secondary fluorescence calculations [1], and more recent work by Llovet and Salvat [2], have demonstrated that by utilizing a combination of monte-carlo simulations and numerical models, one can significantly reduce the simulation time for arbitrary materials with sufficient precision for quantitative calculations (Fig 1).

Unfortunately the required calculation time is still impractical for on-line calculations when acquiring x-ray intensities on the instrument. However, by taking advantage of a computational method, originally developed in the 1970s for use with early computers, we can utilize pre-calculated binary composition intensities for the calculation of matrix and fluorescence effects for arbitrary compositions in seconds.

The original hyperbolic expression developed by Ziebold and Ogilvie [3] and Bence and

$$C / K = \alpha + (1 - \alpha) * C$$

Albee [4] assumed a constant correction term (alpha) for the range of a binary composition to allow empirical calibration with a single standard and this method worked well at the time for most silicates and oxides. Further work by Mark Rivers at UC Berkeley (pers. comm.) showed that the above expression could be easily rearranged to the more flexible expression shown here, which allowed the use of a linear two

$$\alpha = (C / K - C) / (1 - C)$$

coefficient fit which greatly improved the accuracy of the calculation over the entire compositional range of the binary. Subsequent work by Armstrong [5], utilized a three coefficient polynomial fit to the expression from Rivers, a modification which allowed the analyst to handle even cases of extreme absorption and fluorescence.

Therefore, by utilizing a range of binary concentrations from 1 to 99% in the matrix element of interest, pre-calculated binary k-ratios based on these Penelope/Penepma fundamental parameter methods can be utilized as alpha-factors components for the on-line correction of bulk matrix and secondary fluorescence effects in real time.

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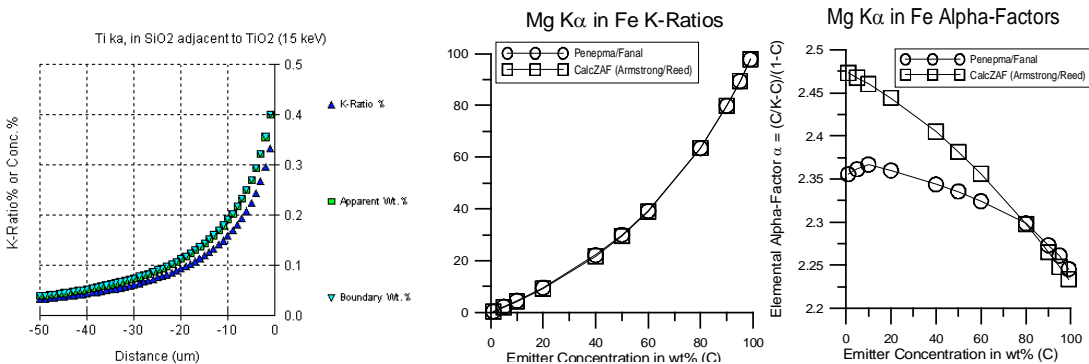


Figure 1. Ti K α intensity in pure SiO₂ adjacent to TiO₂ as a function of distance from the boundary calculated in seconds based on a combination of previously calculated materials from monte-carlo simulation and numerical expressions for extraction of intensities for arbitrary beam energies and distances. The concentrations reported here are based on the "apparent" observed concentrations (and matrix corrections) as would be reported by typical matrix correction methods which assume that all emitted intensities are emitted from the beam incident material. When implemented as an iterative correction, our method would produce a fully rigorous matrix correction in real time.

Figure 2. K-ratios and Alpha-factors from Penepma/Penfluor/Fanal and CalcZAF (Armstrong/Reed) for the binary system Mg K α in Fe from 1 to 99 wt. % of the emitting element.