

High Speed Monte Carlo Matrix and Secondary Fluorescence Corrections by the Binary Composition Method

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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 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), are 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.

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, we can utilize pre-calculated intensities of binary compositions to determine matrix and fluorescence effects for arbitrary complex compositions. The original hyperbolic expression developed by Ziebold and Ogilvie [3] and Bence and Albee [4] assumed a constant correction term (alpha) for the range of a binary composition to allow empirical calibration with a single standard.

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

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 here,

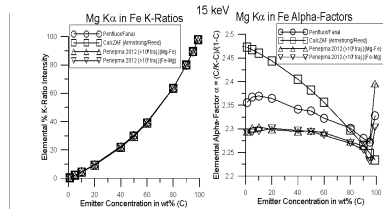
$$\alpha = (C/K - C) / (1 - C)$$

which allowed the use of a linear two 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.

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.

- [1] J.A Escuder, F Salvat, X Llovet, J J Donovan, "Numerical Correction for Secondary Fluorescence Across Phase Boundaries in EPMA", 11th European Workshop on Modern Developments and Applications in Microbeam Analysis IOP Publishing IOP Conf. Series: Materials Science and Engineering 7 (2010)
- [2] X Llovet, P Pinard, J. Donovan and F Salvat, "Secondary Fluorescence in Electron Probe Microanalysis of Material Couples", Journal of Physics D: Applied Physics, 2012
- [3] T O Ziebold and R E Ogilvie, "An Empirical Method for Electron Microanalysis of silicates, oxides, carbonates, phosphates, and sulfates", Analytical Chemistry, 42, 1970
- [5] J T Armstrong, "Bence-Albee after 20 years: Review of the Accuracy of a-factor Correction Procedures for Oxide and Silicate Minerals," Microbeam Analysis—1988
- [6] J.L Pouchou and F Pichoir in "Electron Probe Quantitation", ed. K. F. J. Heinrich and D. E. Newbury, Plenum Press, New York (1991), pp. 31-75.

High Speed Matrix Corrections



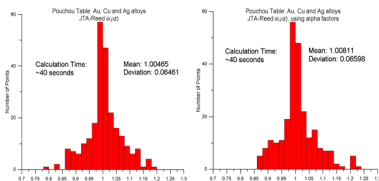
Left: Plot of Elemental K-Ratio %, for a range of Mg (emitter) - Fe (absorber) binary compositions from 1 to 99%. Note that the differences between the models are not easily discerned.

Right: Plot of alpha factors (C/K-C)/(1-C). The scatter at high concentrations is due to precision from small differences in the calculated primary intensities which will have little or no effect in actual compositions since the contribution of the absorbing matrix element is essentially zero as the emitter concentration approaches 100% when summed in the beta factor calculation for complex materials.

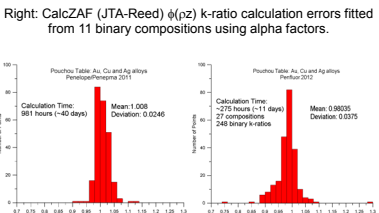
For complex matrices the compositional alpha factors are combined as a beta factor using the expression here:

$$\beta_B = \sum_1^{n_A} (\alpha_{1(B,A)} + C_A * \alpha_{2(B,A)} + C_A^2 * \alpha_{3(B,A)}) * C_A$$

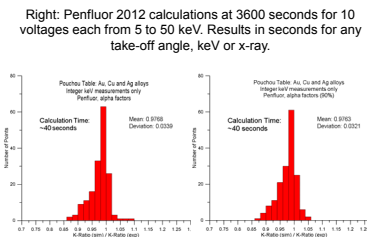
Where $\alpha_1, \alpha_2, \alpha_3$ are the polynomial fit coefficients for the emitting element in the matrix element, and C is the concentration of the matrix element.



Left: CalcZAF (JTA-Reed) $\phi(\rho z)$ k-ratio calculation errors for the Au, Cu, Ag alloy measurements from Pouchou tabulation [6].



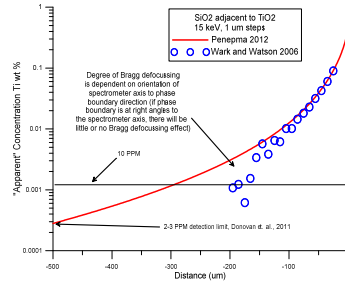
Left: Penepma 2011 0.01% precision limited k-ratio calculation errors for the Au, Cu, Ag alloy measurements from Pouchou.



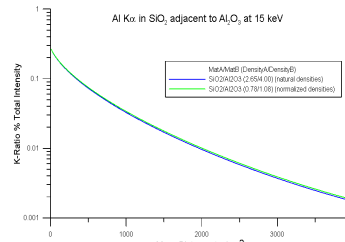
Left: Penfluor 2012 k-ratio (fitted to alpha factors) calculation errors for the Au, Cu, Ag alloy (integer only) keV measurements.

Right: Penfluor 2012 k-ratio (fitted to 90% alpha factors) calculation errors for the Au, Cu, Ag alloy measurements.

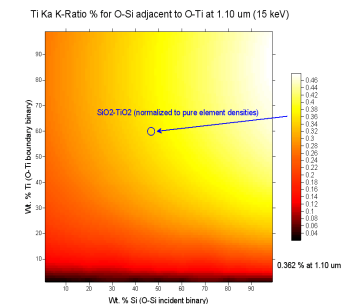
High Speed Boundary Corrections



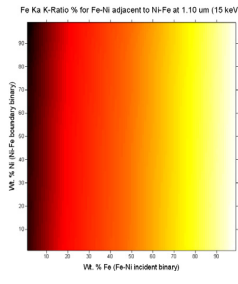
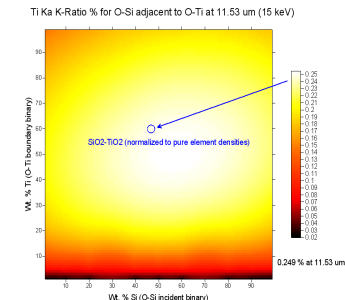
Ti K α intensities in SiO₂ adjacent to TiO₂ both empirically measured (blue circles) and calculated (red line) utilizing monte-carlo calculations for primary electron excitation combined with geometric calculations for secondary fluorescence effects from the TiO₂ boundary material.



Al K α measured in SiO₂ adjacent to Al₂O₃ shows that the density effects can be dealt with by proper normalization of the binary material densities.



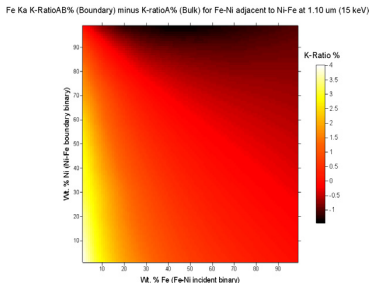
Plot of Ti K α measured in SiO₂ adjacent to TiO₂ for the beam incident compositional range (x-axis) versus the boundary compositional range (y-axis), with stoichiometric SiO₂/TiO₂ noted at 1.10 um (and at 11.53 um below).



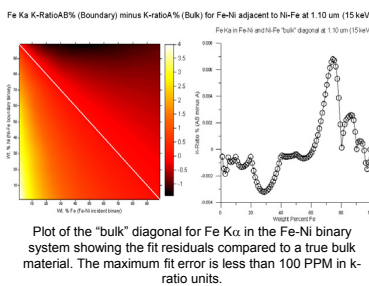
Plot of the Fe K α k-ratio % in the Fe-Ni binary system for the beam incident and boundary compositional binaries from 1 to 99 wt. % showing the effect from the beam incident material.

For secondary fluorescence from boundary corrections, the approach is to subtract from the measured k-ratio (K_{raw}), the difference between the calculated boundary (K_{AB}) and bulk (K_A) intensity k-ratios from binary Monte-Carlo simulations using the expression:

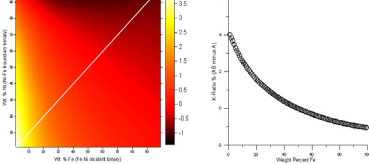
$$K_{corr} = K_{raw} - (K_{AB} - K_A)$$



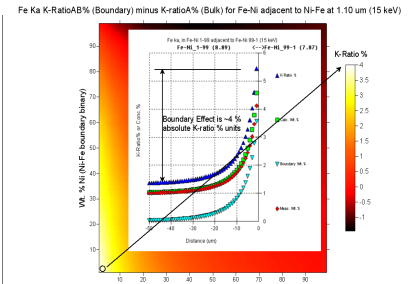
Plot of the Fe K α boundary k-ratio % minus the bulk k-ratio % for the beam incident and boundary compositional binaries.



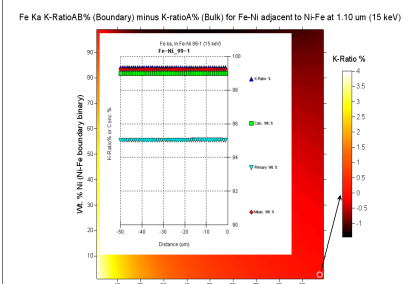
Plot of the "bulk" diagonal for Fe K α in the Fe-Ni binary system showing the fit residuals compared to a true bulk material. The maximum fit error is less than 100 PPM in k-ratio units.



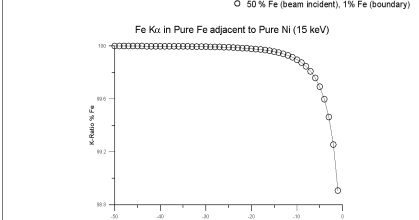
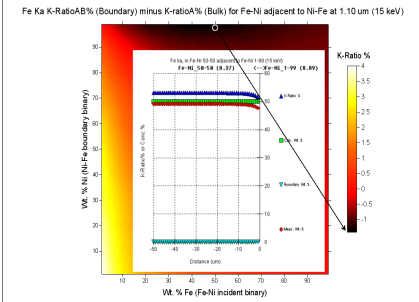
Plot of the "1 to 99" diagonal for Fe K α in the Fe-Ni binary system showing the k-ratio % trend. Note that the boundary effects are not only dependent on the composition of the beam incident material and the boundary material but also the boundary distance and density.



Plot of the Fe K α k-ratio % in the Fe-Ni binary system for an Fe-1N99 beam incident and an Fe99-Ni1 boundary composition showing the maximum boundary effect for a boundary distance of 1.1 um.



Plot of the Fe K α k-ratio % with an Fe99-Ni1 beam incident and an Fe99-Ni1 boundary material binary (a bulk material calculation!) showing the minimum boundary effect. Below the effect due to "missing" self-fluorescence of Fe K α by Ni K α /K β within the beam incident material.



Bonus Question: What physics is causing the intensity to drop off as the pure Ni boundary is approached on the right? Hint: all electrons come to rest within the pure Fe material.