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COMPARISON OF EXPERIMENTAL AND THEORETICAL XEDS CROSS-SECTIONS AND K-FACTORS AS A FUNCTION OF ACCELERATING VOLTAGE

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For nearly fifteen years k-factor measurements have been made by varying the composition of the standards at fixed accelerating voltage and reporting the change in the experimental k-factor with atomic number. An example of this is shown in figure 1a. which compares recent data of Sheridan[1] with various k-factor calculations using cross section parameterizations by Mott and Massey (MM) [2], Green and Cosslett (GC) [3], Brown (B) [4], Powell (P) [5], Schreiber and Wims (SW) [6], and Zaluzec (Z)[7]. From this data a "best model" of the ionization cross-section is frequently proposed for use in quantitative x ray analysis in the AEM , however it is valid only at that fixed voltage. It is usually difficult to judge the validity of the selection of cross-section using this type of plot and difference plots (i.e. [Theory-Expt]/Expt) as shown in figure 1b are more useful for this purpose. These difference plots illustrate that the k-factor at a fixed voltage is not particuliarly sensitive for determination of the correct ionization cross-section parameterization, due to normalization effects which are inherent in it's definition. In fact, calculations show that the relative errors between cross-section models as shown in the difference plot are of the same order of magnitude as those which one would calculate due to inaccuracy in the thickness of the various Si(Li) detector parameters (i.e. Be, Au, Si Dead, Si Active windows). For example, a variation in the Au thickness from 100 to 300 Å can shift the calculated k-factor difference curves by nearly 5%, which is in some cases the difference between models at a fixed accelerating voltage as we can see in figure 1b. On the other hand few, if any, studies to date have sought to determine the systematic variation in the k-factor with accelerating voltage. In this paper experimental measurements of the absolute intensity variation of elemental standards are used to illustrate the differences cross-section models, which are then subsequently compared to experimental variations in the k-factor with accelerating voltage. With the advent of medium voltage analytical microscopes routinely available to the microscopy community, it becomes essential to understand how the k-factor varies with accelerating voltage in order that errors in quantitative analysis can be avoided should experimental or theoretical k-factors from lower voltage instruments be applied to the medium voltage regime.

X-ray intensity measurements for 5 thickness of evaporated polycrystalline aluminium films (227, 415, 656, 1136, and 3082 $\pm$ 30 Å) were made from 50 to 300 kV in a Philips CM30T electron microscope, equipped with a Be-Window Si(Li) detector interfaced to an EDAX 9900 Energy Dispersive Analysis System. Multiple measurements

were taken of each specimen which were mounted in a Gatan Berylium double tilt Liquid Nitrogen Cooled sample stage for the study. Hole count corrections were made to all spectra and were particularly important above 100 kV. Shown in figure 2a is the experimental Al K shell x-ray emission/nA as a function of thickness for the various voltages, while in 2b the data is divided by the film thickness and replotted as a function of voltage to demonstrate multiple scattering effects on the x-ray intensity. Here we can see that as the thickness of the specimen increases above about 600Å the effects of multiple scattering give enhanced intensity over that of the thinner films and hence cannot be directly used for cross-section comparisons. In figure 3a, the Al intensity/nA (which is now a direct measure of the ionization cross-section) for the 200 and 400 Å thick films is normalized at 50 kV and compared to different theoretical calculations of the ionization cross-section. Generally the non-relativistic models (MM, GC, P) severly underestimate the variation in cross-section with voltage while the relativistic parameterization (Z) seems to most closely follow the experimental data. Figure 3b shows similiar data and results from a thick (~600 Å) germanium evaporated film, again as in the Al case, the non-relativistic models underestimate the cross-section. Here multiple scattering will, as in the case of Al, depress the normalized data at the higher kV and hence the relativisitic parameterization still appears to more closely predict the voltage variation.

In addition to the preceeding evaporated elemental thin film measurements, electropolished specimens of NiAl and TiAl were studied to determine the effect of accelerating voltage on the k-factor. Figure 4 shows the experimental variation of the NiKα/AlK and TiKα/AlK intensity ratios as a function of accelerating voltage from 100 to 300 kV. From equation 1, we can see that this ratio is a direct measure of the dependence of the k-factor and the ionization cross-section (σ) with voltage as σ is the only term which varies with electron energy.

$$\frac{I_A}{I_B} = \frac{\kappa_A\, \varepsilon_A\, C_A}{\kappa_B\, \varepsilon_B\, C_B} = \frac{1}{k_{AB}}\,\frac{C_A}{C_B} \qquad \text{where } \kappa_A = \frac{\sigma_A \omega_A \Gamma_A}{W_A} \qquad (1)$$

In equation 1: $\sigma_A, \omega_A, \Gamma_A, W_A, \varepsilon_A$, CA and I_A are respectively the ionization cross-section, fluorescence yield, radiative partition function, atomic weight, detector efficiency, composition and x-ray line intensity for the element A, while k_{AB} is the conventional k-factor. In figure 5, we compare this data with the theoretical variation in the ionization cross-section ratio for NiK/AlK and TiK/AlK shells, here all data is normalized at 300 kV.

These experiments illustrate that the k-factor can vary substantially with accelerating voltage and care must be taken when applying experimental and/or theoretical models determined at lower accelerating voltages to the intermediate voltage regime. Furthermore, relativistically corrected models for the ionization cross-section can successfully predict the voltage dependence of both the relative intensity as well as the k-factor, within the limits of the thin film approximation (no energy loss, absorption and fluorescence). Further work is in progress to extend these measurements to higher atomic

number materials to more precisely determine the applicability of the parameterizated relativisitic model.

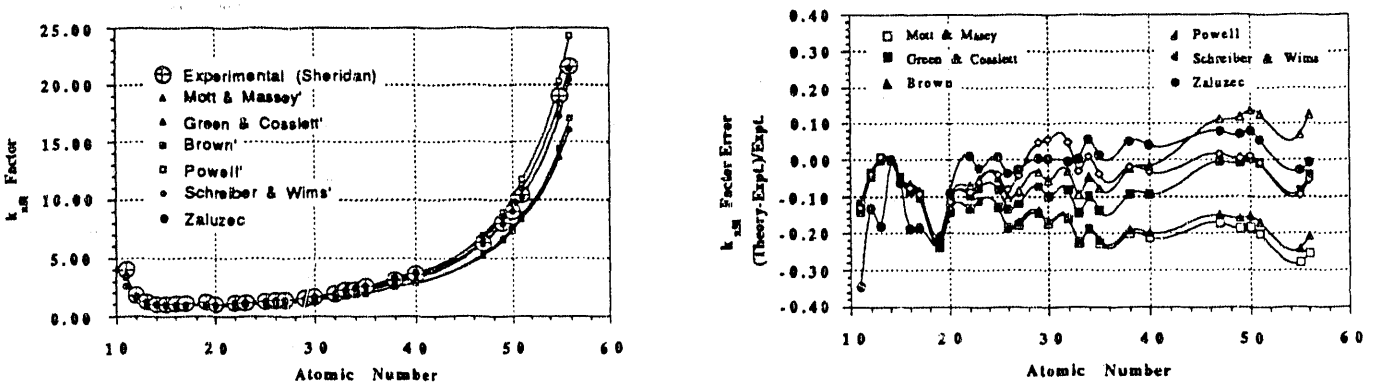

Figure 1a. Experimentally determined k factors calculated using various cross-section models. 1b. Difference plot (Theory-Expt)/Expt. of k-factor showing relative errors.

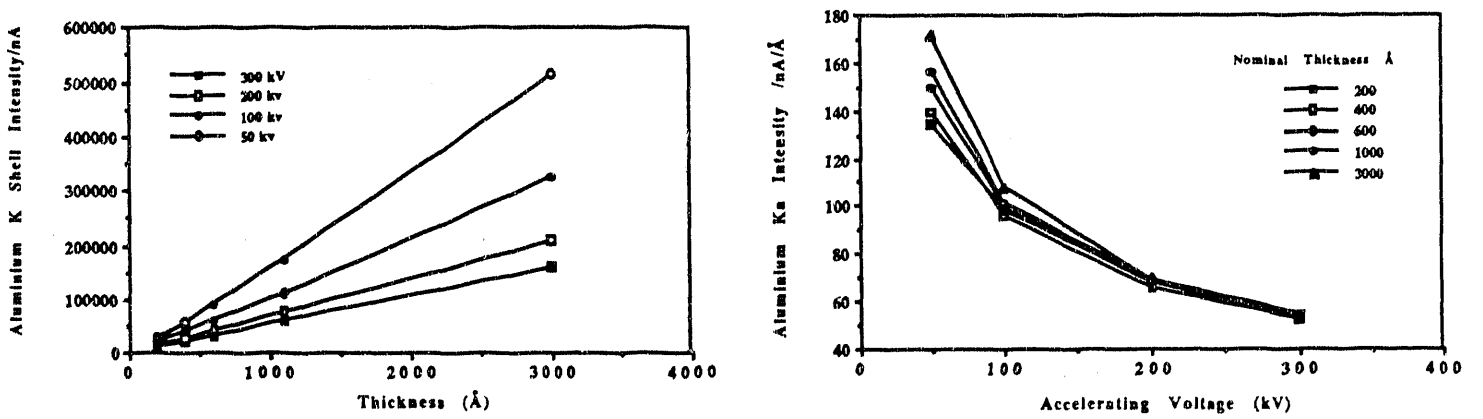

Figure 2a Al K intensity/nA as a function of thickness for various voltages. 2b Al K intensity/na/Å as a function of accelerating voltage for different specimen thicknesses.

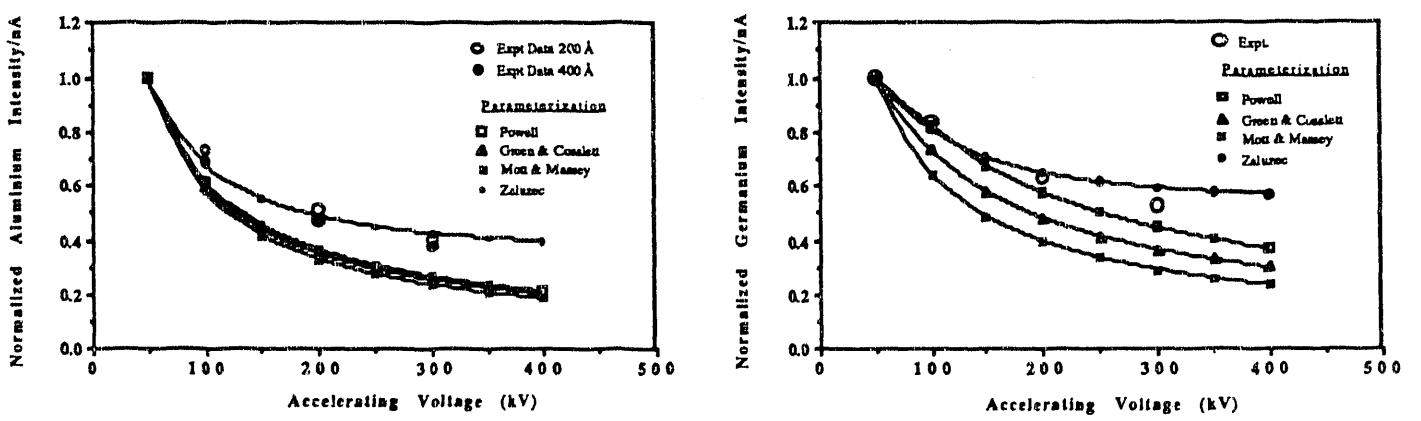

Figure 3a) Comparison of normalized Al intensity/nA with different cross-section parameterizations. 3b) Comparison of normalized Ge intensity/nA with different cross-section parameterizations.

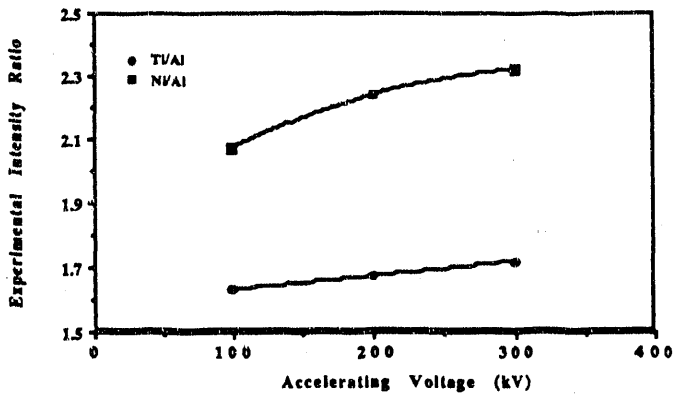

Figure 4. Experimental variation in Ni/Al and Ti/Al K shell x-ray intensity ratios as a function of accelerating voltage.

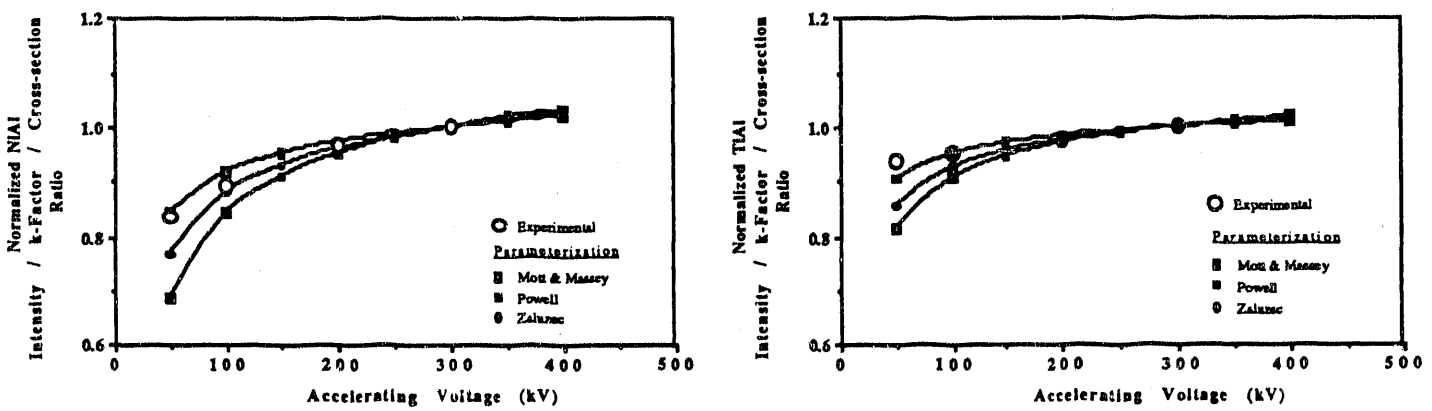

Figure 5. Comparison of calculated and experimental Ni/Al and Ti/Al intensity ratios as a function of accelerating voltage normalized at 300 kV.

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