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Is SEM/EDS Quantitative?

Dale E. Newbury and Nicholas W. M. Ritchie

National Institute of Standards and Technology, Gaithersburg, MD 20899-8370

Scanning electron microscopy/energy dispersive x-ray spectrometry (SEM/EDS) for elemental microanalysis is a critical technique widely applied in engineering, technology, and the physical and biological sciences [1]. Modern computer-aided analysis enables rapid calculation of numerical concentration values, but can such results be trusted as quantitative, which requires both an understanding of and minimization of the error sources in the measurement? Long considered the "gold standard" of accurate x-ray microanalysis, applicable even when severe peak interference occurs, microanalysis by wavelength dispersive x-ray spectrometry (WDS) in the SEM follows a strict protocol: x-ray intensities are measured on unknowns and standards in the form of flat bulk targets under identical conditions of beam energy, spectrometer efficiency, and known dose to determine a suite of "k-values", the ratio of peak intensities, unknown-to-standard, for each element. The k-value is the foundation of quantitative x-ray microanalysis, with concentrations calculated from k-values by the application of matrix corrections (e.g., ZAF, $\phi(\rho z)$, etc.). By following this same rigorous measurement protocol, SEM/EDS has demonstrated measurement of k-values statistically indistinguishable from WDS [2]. The critical requirement for EDS to match WDS is to accumulate high x-ray counts, typically spectrum integrals of 5×10^6 or greater. The silicon drift detector (SDD-EDS) with its greatly improved throughput, a factor of 10 to 100 better compared to Si(Li)-EDS, makes possible such statistically robust k-value measurements within a practical time expenditure, e.g., 50 s. SDD-EDS measurements can now be made with the error budget of WDS measurements. However, for many analysts a flat, polished specimen may not be feasible, and what is really implied by the title question is how significantly the quantitative analysis error budget is compromised when specimens of complex shape must be measured. This study examines the impact of specimen shape on microanalysis accuracy using NIST SRM 470 (K411 glass) in various forms: (1) bulk, polished; (2) bulk abraded by 600-grit silicon carbide; (3) surface cavities; (4) microscopic irregular particles; and (5) macroscopic fragments. K411 was chosen because of the range of major/minor constituents represented and the span of photon energies as listed in Table 1 (inset in Figure 1). SDD-EDS spectra were recorded with a beam energy of 20 keV and a deadtime of ~10% at 100 kHz output count rate, yielding a spectrum integral of $\sim 5 \times 10^6$ counts (0.15 keV – 20 keV) in 50 s. Standards included Mg, Si, and Fe as pure elements, and Ca from NIST SRM 470 (K412), with oxygen calculated by assumed stoichiometry (Fe=2). The spectra were analyzed with NIST DTSA-II applying multiple least squares (MLS) peak fitting and XPP matrix corrections [3]. Results were normalized to 100% as is frequently done in analytical practice. Figure 1 shows a plot of the Fe vs. Mg concentrations for various geometric forms. Because of their wide separation in photon energy, Mg and Fe behave differently with sample geometry and thus provide a sensitive diagnostic for geometric effects. The analysis of 20 locations on flat bulk material (inset) produces a range of approximately 1 percent relative in both Fe (11.33 to 11.46; mean 11.40%) and Mg (8.61-8.82; mean 8.76%), but when the various sample shapes are measured, the range of measured concentration greatly increases: Mg ranges from 0.25% to 11% while Fe is inversely correlated from 75% to 9%. This dramatic increase in error occurs because of the high absorption suffered by Mg compared to Fe, which then artificially elevates the Fe component after normalization. Such a huge range in the apparent composition of a homogeneous material obviously renders such analytical results of little

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practical value. The random counting component of the error budget is typically less than 0.25% relative for the high count spectra used, and the systematic error contribution from the limitations of the matrix corrections is estimated to be less than 2.5% relative. The source of the very large errors for specimens with special shapes is due to the systematic error that results from the severe deviation of the x-ray generation and propagation situation from the model that applies to ideal flat, bulk targets upon which the matrix corrections are based. To avoid or at least minimize errors when analyzing such specimens, the analyst can examine several clues: (1) the shape of the x-ray continuum deviates from "bulk" behavior, especially for photon energies below 4 keV; (2) the raw analytical total deviates significantly from 100%, although this diagnostic is not available when standardless analysis is used for matrix corrections; and (3) x-ray spectrum imaging can reveal areas of unusual absorption which have the most severe impact.

References

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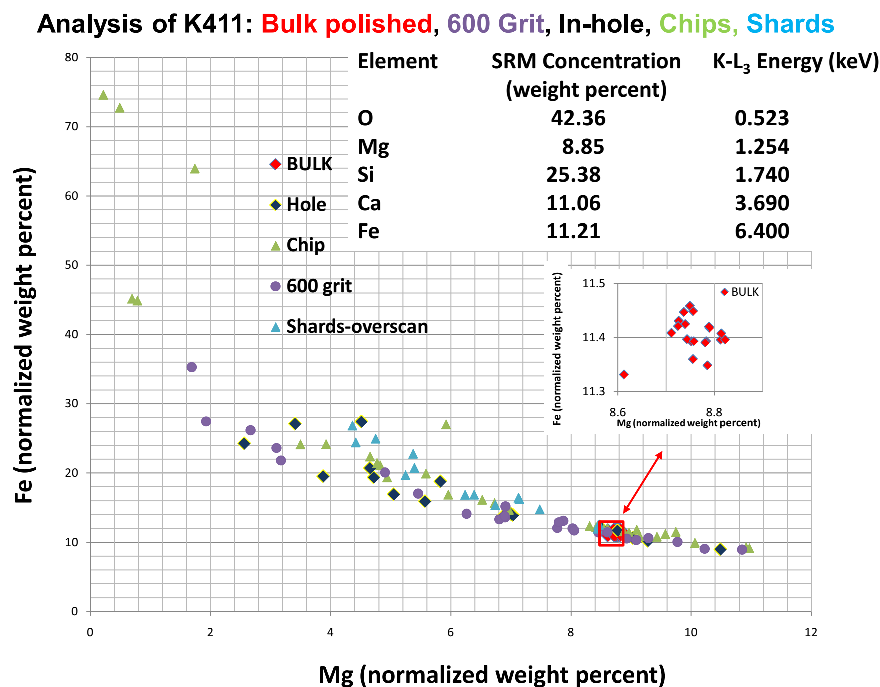

Fig. 1. Fe vs Mg (normalized weight percent) for K411 glass in various forms.

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