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EFFECTS OF CARBON COAT THICKNESS AND CONTAMINATION ON QUANTITATIVE ANALYSIS: A NEW LOOK AT AN OLD PROBLEM

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Due to considerable improvements in electronic stability and detector sensitivity, modern electron microprobes and SEMs have the capability of routinely making x-ray measurements much more precisely than previously possible (often with a precision of as low as a few parts per thousand). The improvements in measurement precision, however, have not necessarily resulted in significant improvements in analytical accuracy. Factors that were once considered secondary now have may have significant importance in the accuracy of high-precision analyses. Among these is the variability in thickness of the carbon (or other conducting element) film evaporated or sputtered on insulating samples and standards. In this paper, we reexamine the effect the conducting surface layer has on emitted x-ray intensities. We show that (1) not accounting for variations in carbon coat thickness between sample and standard can result in systematic analytical errors greater than 1%, and (2) that the effect of carbon coat thickness on emitted x-ray intensities can be adequately corrected for using current $\phi(\rho z)$ models and data reduction programs for thin film analysis.

Other investigators have proposed semi-empirical equations to calculate the magnitude of the effect of variations in carbon coat thickness on emitted x-ray intensities.[1-3] Emitted x-ray intensity is lost both by absorption of generated x-rays by the coating film and by energy loss of the primary electrons during passage through the film. We reevaluated the importance of these factors by (1) making high precision measurements of the emitted x-ray intensities from major x-ray lines of elements in a series of carbon-coated metallic and insulating standards, along with the intensity of C Kα emitted from the carbon coating; (2) comparing these intensities with those measured under identical analytical conditions on uncoated metallic standards; and (3) comparing the data obtained to that calculated using both modern $\phi(\rho z)$ expressions with thin film data reduction programs and Monte Carlo simulations. The experimental measurements agreed very well with the modern correction programs (e.g., the thin film correction program of Waldo[4] using the "PAP" $\phi(\rho z)$ expression[5]. For example, specimens of Si and Ta metals mounted together and coated with an evaporated layer of carbon at a nominal thickness of 200Å produced emitted C Kα intensities (k-ratios relative to graphite of 0.028 and 0.038, respectively) corresponding to film thicknesses of 197.8Å and 197.6Å, respectively (E_0 = 10 keV, $\psi = 40°$). The effect of that coating thickness was calculated to produce k-ratio for Si Kα (relative to uncoated Si metal) of 0.9738, which compares very well to the measured value of 0.9728. (The Waldo-PAP calculations of emitted x-ray intensities for metal specimens coated with a carbon film shows good agreement with the Reed-Sweatman/Long-Kerrick expression for hard x-ray lines [e.g., Cu Kα], but relatively poor agreement for soft x-ray lines [e.g., Al Kα] [Fig. 1]. Our experimental data is much closer to the Waldo/PAP calculations than the Reed et al. expression.)

The calculations show that the effect of carbon coat thickness variations can be significant for essentially all emitted x-ray lines in high precision analyses. For example, for an SiO_2 sample, a carbon coat thickness variation of 100Å results in an intensity variation of about 3.8% for O Kα and 0.5% for Si at E_0 = 15 keV, and 4.1 to 4.6% for O Kα and 1.2 to 1.4% for Si Kα at E_0 = 10 keV. (The magnitude of variation depends on the coat thickness.) At 15 keV, the reduction of intensity per 100Å of C-coat thickness at E_0 = 15 keV is about 0.8% for Al Kα, 0.9% for Ti Kα, 1.2% for Fe Kα, and 1.5% for Cu Kα [c.f., Fig. 2].

Using specially prepared 1-inch-diameter plastic mounts of multiple standards, we tested the ability to obtain uniform carbon coat thicknesses on multiple standards in a single carbon evaporation. Care was taken to have minimize surface topology and maximize surface cleanness. The mounts were placed symmetrically and a constant distance from carbon electrodes and spun symmetrically with respect to the electrodes during evaporation. A nominal thickness of 200Å was coated. The mounts were removed and carbon thickness variations were estimated by the measured emitted C Kα intensity corrected for the substrate electron backscattering using the Waldo program. Adjacently mounted metal specimens showed agreement in apparent carbon coat thickness within 5 to 10Å, regardless of difference in atomic number; however, variations in carbon coat thickness of about 40 to 50Å were measured across the whole mounts. Radial and side-to-side variations were observed. Moreover, isolated small patches on some sample surfaces were observed to have thickness variations of as much as 100Å, suggestive of build-ups of carbon due to local topographic variations. These results suggest that, even when taking special precautions to obtain a uniform coating, variations in carbon coat thickness may occur which would produce percent-level errors in calculated concentrations. Very-high-accuracy analysis of coated samples requires direct monitoring of the coat thickness. Fortunately, the existence of high efficiency layered-dispersion-element pseudo-crystals for detecting carbon and high-quality thin film data reduction programs makes it now possible to directly and accurately correct for the effect of the coating thickness variations.

References

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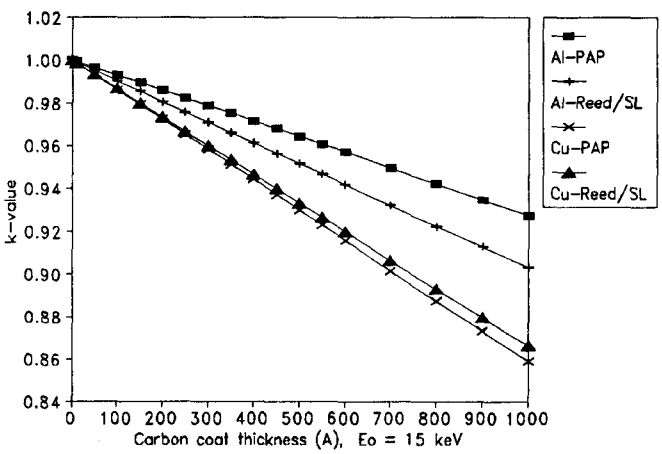

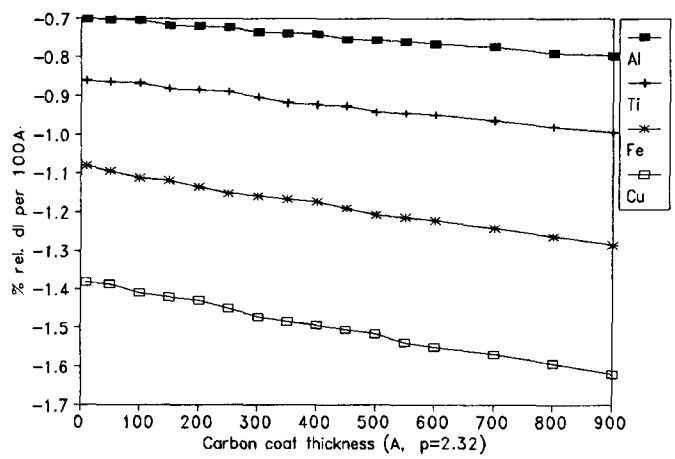

FIG. 1.--Comparison of the effect of carbon coat thickness on emitted x-ray intensities for Al Kα and Cu Kα from the pure metals calculated from the Waldo[4,5] program and the Reed[1-3] expression.
FIG. 2.--Effect of total carbon coat thickness on the relative loss of emitted Kα intensity per 100Å of coat thickness variation for Al, Ti, Fe and Cu in pure element specimens at E_0 = 15 keV.