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The Role of Carbon Film Thickness in Electron Microprobe Analysis

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Abstract

X-ray intensity loss as a function of carbon film thickness was determined for F, Na, Si, Fe, and Sr. Intensity loss is independent of the concentration of an analyzed element in the substrate. Because of X-ray absorption, increasing film thickness will cause greater reduction in X-ray intensity for light elements than for heavier ones. For light elements, X-ray intensity errors of up to 4 percent are possible with film thickness differences of 200 Å between sample and standard. The measured X-ray intensity loss as a function of film thickness is in good agreement with that calculated with an equation developed through consideration of electron and X-ray absorption. Carbon film thickness can be accurately monitored during evaporation by observing the interference colors of carbon films deposited on polished brass.

Introduction

A possible error in quantitative electron microprobe analysis arises from variation in thickness of the conducting film from one mount to the next. In view of the fact that the conducting film absorbs incident electron energy and X-radiation emitted from the substrate, recorded X-ray intensity will be inversely proportional to film thickness. Reed (1972) has pointed out a problem in quantitative analysis at low acceleration potential arising from variation in thickness of the carbon film. To alleviate analytical problems arising from film thickness variation, it has been suggested that samples and standards should be carbon coated during the same evaporation; however, this is often inconvenient, especially when analyzing a large number of samples.

The present study was undertaken to provide experimental data on the role of carbon film thickness in quantitative electron microprobe analysis, and to evaluate certain aspects of the film evaporation procedure.

Experimental Details

Carbon film thickness was determined during evaporation using a Sloan Instrument Corporation thickness monitoring system (trade name: "Iotron")[2] which measures film thickness by change in frequency of a quartz crystal oscillator. The sample and crystal oscillator were directly adjacent to one another and were located 8 inches above the carbon arc. Prior to evaporation the frequency of the crystal oscillator within the bell jar was nulled with that of an oscillator in an external console, and the frequency difference between the two oscillators, a function of the mass of carbon film deposited on the crystal oscillator, was monitored on a meter. This instrument was calibrated by film thickness measurements of several mounts using a "Dektak" film thickness monitor manufactured by the Sloan Instrument Corporation.[3] The Dektak provides a direct measurement of film thickness by a diamond stylus tracking over a vertical edge of the carbon film.

Because of progressive blunting during evaporation by the initially sharp tip of the carbon rod, the efficiency of carbon evaporation diminished with time. Thus, a maximum film thickness of *ca* 400 Å was obtained in a single evaporation. Consequently, deposition of film thickness above 400 Å required several successive evaporations, each starting with a sharpened carbon rod.

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[3] Measurements were made by Mr. Gary Breitweiser of Sloan Research Industries, Inc.

For each element investigated, several mounts of a particular substance containing this element were prepared. The mounts were polished together to avoid any problems arising from variation in the quality of polish from one mount to the next. Chemical homogeneity was assured by coating the mounts with the same film thickness, and then comparing numerous spot analyses within each mount, and average intensity measurements from one mount to the next. Each mount was then coated with the desired film thickness, and the X-ray intensity of each mount was compared to that of the same substrate material with a reference film thickness of 300 Å. This reference film thickness was chosen because initial investigation showed conductivity problems with film thickness less than about 200 Å.

Analyses were made with an ARL-AMX microprobe. A list of the substrate materials, with the corresponding X-radiation measured, is given in Table 1.

Experimental Results

Results of this study are plotted in Figure 1. Analysis of counting statistics suggests a reasonable error of ±1 percent in the X-ray intensity loss for points plotted in Figure 1 for Sr, Fe, Si, and Na; because of low count rates, error in X-ray intensity loss for F is larger (about ±2 percent). Primary sources of error in film thickness measurement arise from: (a) relative error resulting from inaccuracy in reading the meter on the film thickness monitoring equipment, and (b) absolute error in film thickness determination with the Dektak (used in calibrating the crystal oscillator unit). Taken together these factors suggest a reasonable total error of ±100 Å in the film thickness values of points plotted in Figure 1.

It is clear from Figure 1 that, for fixed values of film thickness and acceleration potential, there is a general inverse correlation between X-ray intensity loss and atomic number. Furthermore, since the intensity loss line determined for Fe in pyrite (Fe = 46.6 wt percent) is identical to that of Fe in amphibole (Fe = 25.4 wt percent), X-ray intensity loss is independent of the concentration of the analyzed element, and of different matrix compositions, in the substrate.

Sweatman and Long (1969, p. 335) derived the following equation for calculating the percent intensity loss for a given film thickness:

$$\Delta I = \frac{8.3 \times 10^4 \cdot \rho z}{V_0^2 - V_c^2} \cdot \exp\left[-\left(\frac{\mu}{\rho}\right)\rho z \operatorname{Csc} \theta\right],$$

where:

ΔI = percent X-ray intensity loss[4]
ρ = density of the film (in mg/cc)
z = thickness of the film (cm)
V_0 = acceleration potential (Kv)
V_c = critical excitation potential for the analyzed element (Kv)
μ/ρ = mass absorption coefficient of carbon for the particular radiation concerned
θ = takeoff angle (52.5° in our microprobe).

Part of the above equation was derived from Reed (1964) by integrating the ϕ *vs* ρz curves for Al, Au, and Cu given by Castaing and Descamps (1955) and then plotting a graph of percent loss in X-ray intensity generated in the tracer as a function of $\rho z / V_0^2 - V_c^2$ for the material covering the tracer layer. That electron energy loss is proportional to the square of energy is supported by Cosslett and Thomas (1964). Taking the slope of an average line on this diagram for Au, Cu, and Al, Reed (1964) derived the equation

$$\Delta I_{(\text{electron absorption})} = \frac{8.3 \times 10^4 \cdot \rho z}{V_0^2 - V_c^2};$$

thus, considering electron absorption only, the intensity (I_E) is:

$$I_E = \frac{I_0}{100}\left(100 - \frac{8.3 \times 10^4 \cdot \rho z}{V_0^2 - V_c^2}\right).$$

An additional factor in intensity loss results from

TABLE 1. Substrate Materials Used for X-Ray Intensity Measurements

Radiation	Mineral	Composition (wt. %)
F(Kα)	Fluorite	F = 48.7*
Na(Kα)	Albite	Na_2O = 11.75
Si(Kα)	Albite	SiO_2 = 68.22
Fe(Kα)	Pyrite	Fe = 46.6*
	Amphibole	Fe_2O_3 = 15.96; FeO = 18.52
Sr(Lα)	Strontianite	Sr = 59.3*

*Calculated from ideal stoichiometry.

[4] ΔI may be considered as the percent X-ray intensity loss. Thus, $\Delta I = 100 - 100 \cdot I_f/I_0$, where I_0 is the intensity recorded for a specimen with an infinitely thin film, and I_f is the recorded intensity for a specimen with a given film thickness (z).

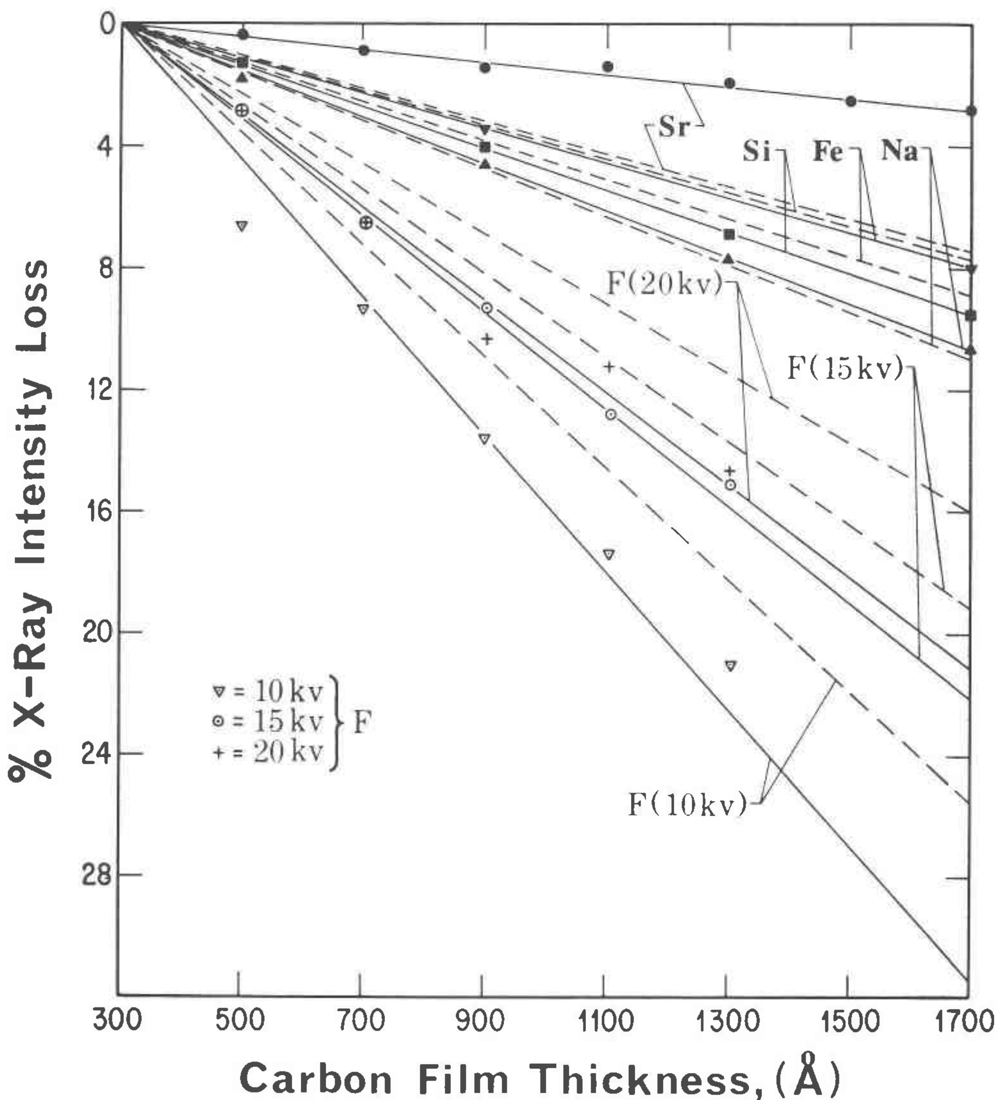

FIG. 1. Plot of measured X-ray intensity loss (solid lines), and intensity loss calculated with equation (1) in text (dashed lines). Except where noted, all lines were determined at an accelerating potential of 15 kv.

absorption by the film of the X-radiation emerging from the substrate. This is readily calculated using Beer's law for X-ray absorption:

$$I_f = I_E \cdot \exp\left[-\left(\frac{\mu}{\rho}\right)\rho z \; 10^{-3} \text{ Csc } \theta\right].$$

Thus the total intensity loss derived by combining both electron and X-ray absorption (and thus a revised form of the equation presented by Sweatman and Long, 1969) is:

$$\Delta I_{(\text{total})} = 100 - \frac{I_f}{I_0} \cdot 100$$

$$= \frac{8.3 \times 10^4 \rho z}{V_0^2 - V_c^2} \cdot \exp\left[-\left(\frac{\mu}{\rho}\right)\rho z \; 10^{-3} \text{ Csc } \theta\right] + 100 - 100 \cdot \exp\left[-\left(\frac{\mu}{\rho}\right)\rho z \; 10^{-3} \text{ Csc } \theta\right] \quad (1)$$

Shown in Figure 1 are curves calculated with this equation using the (μ/ρ) values tabulated by Birks (1971). The carbon film density of 1.3×10^3 mg/cc used in these calculations was derived by combining two sources of data: (a) by fitting Dektak film thickness to the corresponding frequency change

(Δf) recorded with the crystal oscillator unit, and using the equation:

$$\Delta f = \frac{\rho z}{2},$$

which yields a maximum carbon film density of about 1.3×10^3 mg/cc, and (b) by comparing this value with the lowest value for the density of evaporated carbon films reported in the literature, 1.35×10^3 mg/cc (Leder and Suddeth, 1960). Using the same procedure as Reed (1964), but with the ϕ *vs* ρz curves for Al from Castaing and Henoc (1966), and for Pb from Vignes and Dez (1968), we obtain the equation:

$$\Delta I_{(\text{electron absorption})} = \frac{6.2 \times 10^4 \cdot \rho z}{V_0^2 - V_c^2}$$

Intensity loss lines calculated with Reed's electron absorption constant (8.3×10^4) are somewhat closer to the measured intensity loss lines than are the corresponding lines calculated with the electron absorption factor derived above (6.2×10^4). Equation (1) shows that the steep slope of the F intensity loss line in relation to that of other elements investigated primarily reflects the strong X-ray absorption of the carbon film for soft X-rays. Perhaps the most pertinent conclusion from this analysis is that within the film thickness range commonly used for quantitative microprobe analysis (about 200–500 Å), equation (1) predicts X-ray intensity loss to within one percentage unit of the measured value.

The importance of acceleration potential is shown by comparing the intensity loss lines for F at 10 Kv, 15 Kv, and 20 Kv (Fig. 1). There is general agreement between the measured and calculated lines for the above acceleration potentials, supporting the square-law voltage factor for electron energy loss given in equation (1).

A possible complication in this study would be differences in film "sticking coefficients" from one substrate to the next, resulting from differences in such properties as submicroscopic surface texture and/or differences in surface charge. Thus, for a given frequency change measured with the crystal oscillator, the thickness of carbon film deposited on the adjacent sample may depend upon the substrate material. To check on this, mounts of substances measured in this study were subjected to the same evaporation procedure, and the film thickness of each mount was determined with a Dektak thickness

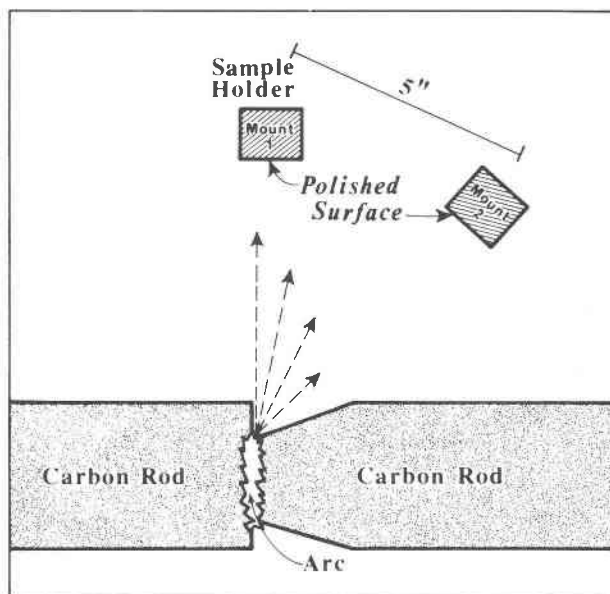

FIG. 2. Schematic sketch showing relation of mounts to carbon arc during evaporation to examine relative film "sticking coefficients" of various substrates. Dashed lines represent vectors of emergent carbon from the arc; the length of each vector is proportional to the amount of carbon/unit-time which passes in that direction. For illustrative purposes, the size of the carbon rods is considerably expanded in relation to the mounts.

monitor.[5] To investigate the possible effect of variation in film thickness according to position in the bell jar, an additional mount of iron was placed 5 inches away from the sample holder, and 8 inches away from the carbon arc (Fig. 2). The substrate materials, with corresponding film thickness, are as follows: albite (1930 Å), strontianite (1900 Å), fluorite (1760 Å), riebeckite (1990 Å), pyrite (1920 Å), iron (1930 Å; mount #1 in Figure 2), and iron (1200 Å; mount #2 in Figure 2). Thus, while most mounts in the sample holder adjacent to the crystal oscillator had film thicknesses within a reasonably confined range (1900 Å–1990 Å), the film thickness on fluorite was at least 150 Å less than that on other mounts within the sample holder. Thus, the sticking coefficient for fluorite appears to be noticeably lower than that for the other substrate materials. In Figure 1 this would have the effect of slightly increasing the slope of the F intensity loss lines in relation to the lines of the other elements investigated. For all practical purposes, however, it

[5] Measurements were made by G. Breitweiser of Sloan Research Industries, Inc.

appears that variation in the carbon film sticking coefficient between the substances investigated is a relatively unimportant factor. There is, however, a significantly thinner film on the iron mount placed 5 inches away from the sample holder (1200 Å) than on the iron within the sample holder (1930 Å). We attribute this discrepancy to the geometry of the carbon arc, as shown in Figure 2. Concomitant with progressive blunting of the initially sharp carbon rod (shown in the lower portion of this diagram), there is a progressive "channelling" of the emitted carbon vapor in a vertical direction. Therefore, in each evaporation there will be a thicker carbon film deposited on the mount within the sample holder (vertically disposed above the arc) than on the mount 5 inches away from the sample holder.

Conclusions

An important conclusion to be drawn from this study is that film thickness differences between sample and standard mounts are more important in the quantitative analysis for light elements than for heavy elements. For example, differences in film thickness of 200 Å between sample and standard could lead to a corresponding error of 4 percent in the X-ray intensity of F($K\alpha$). Many microprobe laboratories estimate the thickness of carbon film by the darkness of an evaporated film on porcelain. Unfortunately, this crude method provides an estimate of film thickness accurate to within only about ±150 Å. A much more accurate way to determine the film thickness is through interference colors of carbon films deposited on a polished brass surface (Table 2). The interference colors are greatly enhanced by placing a small oil droplet on the brass surface before evaporation. With this technique, film thickness can be determined to a precision of ±25 Å. The interference color on a brass sample can be continuously viewed during evaporation in a clean bell jar, with illumination provided by the carbon arc. Using this method it is possible to coat large numbers of samples in separate evaporations with essentially the same film thickness.

From our interpretation of the shadowing effects produced by the carbon rod (Fig. 2), all mounts in a single evaporation should be as close to one another as possible. Furthermore, one should avoid attempting to coat large numbers of samples in a single evaporation. These problems become more serious as the distance between the carbon arc and samples is diminished. Where uniform carbon films are particularly desired, one should consider evaporation with a carbon filament (McLintock and Orr, in press).

TABLE 2. Interference Colors of Carbon Films on Polished Brass Substrates*

Approximate Thickness	Color
150 Å	Orange
200 Å	Indigo Red
250 Å	Blue
300 Å	Bluish Green
350 Å	Greenish Blue
400 Å	Pale Green
450 Å	Silver Gold

*A color photograph showing interference colors on polished brass substrates is available upon request to the senior author.

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