QUANTITATIVE X-RAY ANALYSIS IN THE ELECTRON MICROSCOPE

J. I. Goldstein, J. L. Costley
Dept. of Metallurgy & Materials Science
Lehigh University, Whitaker Lab. #5
Bethlehem, Pennsylvania 18015

G. W. Lorimer
Dept. of Metallurgy
University of Manchester
Manchester, M1 7HS England

and

S.J.B. Reed
Dept. of Mineralogy & Petrology
University of Cambridge
Cambridge, CB2 3EW England

Abstract

A theoretical approach for X-ray standard-less thin film analysis in the conventional and scanning transmission electron microscope using Cliff-Lorimer k values for Kα and Lα lines has been developed. The calculated k values for Kα radiation at 40 and 100 kV, using the Green-Cosslett QK show excellent agreement with measured data above X-ray energies of 1.7 keV. The calculated k values for Lα radiation at 100 kV, using the Mott-Massey or Bethe-Powell QL and QK show good agreement considering the uncertainties in cross sections and the Lα intensity ratio.

Equations to calculate and correct for X-ray absorption have been developed as a function of film thickness and X-ray take-off angle α. It is the difference in mass absorption coefficients between the two measured X-ray lines A and B which is primarily responsible for the variation in intensity ratios in the specimen as a function of film thickness. The absorption correction must be applied if values of the difference in mass absorption coefficients of two elements in a thin film multiplied by the cosecant of the take-off angle are greater than 200 to 500 cm²/g for most electron microscope thin films.

Calculations of electron scattering as a function of operating voltage, film thickness and for specimens of varying atomic numbers have been made. For typical thin foils observed at 100 kV, the predicted beam spreading is large, ~200 to 1200Å. Therefore there appears to be little advantage in using electron beams less than 100Å in diameter unless very thin films can be obtained.

Key Words: Electron Microscopy, X-Ray Microanalysis, Thin Film, X-Ray Absorption, Resolution, Energy Dispersive Spectrometer, Standardless Analysis, Quantitative Microanalysis

X-ray Production in Thin Films

The number of K or L shell ionizations of element X (dnx) per increment of electron path length (dt) is equal to the product of the K or L shell ionization cross section (QK or QL), and the number of atoms per unit volume. For a pure element X

\[ dn_x = Q_k \cdot N \cdot p \cdot dt/A_x \]

where N is Avogadro's number, \( p \) is the density of the specimen and \( A_x \) the atomic weight of the element X. For a multi-element specimen, the number of atoms of X per unit volume in \( c_x d_t/A_x \) where \( c_x \) is the mass concentration of element X. The total number of ionizations per incident electron may be calculated by integrating Eq. (1).

If the thickness of an electron microscope thin film is very much less than the electron range, that is if the electrons lose only a small fraction of their energy in the film, Qk can be assumed constant. The total number of ionizations per second produced along the trajectory of the electron Δt, which is assumed to be the thickness of the thin film, is given by:

\[ n_x = \text{const.} \cdot c_x Q_k \cdot \Delta t / A_x \]
I = const. C \times a \times A \times B 

where a is the ratio of K intensity to total K intensity, \( \frac{K_X}{K_Y + K_B} \); and \( a \) is the ratio of L intensity to total L intensity, \( \frac{L_X + L_A}{L_Y + L_B} \).

\[ I_{X,Y} = \text{characteristic X-ray intensity of element } X. \]

\[ a = \frac{K_X}{K_Y + K_B} \]

\[ I_{A,B} = \text{characteristic X-ray intensity of elements } A \text{ and } B. \]

\[ C_{A,B} = \text{mass concentration of elements } A \text{ and } B. \]

\[ k_{AB} = \text{scaling factor relating intensity ratios of elements } A \text{ and } B. \]

\[ k = \text{scaling factor relating intensity ratios of element } X \text{ to } Si \text{ and weight fraction ratios of elements } X \text{ and } Si. \]

\[ \mu/p = \text{mass absorption coefficient (cm}^2/g). \]

\[ E_0 = \text{operating voltage (kV) or energy (eV).} \]

\[ E_K = \text{binding energy of electrons in the K shell (eV).} \]

\[ E_{\text{over}} = \text{overvoltage, ratio of operating energy } E_0 \text{ to } E_K, \text{ the binding energy.} \]

\[ Z_K = \text{number of electrons in the K shell.} \]

\[ \phi_{\text{K-M}} = \text{constants in the QK cross section formula.} \]

\[ Q = \text{Mott-Ranseaue QK(cm}^2). \]

\[ Q_{OC} = \text{Green-Cosslett QK(cm}^2). \]

\[ Q_{BP} = \text{Bethe-Powell QK(cm}^2). \]

\[ Q_{RP} = \text{Reuter QK(cm}^2). \]

\[ Z = \text{atomic number.} \]

\[ Z_{L} = \text{number of electrons in the L shell.} \]

\[ \phi_{\text{L-M}} = \text{constants in the QL cross section formula.} \]

\[ Q_{L}(X,Y) = \text{Mott-Ranseaue QL(cm}^2). \]

\[ Q_{LP}(X,Y) = \text{Bethe-Powell QL(cm}^2). \]

\[ \phi = \text{depth distribution of X-ray production.} \]

\[ \alpha = \text{take-off angle.} \]

\[ k_{AB,\text{IF}} = \text{k}_{AB} \text{ ratio for an infinitely thin film.} \]

\[ \delta_{X-B} = \text{difference in mass absorption coefficients of two elements in a thin film multiplied by the cosecant of the take-off angle.} \]

\[ \theta = \text{scattering angle.} \]

\[ P = \text{probability of scattering through an angle } > \theta. \]

\[ b = \text{beam broadening (cm).} \]

Multiplying \( n_X \) by the fluorescence yield \( \psi_X \) or \( \psi_L \) gives the characteristic X-ray intensity in photons per incident electron generated in the film. If one assumes that the analyzed film is infinitely thin, the effects of X-ray absorption and fluorescence can be neglected, and the generated X-ray intensity and the X-ray intensity leaving the film are identical. This assumption is known as the thin film criterion. A further minor effect which must be taken into account when considering K excitation is the change in the K intensity as a fraction of the total K intensity (K_X + K_Y), since it is the K intensity that is measured. The K intensity is therefore given by:

\[ I_X = \text{const. } (C_X/C_Y) \cdot a \cdot t / A_X \]

where \( a \) is the ratio of K intensity to total K intensity, \( \frac{K_X}{K_Y + K_B} \). A similar ratio must be used when L intensity is measured.

Cliff and Lorimer have outlined a simple technique to carry out the quantitative analysis of thin foils with the analytical electron microscope. For very thin foils where X-ray absorption and fluorescence can be neglected, the following expression may be used:

\[ \frac{I_A}{I_B} = (k_{AB})^{-1} \cdot \frac{C_A}{C_B} \]

where \( I_A \) and \( I_B \) are the measured characteristic X-ray intensities, and \( C_A, C_B \) are the weight fractions of two elements A and B in the thin film. The constant \( k_{AB} \) varies with operating voltage but is independent of sample thickness if the two intensities are measured simultaneously and if the thin film criterion is satisfied. This method has been often referred to as the standardless method in that pure bulk standards are not needed for the analysis.

Cliff and Lorimer and other authors have been successful in applying the simple expression given in Eq. (4) to a number of materials problems. The method used is to obtain X-ray intensity ratios from a number of thin specimens of known composition and then calculate the scaling factors \( k_{AB} \) from Eq. (4), by which each intensity ratio must be multiplied to give relevant weight fraction ratios.

Calculation of Calibration Curves-K, L Lines

A calibration curve using the ratio of the K \(_X\) radiation from various elements X relative to Si, i.e.

\[ k = \left( \frac{C_X}{C_Si} \right) \cdot \left( \frac{I_X}{I_Si} \right) \]

has been obtained in an EMMA-4 instrument using 100 kV excitation by Cliff and Lorimer.
tions (3) and (4) along with appropriate consid-
erations of EDS detector effects can be used to
calculate theoretical values of $k$ where $k = k_{AB}$
and $A$ and $B$ represent elements $X$ and $Si$ respec-
tively. These results can be compared to the
measured $k$ values of Cliff and Lorimer. A
similar analysis was developed in part by Russ.7

It can be assumed that all X-ray photons less
than 15 keV energy entering the active region of
the Si(Li) detector are detected. However some
X-ray photons may be absorbed in the Be window,
gold surface layer or silicon dead layer on the
way in. Of these the Be window is the most im-
portant. Window absorption is significant for
the light elements Na, Mg and Al. Values of $k$
can be calculated by substituting Eq. (3) in Eq.
(5) and correcting for window absorption as given
by:

$$k = \frac{A \left( Q_{K,\infty} \right) e^{-\mu_{Si}/p_{Be} \rho_y}}{A_{Si} \left( Q_{K,\infty} \right) e^{-\mu_{\infty}/p_{Be} \rho_y}}$$

where $\mu_{Si}/p_{Be}$ and $\mu_{\infty}/p_{Be}$ are the mass absorption co-
efficients of Si and element X in the Be foil, $p$
is the density of Be and $y$ is the Be foil thick-
ness.

Having obtained the theoretical expression
for $k$, we will insert various experimentally de-
termined values in Eq. (6) and compare the cal-
culated $k$ values with the experimentally measured
values of Cliff and Lorimer. The following
paragraphs discuss the choice of values for $w$, $a$,
$\mu/p$ and $Q$ for the calculation.

The fluorescence yield for K shell fluores-
cence is given to a sufficient accuracy by the
expression first proposed by Wentzel8 as:

$$w_K = \frac{Z^6}{(b + Z^4)}$$

where $b$ is a constant equal to 10$^6$. The values of $a$
for atomic numbers 22 and above are taken from
Slivinsky and Ebert,9 and for atomic numbers
15 and 20 from Heinrich et al.10 The $a$ values
for Na, Mg, Al and Si were extrapolated using
data for higher atomic numbers. The mass absorp-
tion coefficients $\mu/p_{Be}$ were taken from the ta-
bles of Heinrich.11 The Be window thickness of
most EDS units including that of the EMMA-4 is
7.5 $\mu$m (0.3 mils).

As discussed by Powell12 the formula for
the cross section $Q_K$ for the K shell can be written
in the following form:

$$Q_K = 6.51 \times 10^{-14} Z_K^2 b_K \left( \frac{1}{E_K^2} \right) \ln \left( \frac{c_K U_R}{d_K R} \right) \text{ cm}^2$$

In this equation the overvoltage $U_R$ is the ratio
of operating energy $E_K$ to $E_K$ the Binding energy
of electrons in $K$ shell, and $Z_K$ is the number
of electrons in the K shell. The parameters $b_K$
and $c_K$ are assumed to be constant for the K shell.

For calculations of $k$ using $Q_K$, the term $6.51 \times$
$10^{-14} Z_K b_K$ is a constant.

Several K shell ionization cross-section
formulas have been proposed each with a different
value of $c_K$. In a recent paper by Powell12 an
evaluation of various ionization cross-section
formulas where $U_K$ is greater than 4 was given.
The formulas for $Q_K$ include those of Mott and
Massey,13 where $Q_{KM} = \text{(const)} \left( \frac{1}{E_K^2} \right) \ln
\left( \frac{2.42 U_K}{E_K} \right)$ and Green and Cosslett,14 where $Q_{GC} = \text{(const)} \left( \frac{1}{E_K^2} \right) \ln \left( \frac{U_K}{E_K} \right)$. Powell12 has made
works to determine whether inner-shell ionization
cross-section data can be fitted to a linearized
form of the Bethe equation, Eq. (8). For the
range 4$\leq U_K \leq 30$, the following formula
Bethe-Powell, where $Q_{BP} = \text{(const)} \left( \frac{1}{E_K^2} \right) \ln
\left( \frac{0.65 U_K}{E_K} \right)$ was proposed. Reuter15 has also pro-
posed a formula for $Q_K$, $Q_K = \text{(const)} \left( \frac{1}{E_K^2} \right) U_K$
ln $(U_K)$, which has been employed for thin films
examined in the electron microprobe at $U_K \leq 4$.
Kysel16 has evaluated ionization cross-sections
for use at low overvoltages and found that Reuter’s
$Q_K$ was more accurate.

Table I presents the calculations of $k$ from
Eq. (6) for $E_K = 100$ keV and K radiation using
the various ionization cross-section formulas.
Measured $k$ values from Cliff and Lorimer2 are also
included in the Table. These data were taken on an EMMA-4 instrument; the specimen was normal
to the electron beam and the X-ray detector was
take a takeoff angle of 45°. The high energy Ag and
Sn$\gamma$ radiation is partially transmitted by the
Si(Li) X-ray detector crystal. The loss of X-ray intensity can be calculated using an ab-
sorption correction for Ag$\gamma$ and Sn$\gamma$ in Si for a
0.3 cm thick Si crystal. The mass absorption co-
efficients were extrapolated from the tables of
Heinrich11 yielding 3.70 and 2.57 cm$^2$/g for Ag$\gamma$
and Sn$\gamma$ respectively. The calculated and mea-
ured $k$ values are plotted versus the energy of

| TABLE 1 |

Calculated and Measured $k$ Values, 100 keV

<table>
<thead>
<tr>
<th>$Z$</th>
<th>$Q_{KM}$</th>
<th>$Q_{GC}$</th>
<th>$Q_{BP}$</th>
<th>$Q_K$</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-Na</td>
<td>1.69</td>
<td>1.66</td>
<td>1.63</td>
<td>1.4</td>
<td>5.77</td>
</tr>
<tr>
<td>12-Mg</td>
<td>1.27</td>
<td>1.25</td>
<td>1.24</td>
<td>1.13</td>
<td>2.07</td>
</tr>
<tr>
<td>13-Al</td>
<td>1.13</td>
<td>1.12</td>
<td>1.11</td>
<td>1.06</td>
<td>1.42</td>
</tr>
<tr>
<td>14-Si</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>15-P</td>
<td>0.99</td>
<td>0.99</td>
<td>1.0</td>
<td>1.04</td>
<td>1.0</td>
</tr>
<tr>
<td>20-Ca</td>
<td>0.98</td>
<td>1.02</td>
<td>1.06</td>
<td>1.30</td>
<td>1.0</td>
</tr>
<tr>
<td>22-Ti</td>
<td>1.0</td>
<td>1.16</td>
<td>1.21</td>
<td>1.57</td>
<td>1.08</td>
</tr>
<tr>
<td>25-Mn</td>
<td>1.20</td>
<td>1.31</td>
<td>1.38</td>
<td>1.91</td>
<td>1.22</td>
</tr>
<tr>
<td>26-Fe</td>
<td>1.22</td>
<td>1.33</td>
<td>1.42</td>
<td>2.0</td>
<td>1.27</td>
</tr>
<tr>
<td>28-Ni</td>
<td>1.30</td>
<td>1.44</td>
<td>1.55</td>
<td>2.27</td>
<td>1.67</td>
</tr>
<tr>
<td>29-Cu</td>
<td>1.42</td>
<td>1.59</td>
<td>1.73</td>
<td>2.56</td>
<td>1.58</td>
</tr>
<tr>
<td>32-Ge</td>
<td>1.75</td>
<td>2.01</td>
<td>2.23</td>
<td>3.65</td>
<td>1.92</td>
</tr>
<tr>
<td>42-Mo</td>
<td>3.66</td>
<td>4.65</td>
<td>5.66</td>
<td>9.51</td>
<td>4.3</td>
</tr>
<tr>
<td>47-Ag</td>
<td>5.89</td>
<td>7.91</td>
<td>10.3</td>
<td>17.5</td>
<td>8.5</td>
</tr>
<tr>
<td>50-Sn</td>
<td>8.60</td>
<td>12.1</td>
<td>16.6</td>
<td>27.7</td>
<td>10.6</td>
</tr>
</tbody>
</table>
The Na, Mg and Al data are affected by absorption in the Be window, which decreases the measured intensities and hence increases the calculated k values. Nevertheless the calculated k values for Na, Mg and Al fall well below the measured values of Cliff and Lorimer. In the EMMA-4 instrument, which was used to obtain these k values, a 2 μm thick window of KThIFOIL, a polycarbonate of density 1.2 g/cm³, is present between the specimen and detector. The effect of this window would be to absorb low energy X-rays preferentially to higher energy X-rays and to increase the measured k values. However even for Na, the calculated k value (Table 1) is increased by no more than 50%.

Figure 3 shows the calculated k curves and measured k values obtained at an operating voltage of 40 kV on the EMMA-4 instrument. As in the case of the 100 kV data, the Green-Cosslett QK appears to fit the data best above X-ray energies of 1.7 keV. The Bethe-Powell and Reuter (not shown in Fig. 3) curves fall significantly higher than the measured data. It should be noted however that for Na, the overvoltage QK is less than 4, which perhaps causes some error in the calculated k value.

Figure 4 shows a comparison of calculated k vs. X-ray energy curves for operating voltages of 40, 100 and 200 kV using the Green-Cosslett QK. The 200 kV curve was calculated using a relativistic correction for beam energy E₀ because QK is a function of operating voltage. As operating voltage increases the k values above 1.7 keV decrease. The effect of high overvoltages in the cross-section calculation becomes significant causing the k values to approach 1.0.

The calculated values using the Green-Cosslett QK appear to fit the data best above X-ray energies of 1.7 keV. The Bethe-Powell curves fall significantly higher than the measured data and the calculated k values from the Reuter cross-sections are more than 50% higher than the measured values for X-ray energies over 4 keV.
It is apparent therefore that k curves calculated from Eq. (6) using the Green-Cossett QK can be used for X-ray chemical analysis of thin films in various types of electron microscopes. Analysis techniques for Na, Mg and Al whose characteristic X-rays have energies < 1.6 keV however require further study.

Curves of k versus X-ray energy can also be calculated for L lines using Eq. (6). The fluorescence yield for L shell fluorescence can be obtained by setting \( b = 10^8 \) in Burhop’s expression, Eq. (7). Comparison of values with the most recent review shows a reasonable agreement. The intensity ratio a for L\(_2\) radiation, I\(_{L2}/(I_{L2} + I_{L3})\), were obtained from the L intensity values compiled by White and Johnson. \( Q_L \) can be calculated from Eq. (8) by substituting the correct parameters for the L shell. In this equation \( Z_L \) is the number of electrons in the L shell, \( U_L \) is the overvoltage for the L lines and the parameters \( b_L \) and \( c_L \) are assumed to be constant for the L shell. As Powell has pointed out, relatively few measurements exist for L-shell ionization. The calculation of k for the L\(_2\) lines however requires that absolute values of \( Q_L \) for element X and QK for Si be used in evaluating k (Note Eq. (6)). Therefore the Bethe parameters, \( b_K \), \( b_L \), \( c_K \) and \( c_L \), in Eq. (8) must be used. Mott and Massey give values of \( b_K \approx 0.35 \), \( b_L \approx 0.25 \), and \( c_K \approx 2.42 \). After evaluating the available experimental data, Powell suggests values of \( b_K \approx 0.9 \), \( b_L \approx 0.6-0.9 \), \( c_K \approx 0.65 \) and \( c_L \approx 0.6 \) appropriate for 4 \( \leq U_L \) \( \leq 20 \) and 4 \( \leq U_K \) \( \leq 20 \). For calculation purposes we will assume \( b_L \approx 0.75 \).

Figure 5 shows the calculated curves of k vs. X-ray energy for L\(_2\) radiation, using the QK, QK of Mott-Massey and Bethe-Powell. Also plotted on the figure are data for L\(_2\) radiation measured in the EMMA-4 instrument operated at 100 kV. The silver value was measured by estimating the correct window for AgK\(_\alpha\) and is subject to some degree of error. The k factors for the L lines were obtained from the following samples: W from W, Fe carbides on an extraction replica, Ba from BaSi\(_2\) particles, Sm from a Sm-Co alloy thin foil, Pb from a Pb-Sn splt quenched alloy thin foil and Au from a Au-Fe alloy thin foil.

The agreement between calculated and measured data is quite good considering the uncertainties in the \( b_L \), \( c_L \) constants for the X-ray cross-sections and the quality of the data available for the L\(_2\) intensity ratio a. It appears that one can use the calculation scheme for k values of L\(_2\) lines successfully. However the L\(_2\) data obtained by Sprys and Shorton measured on a Philips 300 electron microscope falls well below both the calculated and measured data. In the Philips instrument the specimen is tilted and the X-ray detector is at a 90° angle to the electron beam.

Tixier and Philibert have noted that absorption effects can occur even when the foil is transparent to the impinging electron beam if the combination of mass absorption coefficient and film thickness is large enough. Experiments have shown that for the case where the mass absorption coefficient for one of the X-ray lines 4 or 5 in Eq. (4) is large, AuK\(_\alpha\) in Cu-75.5 wt% Au, \( \alpha_{AlK\alpha} \) in CuAl\(_2\), \( \alpha_{AlK\alpha} \) in NiAl, \( \alpha_{FeK\alpha} \) in (FeNi)\(_3\)P, absorption effects were observed. In such cases the value of \( k_{AB} \), Eq. (4), will vary with foil thickness since one or both measured intensities \( I_A \), \( I_B \) vary with thickness. Therefore in some cases the standards analysis technique will be inaccurate without a correction for the effect of absorption.

König considers the depth distribution of X-ray production \( \Phi(\rho t) \) and also the absorption of X-rays in the thin film at a take off angle \( \alpha \), estimating the correct window for AgK\(_\alpha\) and is subject to some degree of error. The k factors for the L lines were obtained from the following samples: W from W, Fe carbides on an extraction replica, Ba from BaSi\(_2\) particles, Sm from a Sm-Co alloy thin foil, Pb from a Pb-Sn splt quenched alloy thin foil and Au from a Au-Fe alloy thin foil.
the angle between the detector axis and the specimen surface. An equation of the following form was developed:

\[
k_{AB}^{k}_{T,F} = \left[ \frac{\int t \cdot \phi_{B}(pt) e^{-\mu/\rho A_{SPEC} csc \alpha(\rho)} dt}{\int t \cdot \phi_{A}(pt) e^{-\mu/\rho B_{SPEC} csc \alpha(\rho)} dt} \right]
\]

(9)

where \(\mu/\rho A_{SPEC}\) and \(\mu/\rho B_{SPEC}\) are the mass absorption coefficients for the characteristic X-rays of elements A and B respectively in the thin film (SPEC) and \(p\) is the density of the thin film. The term \(k_{AB}^{k}_{T,F}\) is the \(k_{AB}\) ratio for an infinitely thin film, that is \(t \rightarrow 0\).

Experimental values of \(\phi(pt)\) have not been measured at high voltages (>50 kV) used for the X-ray analysis technique. König25 and Yakowitz and Newbury26 suggest methods for calculating \(\phi(pt)\) based on experimental values at ≤30 kV operating potential. These approximate methods show that, unless the film is transmission thick to the electron beam, \(\phi(pt)\) will approach a value of 1.0 to 1.10 at 100 kV and above. For almost all cases, considerations of \(\phi(pt)\) for high voltage thin film analysis are unnecessary. One can assume that X-ray production is uniform throughout the film and that \(\phi_{A}(pt) \approx \phi_{B}(pt) \approx 1.0\).

The effect of absorption can be calculated by integrating Eq. (9) assuming \(\phi_{A}(pt) = \phi_{B}(pt) = 1.0\). Therefore

\[
k_{AB} = k_{AB}^{k}_{T,F} \cdot \left(\frac{\mu/\rho A_{SPEC} - \mu/\rho B_{SPEC}}{1-e^{-\mu/\rho A_{SPEC} csc \alpha(\rho)}} \right)
\]

(10)

The effect of absorption can also be calculated to a first approximation if one considers that the average depth of X-ray excitation occurs at one-half the thickness of the film. If the path length for absorption in the film is \((t csc \alpha)/2\), Eq. (9) reduces to

\[
k_{AB} = k_{AB}^{k}_{T,F} \cdot e^{-\Delta \alpha B - A} (\rho/2)
\]

(11)

where

\[\Delta \alpha B - A = (\mu/\rho B_{SPEC} - \mu/\rho A_{SPEC}) \cdot csc \alpha\]

Equation (11) yields \(k_{AB}^{k}_{T,F}\) ratios very similar to those given by Eq. (10). From Eq. (11) it can be observed that it is the difference in mass absorption coefficients between elements B and A which is primarily responsible for the variation in intensity ratios in the specimen as a function of film thickness.

Figure 6 shows the variation in the ratio \(k_{AB}^{k}_{T,F}\) with mass thickness \(\rho/2\) for different values of \(\Delta \alpha B - A\). If a variation in the \(k\) ratio of 10% can be tolerated in an analysis, \(\Delta \alpha B - A\) values must be less than 200 to 500 for most electron microscope thin films which have thicknesses less than the thin film limit. For thin films with \(\rho/2\) values less than 0.04 mg/cm², \(\Delta \alpha B - A\) values of up to 2000 can be tolerated. Figure 6 should prove useful in predicting whether X-ray absorption will be important in an analysis involving two elements A and B in a material of a given thickness.

In order to calculate the effect of absorption using Eq. (10) or (11) in a specimen where absorption is significant it is necessary to measure the specimen thickness at each analysis point. Several techniques for measuring specimen thickness have been developed. Lorimer et al.23 have a technique of tilting the specimen after analysis to measure the separation between pairs.
of contamination spots and calculate the corresponding thickness. Joy and Maher have suggested a technique for measuring crystal thickness using a calibration curve developed from the relative transmission of the primary electron beam through the specimen. Other techniques include the trace method, counting extinction contours in a wedge shaped crystal or stereomicroscopy. These techniques are seldom accurate to within ±10%. Kelly et al. have described a method which makes use of measurements of spacing of intensity oscillations in convergent beam diffraction patterns obtained with the STEM. Foil thicknesses to ±2% can be determined as shown by Rao. Depending on the specimen distortion, spot analysis position and specimen tilt, it should be possible to use one of these techniques for thickness measurement.

X-ray absorption effects have been reported in several alloy systems, although little data have been measured as a function of foil thickness. Table 2 summarizes the values of $\mu^A / \rho^A_{\text{SPEC}}$ and $\mu^B / \rho^B_{\text{SPEC}}$ for each of these alloy systems. Except for the Fe-Ni system, large absorption effects are predicted, see Figure 6, in which the ratio $k_{\text{AB}} / k_{\text{AB}}^\dagger$ will increase.

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>A</th>
<th>$\mu^A / \rho^A_{\text{SPEC}}$ (cm$^2$/g)</th>
<th>B</th>
<th>$\mu^B / \rho^B_{\text{SPEC}}$ (cm$^2$/g)</th>
<th>$\Delta k_{\text{B-A}}$ (cm$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-75.5 wt% Au</td>
<td>Cu$_{\text{Kr}}$</td>
<td>1352</td>
<td>Cu$_{\text{Kr}}$</td>
<td>170.6</td>
<td>-1672</td>
</tr>
<tr>
<td>CuAl$_2$</td>
<td>Cu$_{\text{Kr}}$</td>
<td>3056</td>
<td>Cu$_{\text{Kr}}$</td>
<td>51.8</td>
<td>-4249</td>
</tr>
<tr>
<td>NiAl</td>
<td>Ni$_{\text{Kr}}$</td>
<td>3435</td>
<td>Ni$_{\text{Kr}}$</td>
<td>59.5</td>
<td>-4774</td>
</tr>
<tr>
<td>FeNi</td>
<td>Fe$_{\text{Kr}}$</td>
<td>218</td>
<td>Fe$_{\text{Kr}}$</td>
<td>80.8</td>
<td>-194</td>
</tr>
<tr>
<td>(FeNi)$_3$P</td>
<td>P$_{\text{Kr}}$</td>
<td>1643</td>
<td>Ni$_{\text{Kr}}$</td>
<td>199.4</td>
<td>-2044</td>
</tr>
</tbody>
</table>

$\alpha = \text{till angle } = 45^\circ$

Jacobs and Baborovksa showed that the measured intensity ratio $I_{\text{Au}} / I_{\text{Cu}}$ decreased with increasing foil thickness, at ~0.3 μm thickness the intensity decreased to ~0.75 of its value for a very thin foil. Predictions using Eqs. (10-11) indicate a decrease to ~0.67 of the thin foil value. Measurements of Lorimer et al. indicate that the intensity ratio $I_{\text{Cu}} / I_{\text{Al}}$ decreases with increasing foil thickness. This increase is also predicted by Eqs. (10-11), and that the mass absorption coefficient of Al$_{\text{Kr}}$ is so large, see Table 2. The large measured increase in the intensity ratio of Ni$_{\text{Kr}} / I_{\text{Al}}$ and $I_{\text{Ni}} / I_{\text{Fe}}$ with increasing foil thickness for NiAl and (FeNi)$_3$P respectively is also predicted by Eqs. (10-11) and the pertinent data is given in Table 2. Goldstein et al. measured an increase in $k_{\text{AB}} / k_{\text{AB}}^\dagger$ of ~4% for a 0.5 μm foil specimen of a 50-50 NiFe alloy. A 4% increase is also predicted for a 0.3 μm foil using Eq. (11) and the mass absorption coefficients of Table 2.

From the preceding discussion a criterion was developed which can be used for predicting the effect of absorption. If absorption corrections are necessary, they can be made using Eq. (10) or (11) as long as the foil thickness is measured.

### Beam Spreading in Thin Films

Very little systematic work, either theoretical or experimental, appears to have been done in connection with the question of spatial resolution in the X-ray analysis of thin films as a function of film thickness. The dominant process causing beam spreading is elastic scattering by atomic nuclei. This process has been treated exhaustively in the literature, but almost entirely in the context of electron microscope image formation, where small-angle scattering (e.g., ~1°) is of greatest importance, and electrons scattered out of the objective aperture are of no interest. By comparison all electrons potentially contribute to X-ray production, indeed it is those scattered at the greatest angles which define the effective width of the X-ray source. For elastic scattering at relatively large angles screening of the nucleus by outer electrons may be neglected, and the formula derived by Rutherford for Coulomb deflection by a point charge is applicable. This may be expressed in the following form:

$$p = 9.76 \times 10^9 \frac{Z^2}{A} \frac{1}{E_0} \cot^2 \left( \frac{\theta}{2} \right) \text{pt}$$

(12)

where $Z$ = atomic number, $A$ = atomic weight, $E_0$ = electron energy in eV, $p$ = density in g/cm$^3$, $t$ = thickness in cm, and $p$ is the probability of scattering through an angle $> \Phi$. The effective X-ray source size may be defined as that within which 90% of the electron trajectories lie. Substituting $p = 0.1$ in Eq. (12):

$$t = 2.56 \times 10^{-12} \frac{A}{Z^2} \frac{E_0^2}{P} \frac{\theta^2}{2} \text{ cm}$$

(13)

using the approximation $\cot(\theta/2) \sim 2/\theta$.

The effective beam broadening $b$ may be estimated by assuming that scattering takes place at the center of the film (Fig. 7), that is $b = t\Phi$, and from Eq. (13)

$$b = 6.25 \times 10^5 \frac{Z^2}{E_0} \left( \frac{\theta}{2} \right) \frac{\theta}{3} \text{ cm}$$

(14)
Fig. 7. Model for beam broadening (b) in a thin film of thickness t due to single scattering through an angle $\phi$ at the center of the film.

Figure 8 shows the relationship between b and t calculated for carbon, copper and gold at 100 kV. For other electron potentials, the broadening varies inversely as $E_0$. For high voltages a relativistic correction for beam voltage $E_0$ may be necessary. For a given $E_0$ and t the broadening is about 10 times greater for gold than for carbon.

![Diagram](image)

Fig. 8. Broadening (b) calculated as a function of thickness (t) at 100 kV. Dotted line represents approximate upper thickness limit for single scattering model.

Table 3 gives calculated values of beam spreading for a zero diameter electron beam as a function of various film thicknesses and pure element targets. For 500Å Au, 3000Å Cu and 5000Å Al films which are typical of electron microscope thin film specimens observed at 100 kV, the predicted beam spreading and hence the X-ray source size is large (~760 ro 1200Å). With this amount of beam spreading, there is no advantage in using impinging electron beams less than 100Å in diameter unless very thin films, <100Å for Au, <200Å for Cu and <500Å for C can be obtained.

**TABLE 3**

<table>
<thead>
<tr>
<th>Element</th>
<th>100Å</th>
<th>500Å</th>
<th>1000Å</th>
<th>3000Å</th>
<th>5000Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1.6</td>
<td>18</td>
<td>51.3</td>
<td>267</td>
<td>574</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2.6</td>
<td>29</td>
<td>81.2</td>
<td>422</td>
<td>909</td>
</tr>
<tr>
<td>Copper</td>
<td>6.8</td>
<td>76</td>
<td>214</td>
<td>1117</td>
<td>*</td>
</tr>
<tr>
<td>Gold</td>
<td>15.5</td>
<td>173</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* $\phi > 20^\circ$

It is difficult to define exactly the range of thicknesses for which the single scattering model is valid. It may be argued from the dependence of p on $\phi$ in Eq. (12) that for $p < 1$ the probability of two deflections through angles less than $\phi$ combining to give a total deflection greater than $\phi$ is less than that of a single deflection greater than $\phi$, which justifies the use of the single scattering model, at least up to $p = 0.1$. However the model clearly must break down at some point. We tentatively propose a limit corresponding to $\phi = 20^\circ$ on the basis that at larger angles the path length, and hence the probability of scattering, becomes significantly increased. Furthermore, the probability of scattering through a large enough angle to travel significant distances laterally within the film becomes appreciable, whereas for $\phi < 20^\circ$ less than 1 in 30 of the 10% of incident electrons scattered at an angle greater than $\phi$ are scattered through 90° or more. It is clearly desirable that Monte-Carlo calculations should be carried out to investigate the border-line region of the single scattering model and beyond.

**Acknowledgments**

We thank G. Cliff, D. Kaiser, D. Williams, C. Pande for helpful discussions and suggestions. This work was supported in part by NASA Grant NGR 39-007-043.
References

DISCUSSION WITH REVIEWERS

Reviewer I: Are you justified in assuming that the effects of absorption can be calculated by assuming the average depth of X-ray excitation occurs at one-half the film thickness? What effect does varying this average depth have on the calculated effect of absorption?
Authors: Yes, calculations using Eqs. (10) and (11) for absorption effects yield \( k_{AB}/k_{ABT,F} \) values that are very similar. Eqn. (10) integrates the absorption effect throughout the thin film. Varying the average depth from a position at one-half the film thickness would yield incorrect values for absorption, particularly if \( A_{AB} \) was greater than 500.

Reviewer II: There is a variation in Be window thicknesses on solid state detectors from unit to unit and even within the same unit. Could a small change in effective Be window thickness bring the k values for the light elements Na, Mg and Al into close agreement with measured k values listed in Table 1?
Authors: No, even a 50% increase in Be window thickness from 7.5 \( \mu \)m (0.3 mil) to 11.25 \( \mu \)m will only increase k for Na by 25%. An increase of k by about 350% for Na is necessary to obtain close agreement between calculated and measured values (Table 1). Similar results are found for the elements Mg and Al.

Reviewer III: Is there any chance that agreed values for ionization cross sections can be derived? The proliferation of values that you catalog suggests that much more experimental work at high kV is called for.
Authors: The review of Powell, text reference 12, summarizes the best ionization cross section formulas to date. It is agreed that more experimental work at high kV is a must if we are to substantially progress in quantitative analysis.

Reviewer IV: Could the poor agreement with the theory for Na, Mg and Al be due to absorption in the calibration specimens?
Authors: No. Using Eq. (10) one can calculate the effect of absorption and the ratio \( k_{AB}/k_{ABT,F} \). For a typical silicate, thinned for electron microscopy, the film thickness is 1000 to 1500\( \AA \). For the hornblende sample analyzed by Cliff and Lorimer, text reference 2, the effect of absorption is to increase the k ratio for Na by only 6% for a 1000\( \AA \) film. Even for a 5000\( \AA \) film, the absorption correction only raises k by 30%. An increase of 350% is necessary to obtain agreement between calculated and measured k values. The effect of absorption is even less significant for Mg and Al.

Reviewers III and IV: Would the authors please explain how a potential is relativistically corrected?
Authors: The relativistic correction of a potential is merely the use of increased values of accelerating potential \( E_0^\ast \) which give the actual electron wavelengths that interact with the specimen. The electron wavelength \( \lambda \) is related to the accelerating voltage \( E_0 \) by \( \lambda = h/(2m_eE_0) \) and this relationship is used in the calculation of Q and b. As the operating or accelerating voltage approaches 100 kV, the actual wavelength is less than the calculated wavelength due to relativistic effects. Therefore it is necessary in the calculation to "correct relativistically" the accelerating voltage, such that the correct value of \( E_0^\ast \) actually incident on the specimen is used. This is given by \( E_0^\ast = (1+0.9785 \times 10^{-6}E_0)E_0 \) (Eo in volts), text reference 17.

Reviewer V: Would not beam damage and loss of the element of interest in thin films due to the action of the beam be an important factor to be considered in the correction?
Authors: The reviewers point is well taken however in metals this effect is minimal. In this paper we have assumed that we are using intensity ratios obtained from specimens for which such effects have been taken into account.

Reviewer V: Would it not be generally best to use beam diameters less than 10 nm (100\( \AA \)) for thin film analysis?
Authors: Yes; however the X-ray intensities obtained from such small spot sizes on thin films may be too low for obtaining statistically meaningful data. This statement is particularly true for standard tungsten filament guns. In addition beam spreading effects, as discussed in the paper, enlarge the effective size of even the smallest beam diameter.

Reviewer VI: In analyzing a thin specimen, the irradiated volume is quite small. Would the authors please comment on count rates and analysis times needed to get good statistics?
Authors: To obtain adequate X-ray statistics it is considered that a minimum of 10,000 counts above background should be accumulated for the elements of interest. Peak counts below 1000 are unacceptable for quantitative analysis. Counting times of 100 sec. are not unusual unless specimen contamination is a limiting factor.

Reviewer VI: How useful would the authors' technique be in the identification and analysis of a small particle embedded in a thin foil?
Authors: The analysis technique described in this paper can be used if the following criteria are met; only the sample (particle) is bombarded by the impinging beam and the surrounding matrix is not analysed, all the elements present in the particle including the light elements (O, N, C etc.) are known, specimen contamination is not significant and the foil containing the specimen is thin. If the particle is truly surrounded by the matrix within the thickness of the foil, the technique can not be used.

For additional discussion see p. 200.

Reviewer VI: What modifications to the equations are necessary in dealing with ternary or higher order systems?
Authors: No modifications need be made to the Equations (4) and (5) in the paper. Equation (5) can be used to obtain $k_{AB}$ constants for Eqn. (4). If three elements A, B and C are analyzed, Eqn. (4) is used twice, once for $K_{AB}$ and once for $K_{AC}$. As long as $C_1 + C_2 + C_3 = 100\%$, and $k_{AB}$, $k_{AC}$ can be obtained, ternary systems can be calculated. For higher order systems the number of expressions (4) used is equal to the number of components A, B, C... minus one.

Reviewer III: Have you attempted to verify your predictions about spatial resolution by means of any direct experiments? Could you suggest a suitable test specimen for this purpose?
Authors: Yes, we have in many cases moved the electron probe across interfaces between phases where a discontinuity in composition occurs. For the EMMA-4 instrument, the probe size is sufficiently large (1000-1500Å) that beam broadening is not a significant factor. For the Philips EM 300 instrument, we have observed broadening of about 250Å with a 300Å nominal probe size when analyzing the Ni content at the α/γ interface of γ plates in a heated FeNiCo alloy. The broadening b compares favorably with calculated values, Table 3, for nominal 1000Å films. We suggest that probe traces across suitable two phase interfaces parallel to the electron beam will enable one to study broadening effects.

Reviewer IV: The discussion following Eqn. (9) indicates that $\Phi(pt)$ has been defined such that $\Phi(0) = 1$. Is this the generally accepted definition?
Authors: The authors did not define $\Phi(pt)$; they just stated that in thin films used for X-ray analysis the value of $\Phi(pt)$ equals 1.0.

Reviewer I: Will the authors make estimates of the accuracy and sensitivity of the quantitation technique described? Is it possible to give an example of the smallest detectable mass of a given material that can be quantified?
Authors: Any estimate of accuracy and sensitivity must assume all other factors such as contamination, continuum background subtraction, overlapping X-ray peaks, specimen-beam drift, etc. have been eliminated or corrected. At this time many of these factors remain a subject of investigation. Nevertheless, we have shown that for K lines agreement between calculated and measured $k$ values is better than 10% for elements with $Z$ greater than 13. Compositional accuracy will be within ±10% relative. Assuming integrated peak counts exceeding 10,000, the sensitivity is better than 1-2% relative.

Our quantitation technique is not aimed at obtaining a low minimum detectable mass. However we can make an estimate of minimum detectable mass for the general operating conditions we use in analysis. Using typical count rates from a standard tungsten filament instrument, operating at 80 or 100 kV, the presence of approximately 1 wt% of an element can be detected. This value is typical when peak overlaps do not occur and the continuum background subtraction is made. For a typical 300Å sized electron probe incident on a 1000Å thin foil of steel and for 100 sec. counting times, the minimum detectable mass is about $10^{-18}$ g. With a higher brightness gun, the excitation area and minimum detectable mass can be decreased while retaining a sensitivity of 1 wt% for an element of interest. See Joy and Maher, p. 325 in this volume.