QUANTIFICATION OF ENERGY-DISPERSIVE SPECTRA FROM THIN-FOIL SPECIMENS

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A major driving force for the development of the analytical electron microscope (AEM) was that the quantification procedure for the x-ray energy-dispersive spectrometer (EDS) output obtained from thin specimens should be simple in comparison with the process for bulk specimens, because in many cases, the absorption and fluorescence corrections that are required when bulk specimens are analyzed can be ignored. The degree to which this assumption is justified, the methods used for quantification, and current limits to the quantification process are discussed in this article. The article is tutorial in nature, but in the rapidly changing AEM field, opinions on the best method to perform certain operations vary substantially, as reflected in the amount of discussion in the sections below. Current extraneous problems that still exist concerning x-ray analysis in the AEM, such as spurious x-ray signals entering the detector and artifacts introduced during specimen preparation, are discussed elsewhere in this volume by Allard and Fraser, respectively.

Selection of Experimental Parameters

Prior to quantitative x-ray analysis in the AEM, there are a number of instrumental variables that can be optimized to insure that, for example, quantification is accurate, or that the best conditions exist for detecting trace element segregation. As described by Statham in this volume, x-ray counting statistics may be the limiting factor in quantification. Therefore, it is essential to maximize the count rate of the characteristic x rays of interest. However, the time to acquire the x-ray counts must also be short enough to insure that specimen drift or contamination does not degrade the desired spatial resolution. Spatial resolution is optimized by small probes and thin specimens, conditions that are exactly the opposite of those required to generate high count rates. In general, therefore, a compromise experimental set-up is often required by which reasonably accurate quantification (about ±5% relative accuracy) can be achieved at a reasonable spatial resolution (about 10-30 nm).

The quantification process, as we shall see, requires acquisition of the maximum characteristic x-ray intensity above the continuum background. Therefore, the peak-to-background ratio (P/B) should be maximized along with the absolute count rate. As a rule of thumb, the total x-ray count rate over the whole of the energy spectrum (up to $E_0$, the accelerating voltage) should not exceed about 3000 counts per second, since the x-ray detector resolution may be impaired. Even in thin foil specimens using small probes, this count rate can often be achieved in modern AEMs, so caution is required. Under these circumstances the count rate in a small peak may be so low that long times (300-500 s) may be required to accumulate sufficient counts for quantification. Then spatial resolution may be lost, and it is more than ever essential to insure that the AEM is optimized for x-ray analysis. The relevant instrumental variables over which the operator has control will now be discussed.

Choice of Accelerating Voltage. Several theoretical treatments (e.g., Joy and Maher) predict that P/B increases with voltage but there is a lack of conclusive experimental evidence for it. However, there is no evidence that P/B decreases with increasing voltage, and given that the gun brightness ($A m^{-2} sr^{-1}$) is a linear function of $E_0$, there is good reason to operate at the highest voltage available, particularly if the number of
generated x-ray counts is a limiting factor. The fact that spatial resolution also improves with voltage is an added advantage.

Choice of Electron Gun. The choice for the average user is between a conventional W hairpin filament and a LaB₆ gun. The latter is brighter by a factor of about 10 at 100 kV, but substantially more expensive. However, if properly operated and maintained, a single LaB₆ source will operate for many months compared with the several days commonly obtained from a W hairpin. The relatively poor brightness of the W gun can be offset partially by the fact that operation at emission currents of 100 µA or more is not unreasonable for short periods of time, if a reduced filament life is acceptable. However, operating a LaB₆ gun much above 10µA emission may result in premature breakdown. (This difference in emission current does not totally offset the inherent brightness difference, since the probe diameter formed by a LaB₆ source is at least half that from a W source.) In a multi-user laboratory/teaching institution such as ours we still find it more practical to operate with a W filament, and have rarely encountered x-ray statistical limitations in our microanalyses. However, few of the problems we address require working at the lowest sensitivity, levels where the W gun would be a limiting factor. The field-emission gun as an alternative source is expensive, requires ultrahigh-vacuum conditions, and is available in very few laboratories. But in situations where the highest spatial resolution in both images and microanalysis is demanded, and minimum detectability problems are encountered, it is the best electron source to use.

Choice of Probe Parameters. Besides emission current, which is a function of the gun, the operator has a choice of the probe size (C₁ lens strength) and the probe convergence angle 2αₜ (C₁ aperture size). The current in the probe at the specimen can be varied over two orders of magnitude depending on the probe size (Fig. 1). If spatial resolution is a secondary consideration then a large probe size will minimize any x-ray count problems. Similarly, an increase in the value of 2αₜ increases the probe current (Fig. 2) for a fixed probe size. In theory probe size is independent of 2αₜ, but in practice spherical aberration at very high 2αₜ values may result in loss of resolution. In routine operations we use a C₂ aperture about 70 µm in diameter, which gives a probe current of about 10⁻¹⁰ A at a probe diameter of 10 nm. This configuration gives both adequate image resolution and good x-ray statistics.

EDS Variables. The EDS detector itself has a fixed geometry with respect to active area (about 30 mm²) and take-off angle (0°, 20° or about 70°, depending on the specific instrument). The solid angle is usually maximized, again to maximize the number of detected x-ray photons, by being placed as close (within about 15 mm) to the specimen as possible. The detector can be backed off mechanically if the count rate is too high, or if it is considered that extraneous radiation (e.g., backscattered electrons or hard x rays from the illumination system) is penetrating the collimator. Attention should be given to the choice of spectral display variables, in particular the energy range of the display on the multichannel analyzer (MCA) and the experimental counting time. The former should always be as large as possible (at least 40 keV) in the case of an unknown specimen, where the existence of K and L lines above 10 keV may be essential in initial qualitative analysis (e.g., as shown in Fig. 3, it is possible to distinguish between Mo and S L/K overlap at 2.3 keV by observation of the Mo Kα line at 17.5 keV). Selection of the desired energy range for analysis should then maximize the resolution of the display to about 5-10 eV/channel if all the peaks of interest can still be displayed in the 1024 available channels. If the specimen is known, the appropriate energy range can of course be selected immediately.

Counting time is important insofar as it should be minimized to reduce the effects of contamination, specimen drift, and elemental volatilization (in the case of Na and other mobile species). This limitation must be counterbalanced by the need to acquire enough counts for acceptable errors.

Measurement of X-ray Peak and Background Intensities

The only experimental information that is required for quantification of the EDS spectrum are the characteristic peak intensities Iₐ, I₇, etc., of the elements of interest. As discussed in the following section these values can then be converted directly into values of the wt.% of each element Cₐ, C₇, etc., or corrected for absorp-
FIG. 1.--Variation of probe current in Philips EM400T TEM/STEM as function of nominal probe size (courtesy Norelco Reporter).

FIG. 2.--Variation of probe current in Philips EM400T TEM/STEM as function of $C_2$ aperture size ($2a_2$) and probe size ($C_1$ setting) (courtesy Norelco Reporter).

FIG. 3.--EDS spectrum from inclusion in 2% Cr-1 Mo pressure vessel steel. The poor resolution of EDS cannot distinguish between S and Mo at 2.3 keV (a). However, observation of spectrum out to 20 keV (b) demonstrates that Mo is present.
tion, etc., where necessary. The determination of the characteristic intensity requires first that the continuum background (bremsstrahlung) radiation contribution to the peak be removed. This procedure can be carried out by one of several methods, depending on the degree of sophistication of the available computer hardware. A full description of the methods of determining the peak and background intensities has been given elsewhere. In this section we shall deal only with three representative methods of varying sophistication; two require computer curve-fitting and the other uses windows on the MCA display to select specific regions of peaks and equivalent regions of the background.

In current EDS/MCA systems the background intensity variation is usually accounted for in one of two ways. In the first, the detected intensity variation is described mathematically as originally proposed by Kramer and then modified by taking into account absorption in the detector. The second method assumes that the background intensity variation is a "smooth" function compared with the rapidly changing intensity in the characteristic peak. The application of a digital filter to the spectrum then removes any background without substantially affecting the superimposed characteristic peaks. Once the background is removed by either method, the characteristic peak intensity is obtained, again by one of two methods. The first method involves generation of Gaussian peaks and fitting them to the experimental peaks. In the second method, the experimental peaks are compared with library peaks obtained from reference standards. Both these methods can handle complex multielement spectra, and are essential when peak overlap occurs. Figure 4 shows the MCA display when x-ray peaks and the background intensity are determined in this manner. More advanced methods for handling peak overlap, and minimizing the resultant errors, are still evolving; progress will continue as mini-computer capabilities increase.

If the x-ray spectrum obtained is relatively simple (i.e., peak overlaps do not occur) and the continuum background is not changing rapidly (> 2 kV) then quantification can be achieved with an acceptable degree of accuracy (about ±5% relative) by the method of defining the characteristic peak area with a "window" in the spectrum. The windows available on a MCA display should select equivalent (i.e., same number of channels) regions of both the characteristic peaks, including background and a "typical" region of background, as shown in Fig. 5. (This approach is clearly not possible if peak overlap occurs.) When counts are integrated in this manner the optimal window width to maximize the peak counts and minimize background counts is about 1.2 FWHM. This arrangement gives the best sensitivity. If the selected peak contains sufficient counts and the background intensity is not varying rapidly with energy, then this process is more than adequate for obtaining \( I_A \) and \( I_B \) for subsequent quantification. In our experience, data obtained by both curve-fitting and spectral-window techniques are identical, within the necessary corrections when absorption and fluorescence are significant.

In electron-transparent thin films, electrons lose only a small fraction of their energy in the film. In addition, few electrons are backscattered and the trajectory of the electrons can be assumed to be the same as the thickness \( t \) of the specimen film. Under these circumstances the generated characteristic x-ray intensity \( I_A^* \) for element A can be given by a simplified formula:

\[
I_A^* = \text{const.} \quad C_A^* \omega A Q_A a_A t / A_A
\]  

(1)

where \( C_A \) is the weight fraction of element A; \( \omega A \) is the fluorescence yield for the K, L, or M characteristic x-ray line of interest; \( Q_A \) is the ionization cross section (the...
the Be window, gold surface layer, and silicon intensity is related to the generated intensity by

\[ I_A = I_A^* \varepsilon_A \quad \text{(2a)} \]

where

\[ \varepsilon_A = \exp \left[ -\mu / \rho_{Be} \right] \rho_{Be} \cdot \exp \left[ -\mu / \rho_{Au} \right] \rho_{Au} \cdot \exp \left[ -\mu / \rho_{Si} \right] \rho_{Si} \quad \text{(2b)} \]
and \( \mu/\rho \), \( \rho \), and \( X \) are respectively the appropriate mass absorption coefficients of element A in Be, Au, and Si; the densities of Be, Au, and Si; and the thicknesses of the Be window, the gold surface layer, and the silicon dead layer.

From Eqs. (1) and (2), it appears that the composition of element A in an analyzed region can be obtained simply by measurement of the x-ray intensity \( I_A \) and by calculation of the constant and other terms. In practice, however, that is not easy because many of the geometric factors and constants cannot be obtained exactly. In addition, the specimen thickness varies from point to point, which makes continual measurement of \( t \) inconvenient.

If the x-ray intensity \( I_A \), \( I_B \) of two elements A and B can be measured simultaneously, the procedure for obtaining the concentrations of element A and B can be greatly simplified. If one combines Eqs. (1) and (2) to calculate the intensity ratio \( I_A/I_B \), the following relationship for the concentration ratio \( C_A/C_B \) is obtained:

\[
\frac{C_A}{C_B} = \left[ \frac{(Qw/A)_B \cdot e_B}{(Qw/A)_A \cdot e_A} \right] \cdot \frac{I_A}{I_B}
\]

In this case the constants and the film thickness \( t \) drop out of the equation and the mass concentration ratio is directly related to the intensity ratio. The term in the brackets of Eq. (3) is a constant at a given operating voltage and is referred to as the \( K_{AB} \) factor or Cliff-Lorimer factor. Equation (3) is usually given in a simplified form as:

\[
\frac{C_A}{C_B} = K_{AB} \cdot \frac{I_A}{I_B}
\]

This relationship was developed and applied initially by Cliff and Lorimer using an EDS detector. The Cliff-Lorimer ratio method has gained great popularity due to its simplicity. (It must be borne in mind however that the technique is based on the assumption of the thin-film criterion.)

In a binary system, using Eq. (4) we can determine \( C_A \) and \( C_B \) independently since:

\[
C_A + C_B = 1
\]

In ternary and higher order systems the intensities of all the elements whose mass concentrations are unknown must be measured. A series of intensity ratio equations (like Eq. 4) are used in combination with an equation which sums all the mass concentrations to unity (like Eq. 5) to determine the mass concentration of each element.

The ratio method is often referred to as a standardless technique. However this description is strictly true only when \( K_{AB} \) is determined by calculation of the \( Q \), \( w \), etc., factors given in Eq. (3). More often the \( K_{AB} \) factor is determined using standards where the concentrations \( C_A \), \( C_B \), etc., are known. In this case the characteristic x-ray intensities are measured and the Cliff-Lorimer \( K_{AB} \) factors are determined directly from Eq. (4). The standards approach is often more accurate, particularly because \( e_A \) and \( e_B \) vary from one instrument to another and as we have observed may vary even in a single instrument over a period of time.

By convention \( K_{AB} \) factors are compared to Si, i.e., tabulation usually occurs as \( K_{ASi} \), \( K_{BSi} \), etc., and the values are called \( k \) factors. The relationship between \( k \) factors and \( K_{AB} \) factors is given by

\[
k_{AB} = \frac{k_{ASi}}{k_{BSi}} = \frac{k_A}{k_B}
\]
Until recently the only comprehensive range of measured k factors for Kα lines of a number of elements were reported by Cliff and Lorimer and Lorimer et al. These results were obtained with an EMMA-4 analytical instrument which has a relatively large probe size (about 10⁻⁵ mm). Limited work has been carried out on modern analytical instruments but most reported results refer to a single k_AB determination for a system of interest to the investigator.

Recently two sets of k factors have been measured. Figure 6 shows a selection of k factor measurements of Wood et al. plotted as a function of Kα characteristic x-ray energy. The measurements of k were made with a Philips EM400T AEM operated at 120 kV. The values of k_As are all close to 1.0 except for Mg and Na. Figure 7 shows experimental

\[ k_{AB} \] factors where element B is iron. We consider it more useful for the metallurgist to display the k factors in this manner because of the large number of common metals that can be alloyed in a convenient, homogeneous manner with the transition metals. Direct determination of k_Fe is then possible and few interpolations are required. By contrast many interpolations are required to obtain k_As because convenient metallurgical standards often cannot be fabricated. The measurement errors approach ±1% relative in a few selected cases. More typically, measurement errors are in the range ±1 to ±4%.

Since the measurement of the concentration C_A is directly related to the k_AB factor (see Eq. 4), the accuracy of the ratio method is limited to the error in the measurement of k_AB.

For most analyses it is not possible to use these measured and tabulated k factors, since the characteristics of EDS detectors vary from one instrument to another. Also many k factors, particularly for L and M lines, have not been measured and operating voltages other than 100 or 120 kV are used. Therefore it is often advisable for the analyst to measure the necessary k_AB factors directly. In many cases well-characterized alloys or stoichiometric oxides containing the elements of interest are available. When direct k_AB factor measurement is not possible the analyst must resort to using the standardless ratio method and calculate k_AB factors directly.

To calculate k_AB directly, the various terms in the brackets of Eq. (3) must be obtained. Figure 8 shows a comparison between measured and calculated k factors for K lines at a 120 kV operating potential. In this case the Green-Cosslett ionization cross section Q_K was chosen. Values of &omega_K were taken from the fitted &omega_K values of Bambynek et al. with use of the Burhop equation. The values of a and μ/ρ were obtained from Heinrich et al. and Heinrich, respectively. The EDS detector parameters as suggested

FIG. 6.--Variation of experimentally determined k factors with characteristic x-ray energy for selection of elements studied. Operating voltage 120 kV; k factors are relative to Si. Error bars represent 95% confidence limits.
by Zaluzec\textsuperscript{22} were $X_{\text{Ba}} = 7.6$ \textmu m (0.3 mil), $X_{\text{Au}} = 0.02$ \textmu m and $X_{\text{Si}} = 0.1$ \textmu m.

From Fig. 8 it is clear that above Si the calculated and experimental values follow the same trend, increasing with increasing K\textalpha energy. It is not possible to explain the differences between the calculated and measured values shown in Figure 8 with certainty but it appears that errors in the calculation of the ionization cross section may be largely responsible.

Other expressions for $Q_K$ are available. In general the formula for K shell cross section $Q$ can be written in the form:\textsuperscript{23}

$$Q = \text{const } \left( \frac{1}{E_0 E_K} \right) \ln \left( \frac{C_K E_0}{E_K} \right)$$

(7)

where $E_K$ is the binding energy of electrons in the K shell. The parameter $C_K$ is different for different models of the ionization cross section. The values of $C_K$ in Eq. (7) are 2.42, 1.0, and 0.65 for Q Mott-Massey,\textsuperscript{24} Q Green-Cosslett\textsuperscript{17} and Q Bethe-Powell.\textsuperscript{13} Zaluzec\textsuperscript{22} uses a form of Q in which $C_K$ varies with $E_K$. Schreiber and Wims\textsuperscript{15} used measured $k_{\text{AB}}$ values to back-calculate a best-fit ionization cross section. Maher et al.\textsuperscript{25} show that the uncertainties in using the Mott-Massey vs the Zaluzec modified Q equations lead to an error in the calculated $k_{\text{AB}}$ of less than about 15%. Goldstein et al.\textsuperscript{26} report a similar uncertainty when comparing calculated $k_{\text{AB}}$ values using the cross sections of Mott-Massey, Green-Cosslett, and Bethe-Powell.

Until more accurate measurements of $Q_K$ in the 100-200 kV range are made, inaccuracies in $k_{\text{AB}}$ for K\textalpha lines will remain in the range of 10 to 15%. These errors are much larger than those currently obtained for measured $k_{\text{AB}}$ factors. The differences in the values of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Variation of experimentally determined $k$ factors with characteristic x-ray energy for selection of elements studied. Operating voltage 120 kV; $k$ factors are relative to Fe. Error bars represent 95\% confidence limits.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Comparison of experimental results in Fig. 6 with calculated $k$ factors at 120 kV. Error bars represent 95\% confidence limits.}
\end{figure}
ionization cross sections for L and M lines are much larger than those for QK. Therefore, calculated compositions using L and M lines have correspondingly larger errors.

ii. Effects of Absorption. The thin-film criterion states that the effects of x-ray absorption and fluorescence can be neglected. Both Tixier and Philibert\textsuperscript{27} and Goldstein et al.\textsuperscript{26} have given criteria by which it can be determined whether the thin-film approximation has broken down and an absorption correction must be made. Both thin-film criteria give the film thickness at which the intensity ratio $I_A/I_B$ is altered by more than 10% from the ratio obtained from an infinitely thin film (Eq. 3).

The arbitrary assumption that absorption is only significant if $I_A/I_B$ is changed by more than $\pm$ 10% was justified originally, because that was the level of accuracy with which $k_{AB}$ factors and the values of $I_A$ and $I_B$ could be experimentally determined. With recent improvements in STEM electron optics and the development of clean specimen environments, measurements of $k_{AB}$ factors and of $I_A$ and $I_B$ can be made more accurately. As we have already discussed $k_{AB}$ factors can be routinely determined with an error of between $\pm$1-4%. Given this accuracy, the arbitrary definition of significant absorption should be lowered accordingly to $<\pm$5%, and perhaps as low as $\pm$1%. Such a new definition of significant absorption will reduce the thickness of specimens required to avoid absorption corrections, in many cases to small values (e.g., $<10$ nm in NiAl), difficult to obtain in practice. Thus the accuracy of the absorption correction process becomes more critical.

In order to correct for absorption, the $k_{AB}$ factor can be modified by a correction factor (CF) due to preferential absorption of one of the measured x-ray lines from element A or B.

Based on the original work of Tixier and Philibert\textsuperscript{27} and of Konig,\textsuperscript{28} Goldstein et al.\textsuperscript{26} have derived an equation to correct the $k_{AB}$ factor:

\[ CF = \frac{\int_0^t \phi_B(pt) \exp\left[-\mu/\rho\right]_\text{SPEC} \csc \alpha(pt) \, dt}{\int_0^t \phi_A(pt) \exp\left[-\mu/\rho\right]_\text{SPEC} \csc \alpha(pt) \, dt} \]

(8)

where $\phi_{A,B}(pt)$ is the depth distribution of x-ray production from element A or B as a function of specimen density $\rho$ and measured film thickness $t$, and $\alpha$ is the x-ray take-off angle. The terms $\mu/\rho\text{SPEC}_A$ and $\mu/\rho\text{SPEC}_B$ are the mass absorption coefficients of characteristic x rays of element A and B in the specimen.

On the assumption that $\phi_A(pt) = Q_B(t) = 1$ (i.e., x-ray production is uniform throughout the specimen), the integrals in Eq. (8) can be evaluated to give:

\[ CF = \frac{\mu/\rho\text{SPEC}_A}{\mu/\rho\text{SPEC}_B} \frac{1 - \exp[-\mu/\rho\text{SPEC}_B \csc \alpha(pt)]}{1 - \exp[-\mu/\rho\text{SPEC}_A \csc \alpha(pt)]} \]

(9)

To apply the correction factor CF for absorption to $k_{AB}$ the values of $\mu/\rho$, $\alpha$, $\rho$, and $t$ must be accurately known. The following sections discuss the limitations in the application of Eq. (9) and make some suggestions for minimizing the correction.

**Mass Absorption Coefficient.** Values of the mass absorption coefficient are accurately known from earlier studies of x-ray absorption, and may be obtained from any one of several sets of tables available in the literature.\textsuperscript{21,19} It is worth noting here that when
where \( n, \rho, t, \) and \( C_A \) are respectively the absolute electron flux, specimen density, thickness, and concentration in the standard \( S \) or the unknown \( U \). In this case neither \( k_{AB} \) or \( e_A \) values need be calculated. Unfortunately one must know \( n, \rho, \) and \( t \) for both standard and unknown and have a standard for each element measured in the unknown. As discussed previously, accurate measurements of \( t \) are difficult to make. In this case \( t \) must be measured for both the unknown and for all the standards. These disadvantages are so serious that this technique has seen little practical use. Recently Brown et al.\(^5\) have used pure-element Al, Mo, and Ni standards to determine the composition of \( \beta \)-NiAl and \( \delta \)-NiMo alloys. Besides difficulties in preparing pure-metal standards, changes in beam current lead to instabilities in the absolute electron flux. Unless standards preparation become easier and thickness measurements become more accurate the thin film standards technique will not be employed widely. The ratio method will continue to be employed by the vast majority of AEM users.

Limits of Microanalysis

It is pertinent to ask what the limits of EDS microanalysis are; specifically, with what accuracy can the average composition be determined and what is the minimum mass fraction (wt.%) that may be determined?

If x-ray counting statistics obey Gaussian behavior, at the 2\( \sigma \) confidence level, the relative error in the number of counts \( I \) is \( 2^{\frac{I}{N}} \times 100\% \). Since the Cliff-Lorimer relation (Eq. 4) uses the x-ray ratio \( I_A/I_B \), the relative error for this ratio is the sum of the relative errors for \( I_A \) and \( I_B \), and the total relative error in \( C_A/C_B \) for any one measurement is the sum of the errors for \( I_A, I_B, \) and \( k_{AB} \). As we have seen \( k_{AB} \) may be determined experimentally with an accuracy between 1\% and 4\%. For a minimum of \( 10^2 \) counts in each characteristic peak \( I_A, I_B \), the total error is 5-8\%, which is still high in comparison with bulk x-ray microanalysis errors. Still more accurate \( k_{AB} \) factors and as many accumulated counts as possible (concomitant with maintaining resolution) are required if accuracy in \( C_A/C_B \) is to be better than 5\%.

The only theoretical approach to determination of the minimum mass fraction (MNF) was described by Joy and Maher\(^4\) who predicted values of \( 0.2 \sim 3 \) wt.% for species of \( Z = 15 - 40 \) in a Si matrix, depending on the microscope conditions.

Assuming Gaussian statistics (which is debatable at small peak intensities) MNF of element A in a matrix of B may be given by\(^3\)

\[
\text{MNF} = \frac{3(21_A)^2}{I_B} k_{AB} \frac{C_A}{C_B} \tag{13}
\]

where \( I_B \) is the continuum background for element A. This equation shows that the MNF decreases as the characteristic counts or peak-to-background increase. To increase the counts one can use larger probe sizes, brighter electron sources, and moderately thick foils if high spatial resolution is not required. Optimization of the AEM is therefore essential if the MNF limit is to be approached; the considerations outlined in the first section of this article should be followed. Recent work in our laboratory by Michael\(^5\) using a Philips EM400T AEM, where count times are not limited by carbon contamination, has demonstrated that about 0.3 wt.% Mn can be detected in Cu by counting for about 300 s with a 100 nm probe to accumulate over \( 10^3 \) counts. Extrapolation of these data by using Eq. (13) indicates that given sufficient counts, the MNF can approach about 0.1 wt.% with a tungsten filament. High-brightness guns should improve the detectability limits accordingly.

Conclusions

Quantitative x-ray microanalysis in the AEM can be routinely performed by the ratio method with an accuracy of about \( \pm 5\% \). True standardless microanalysis based on calculated \( k_{AB} \) factors is significantly less accurate, and severe practical difficulties exist for
microanalysis based on thin-film standards. Correction for absorption is possible but complicated by several factors of which the most prominent is the difficulty of accurate thickness determination. The fluorescence correction need rarely be applied and there is still uncertainty concerning the best correction to use. The MNF is significantly less than 1%, but depends on instrumental parameters over which the operator has control.

References

1. L. F. Allard, these proceedings, p. 25.
2. H. L. Fraser, these proceedings, p. 37.
3. P. J. Statham, these proceedings, p. 54.


