SPATIAL RESOLUTION AND DETECTABILITY LIMITS IN THIN-FILM X-RAY MICROANALYSIS

J. I. Goldstein, C. E. Lyman, and Jing Zhang

The major advantages of performing x-ray microanalysis in the analytical electron microscope (AEM) are the high compositional spatial resolution and the elemental analysis sensitivity. Unfortunately there is usually a trade-off between these two advantages. This paper discusses the factors involved in the optimization of both spatial resolution and sensitivity during x-ray microanalysis and shows the results of such optimization experiments for several AEM instruments.

X-ray Spatial Resolution

Spatial resolution R depends on the size d of the focused electron probe and the amount of electron beam broadening b in the thin foil specimen.\(^1\),\(^2\) Figure 1 shows schematically the concept of spatial resolution in thin-foil microanalysis. A focused electron probe is shown at the top of the thin foil. The incident electron probe is elastically scattered as it progresses through the thin foil and the beam is at maximum size at the bottom of the thin foil of thickness t. If we assume that x rays are generated throughout the scattering process, x-ray emission occurs from a volume which is a frustum of a right circular cone (Fig. 1). If the intensity in the probe is Gaussian and the electron distribution remains Gaussian while traversing the sample, Reed\(^3\) proposed that the total amount of broadening \(\text{R}_{\text{max}}\) at the bottom of the thin foil is given by

\[
\text{R}_{\text{max}} = \sqrt{d^2 + b^2}
\]  

where b is the amount of beam broadening. As shown by Michael et al.,\(^2\) the measured spatial resolution is an average of the electron probe size over the specimen thickness. In Fig. 1 we define the spatial resolution R as an average of the electron probe size from the top and the total beam broadening (Eq. 1) from the bottom. Thus, R is given by

\[
R = \frac{d + \sqrt{d^2 + b^2}}{2} = \frac{d + \text{R}_{\text{max}}}{2}
\]  

It is important to define the probe size and the resultant beam broadening in a consistent way. Recently, Michael and Williams\(^4\) proposed using the combination of the full-width at tenth maximum (FWTM) probe diameter d with the 90% beam broadening diameter b as determined by

\[
b = 7.21 \times 10^5 \left(\frac{\rho A}{E}\right)^{1/2} \left(\frac{Z}{E}\right)^{1/2} t^{1/2}
\]

where \(\rho\), A, and Z are the average density, atomic weight, and atomic number of the specimen, respectively; E is the beam voltage in eV; and t is the specimen thickness in cm.

There are several ways to determine the probe size d at FWTM in an AEM for a given beam current and a specified operating voltage.\(^5\),\(^6\) One method to measure d is to scan the focused probe across a sharp edge on a thin specimen. Instead of a sharp discontinuous step, a smooth intensity profile is obtained. The width of this profile is a measure of the probe size under the assumption of a perfectly sharp edge. For a dedicated STEM, such as the Vacuum Generators HB-501, this is the only method available to measure the probe size. For a TEM/STEM system, it is also possible to image the probe directly on a photographic plate. If the exposure is controlled to remain within the linear range of the plate, the density level of the probe image on the film is a measure of the probe intensity. The intensity profile of the probe can be obtained and the probe size can be measured using a densitometer. In this study, the probe sizes for the Philips AEMs were measured by this method. Combining the calculation of b and a measurement of d at FWTM, one
can calculate the spatial resolution $R$ using Eq. (2).

To optimize spatial resolution, one should use the smallest probe size $d$, most easily obtained by using a high-brightness field-emission gun (FEG). For thermionic sources the probe current is reduced to inadequate levels at probe sizes $<10$ nm. This reduction occurs because the probe current is proportional to $d^{-3/2}$ for thermionic sources but not for FEG sources. In addition, specimens should be as thin as possible and the highest operating voltage should be used to minimize the beam broadening $b$.

One can determine the spatial resolution $R$ experimentally by measuring composition profiles from specimens with abrupt concentration discontinuities. Figure 2 shows schematically how the x-ray excitation volume for a given element varies as the focused probe is stepped across an interface with an abrupt concentration change. The actual step size should be much less than the spatial resolution $R$ so that the detailed concentration gradient across the interface can be measured. The measured concentration variation takes into account the finite x-ray spatial resolution, and the discontinuity is measured as an error function composition variation across the interface (Fig. 2).

As suggested by Michael et al., the FWTM distance of a Gaussian distribution $R$ scanned across a composition step is a horizontal distance $L$ that can be used to help measure the spatial resolution. If the concentration discontinuity is normalized to 100%, the FWTM across the apparent concentration variation is represented by $L$ between the 2% and the 98% points on the compositional profile (Fig. 3). It may be easier to measure $L$ from the full width at half maximum (FWHM), which is the distance between the 12% and the 88% points on the profile, and then to multiply that value by 1.82 to obtain $L$.

The geometry of the beam and specimen used to measure the spatial resolution across a concentration step is not the same as that shown in Fig. 1. In the experimental setup, the scattering of electrons parallel to the boundary where the discontinuity is present occurs without a degradation of the spatial resolution in one dimension rather than in two dimensions as in Fig. 1. The spatial resolution $R$ given in Eq. (2) can be obtained by multiplication of $L$, the FWTM across the error function, by $1/2$.

Another test specimen for spatial resolution can be conceived as a right cylinder of a second phase in a thin foil. If such a cylindrical second phase could be obtained in various sizes, the spatial resolution would be given as the cylinder diameter where 90% of the signal from the second phase may be obtained for a given probe diameter. Such a spatial-resolution specimen is not yet available.

**Minimum Mass Fraction**

The minimum mass fraction (MMF) is a measure of the elemental analysis sensitivity and represents the smallest concentration of an element that can be measured with a focused electron probe of size $d$ under specified AEM operating conditions ($kV$, probe current, x-ray detector solid angle, counting time, etc.). The analyst can determine the MMF directly for a sample of known composition by making relatively simple measurements on the thin film. The approach used in this study to determine the MMF is to employ a thin film where element $A$ is present and its concentration $C_A$ in the sample is known. The analysis requirement is to detect significant differences between the sample and continuum background generated from the sample. For a single analysis, we can say that $I_A$ is significantly larger than the background continuum radiation $I_B$ for the sample if the value of $I_A$ exceeds $I_B$ by $3(2I_A)^{1/2}$. If we use a thin film where element $A$ is present
FIG. 4.--Measurement of the electron probe intensity profile for a Philips EM430T and a Philips EM400T AEM. (a) EM430T, 300kV, 50μm C2 aperture, spot size 4 setting; (b) EM400T, 120kV, 70μm C2 aperture, spot size 4 setting; (c) EM430T, spot size 5 setting; (d) EM400T, spot size 5 setting.

FIG. 5.--Electron probe intensity profiles of EM430T, spot size 5 setting at different objective lens focusing. (a) Small central peak with tail, (b) approximate Gaussian peak.

and its concentration $C_A$ in the sample is known, then

$$\text{MMF} = \frac{\sqrt{2b^2}}{A} \frac{C_A}{I_A - I_b}$$  \hspace{1cm} (4)

Since the x-ray yield $I_A$ varies with film thickness, the value of MMF varies from one analysis point to the other. Therefore the MMF is not likely to be constant over an entire sample even for the same analysis conditions.

Ziebold$^7$ showed that trace element sensitivity or MMF can also be expressed as

$$\text{MMF} \approx \left[ \frac{P}{P/B} \right]^{-1/2}$$  \hspace{1cm} (5)

where $P$ is the pure element counting rate, $P/B$ is the peak-to-background ratio of the pure element, and $T$ is the counting time. One can decrease (improve) the MMF by increasing all three factors in Eq. (5). Thus, one may obtain improvements in MMF by increasing the electron current density and optimizing the x-ray detector configuration to increase $P$, by increasing the operating voltage to increase $P/B$, and in increasing the analysis time $T$. Unfortunately, the analysis time is limited in most AEM instruments by contamination and specimen drift. In an AEM optimized for chemical sensitivity, the MMF if typically 0.1 to 0.2 wt% for elements near iron in atomic number. In this study the MMF was measured for Ni in an homogenous thin foil of an Fe-25 wt% Ni alloy.

Results: Measurement of $R$ and MMF

Measurements of the electron probe diameter for the Philips 400T at 120 kV and the Philips 430T at 300 kV were made by direct imaging of the probe and measurement of the intensity profile across the photographic negative by a densitometer. To image the electron probe, beam scanning was stopped and the microscope imaging system was switched from diffraction mode to image mode so that, instead of a scan raster, a magnified probe image was obtained on the microscope viewing screen. The objective focus was changed slightly to obtain a focused probe image. The error introduced in the probe diameter by variation of the objective focusing length was minimal. The advantage of using the microscope imaging mode was that at high magnification, the current density on the viewing screen falls within the linear range of the recording film. The intensity profiles of the magnified focused probe were measured with an LKB 222-020 Ultra Scan XL laser densitometer.

Measured probe diameters (FWHM and FWTM) and beam current for the Philips 400T and Philips 430T at various C2 apertures and probe forming conditions in STEM mode are listed in Table 1. For the 70μm C2 aperture used in the EM400T, the measured FWTM of the probe is larger than the calculated value for a Gaussian peak, FWHM × 1.82. The larger FWTM probe size shows that the electron probe has a broad tail distribution because of the larger than optimum C2 aperture size available. For the EM430T with a 50μm C2 aperture, the electron probes are approximately Gaussian.

TABLE 1.--Experimentally measured electron probe parameters of the Philips EM430T and EM400T microscope in STEM mode.

<table>
<thead>
<tr>
<th>STEM setting</th>
<th>EM430T 50 μm C2 aperture</th>
<th>EM400T 70 μm C2 aperture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot Size 4</td>
<td>FWHM 7.0, P=0.263 μA</td>
<td>FWTM 11.8, P=0.263 μA</td>
</tr>
<tr>
<td>Spot Size 5</td>
<td>FWHM 11.8, P=0.263 μA</td>
<td>FWHM 4.0, P=0.052 μA</td>
</tr>
</tbody>
</table>

Figure 4 shows the measured intensity profiles of the electron probes listed in Table 1, at optimum focusing conditions (smallest probe sizes with the minimum tails). For certain
probe size and aperture combinations, the optimum probe for microanalysis was different from that which gives the best STEM image. An example is shown in Fig. 5. The probe in Fig. 5(a), which has a sharp central peak with a large tail will probably give a better STEM image. However, the probe in Fig. 5(b), which is approximately Gaussian and is underfocused by the objective lens by some 200 nm, will allow microanalysis at a higher spatial resolution, since it has no significant tail. As demonstrated previously by Cliff et al., slightly underfocusing from the best STEM image condition improves the spatial resolution of x-ray analysis. For some experimental conditions, usually with large C2 apertures, it is not possible to achieve a Gaussian probe without a tail no matter what underfocusing is used.

The electron probe size of the HB-501 STEM was measured by Michael by use of a small MgO crystal. An optimum probe with FWTM of 1.8 nm was obtained with a 50um virtual objective aperture. This probe size was used for the spatial resolution calculations for the VG STEM. In the calculation of the spatial resolution R of the Philips AEMs, we used the experimentally measured FWTM probe size when the electron probe was approximately Gaussian, and 1.82 times the experimentally measured FWHM probe size when the probe was not Gaussian. The spatial resolutions calculated in this study are the ideal values. The practically achievable spatial resolution may be worse due to factors such as specimen drift and other instabilities of the microscope, as well as nonideal electron probe characteristics as discussed above.

In order to calculate the amount of beam broadening from Eq. (3) one must measure the specimen thickness t at the analysis position. Direct foil thickness measurements were made by the EELS log-ratio technique. This procedure involves measuring the ratio of the total area I under the electron energy loss spectrum from the Fe-Ni thin foil to the elastically scattered peak I0, where

\[ t = \lambda \ln \left( \frac{I}{I_0} \right) \]  

An equation for the total inelastic mean free path \( \lambda \) was derived by Malis based on experimentally measured values of \( \lambda \) for various materials. Absolute thickness can be determined to an accuracy of ±20%. For a measurement of the relative specimen thickness at each analyzing position, the x-ray count method is the most convenient. To use this method, it is necessary to measure a calibration curve of x-ray counts vs thickness for a specimen of similar atomic number. The beam current must be measured by an independent method. In this study, a calibration curve of 0-10 keV x-ray counts per pA vs thickness was measured for a 120s counting time on an Fe-25 wt% Ni alloy for each of the AEM instruments used. The specimen thickness was measured by the EELS log-ratio technique. The calibration curves for the EM430T and HB-501 are shown in Fig. 6. These calibration curves are linear for film thicknesses up to at least 100 nm.

In the Philips 400T and 430T AEMs, the beam current from the LaB6 filament was measured by means of a specimen holder electrically isolated from the microscope column and connected to a Keithley 480 picoammeter. The reading from the picoammeter was corrected for back-scattering to obtain the direct beam current. The beam current was quite stable after an initial period when the beam current was decreasing. In the VG HB-501 STEM, the beam current was measured by insertion of an electrically...
isolated slab of Mo into the beam path and accounting for backscatter. The beam current of the instrument was measured frequently during the experiment to obtain accurate and continuous information.

By combining the calculation of beam broadening $b$, using the measured thicknesses of the Fe-Ni thin foil and the measurement of $d$, we have calculated the x-ray spatial resolution $R$ according to Eq. (2). Calculations of MMF were made from measurements of $I_A$ and $I_B$ at specific analysis points on the Fe-25 wt% Ni thin foil. Figure 7 shows the variations of MMF and spatial resolution $R$ in the Fe-Ni alloy. The data are given for three AEM instruments: a Philips 430T, a Philips 400T, and a VG HB-501.

**Discussion**

The definition of the x-ray spatial resolution $R$ has been stated in several different forms. We prefer the definition given by Eq. (2) and illustrated in Fig. 1 because the spatial resolution can be shown explicitly on a diagram (Fig. 1) and can be considered in such a way that the value of $R$ is not tied directly to an experiment, for example a step in concentration at a planar interface. The spatial resolution given in Eq. (2) is about 40% larger than that defined by Michael et al. for a planar interface and represents a more conservative value of $R$.

As noted in previous studies and in Fig. 7, the chemical spatial resolution and the MMF are not independent of one another. For the data shown in Fig. 7, the electron probe current and the probe diameter (FWTM) for each instrument is held constant. What is varied is the thickness of the Fe-25wt% Ni specimens from 20 to 250 nm. The spatial resolution $R$ approaches the beam diameter $d$ in the thinnest specimens. The MMF decreases continuously as the thickness (and spatial resolution) increases.

The measured electron probe current in the Philips 430T and VG HB-501 are almost the same (0.26 nA vs 0.3 nA). Although operating voltages and EDS collection angles are quite different, the MMF of both instruments is quite similar, 0.15 to 0.20 wt% Ni. As shown in Fig. 7, the variation in optimum x-ray spatial resolution for the two instruments, however, is quite dramatic.

In order to improve the spatial resolution in AEMs with thermionic sources, one should use a small $d$, which minimizes the probe size, and also use a thinner specimen to minimize $b$. Both of these improvements degrade the MMF because a smaller x-ray intensity $P$ is generated. At minimum specimen thickness, the spatial resolution is optimized and controlled by the probe size $d$. The MMF is optimized with thicker samples that force the spatial resolution to be 2 to 5 times optimum (Fig. 7). For this case the MMF is limited by the factors that control the number of x-ray counts collected (e.g., probe current, detector collection efficiency, and collecting time). The usefulness of the FEG is clearly illustrated in Fig. 7.

FIG. 8. Ni composition profile for planar austenite (fcc) precipitate in plessite region of Grant meteorite: (a) STEM image, (b) Ni composition profile.

where spatial resolution $R$ can be improved by almost an order of magnitude from about 15 to 1.8 nm) without any loss of MMF.

Figure 8 shows a Ni composition profile across a planar 10nm-wide precipitate in the plessite region of the Grant iron meteorite. A spatial resolution of roughly 2.5-3.5 nm was obtained from a 20nm-thick sample analyzed in a Vacuum Generators HB-501 FEG AEM (electron probe diameter: 1.8 nm FWTM). This spatial resolution is one of the best (smallest) measured in real specimens. Unfortunately, not enough data points were obtained to define accurately the error function composition curve and the value of $L$ at FWTM (Fig. 3). The lack of an accurate $L$ value leads to the uncertainty in the measured spatial resolution. Use of step sizes of the order of 0.2 $L$ will lead to more accurate fitting of the error function composition variation through the measured data and hence a more accurate value of spatial resolution $L$. Such a small step size may not be practical due to specimen-borne contamination.
A modest amount of specimen drift was present during the measurement although a computer specimen drift correction program was used. This factor also led to an increase in the measured spatial resolution. Finally, the planar precipitate was probably not wide enough for the spatial resolution test, since a flat portion of the composition must be measured on both sides of the discontinuity in order to calculate the error function composition variation. Prospects for improved spatial resolution and chemical sensitivity include combined use of intermediate voltages (300-400 kV) with the field-emission gun, optimization of x-ray intensity by use of higher collection angles and multiple x-ray detectors, longer counting times due to improved stage and electron beam stability, and the development of compact wavelength-dispersive spectrometers (WDS) to increase the peak-to-background of x-ray measurements. Some of these instrumental developments will soon be available. However, the employment of two or more EDS detectors will need to be carefully explored. Both detectors must see the same region of the sample. However, each detector will receive x rays absorbed along different specimen path lengths unless very special geometrical conditions are used. One can examine the effect of the instrumental improvements on the spatial resolution and MMF discussed above. Because of the higher brightness FEG, one will have available a 0.5nA beam current in a 1.0-1.5nm (FWTM) focused probe. With this small probe and high probe current, it should be possible to analyze thin foil specimens 10nm thick and obtain a spatial resolution of the order of the FWTM of the focused probe, 1.0 to 1.5 nm. With the use of a longer counting time (for example, 1200 s, due to increased stage and beam stability) and two EDS detectors at higher collection angles than available at present, it should be possible to obtain a MMF of 0.05 wt% with the improved spatial resolution discussed above. With the improved spatial resolution one should be able to measure x rays from about 1.5 x 10^{-19} g of material. With an MMF of 0.05 wt% for a given element, one could detect the presence of as little as 7.5 x 10^{-23} g of that element. In a specimen of an iron-base alloy, this spatial resolution and MMF allows the detection of as little as one atom of an element of interest in the iron-base alloy. The AEM would then be capable of single-atom analysis, a very exciting achievement. In specimens of average atomic number significantly lower than iron, the detection of single atoms of low atomic number in the analysis volume is more difficult. Some concern must be raised about the effect of specimen preparation techniques on thin-specimen chemistry, electron-beam effects at high operating voltages, less than optimal vacuum at the specimen, and whether increased P/B can be achieved at higher voltage if the hole count becomes worse at such voltages. The hole count on current instruments has not prevented analysis, but for the very best values of MMF it will have an effect since it will tend to reduce the peak-to-background ratio for an element in a local area. For example, the hole count tends to be a more serious problem as the atomic number of the specimen increases. Thus, it is likely that this effect of hole count on MMF will be worse for platinum in alumina than nickel in iron.

Conclusions

This paper has shown detailed measurements of spatial resolution R and chemical sensitivity MNF from FEG and thermionic emission AEM instruments. For all these instruments there is a clear trade-off between R and MMF and an optimum value of R and MMF can be obtained. The FEG instrument is clearly superior, offering higher spatial resolution for comparable values of MMF. Future developments in instrumentation promise an improvement in both factors.

References