36

Spatial Resolution and Minimum Detection

CHAPTER PREVIEW

Often when you do X-ray analysis of thin foils you are seeking information that is close to the limits of spatial resolution. Before you carry out any such analysis you need to understand the various controlling factors and in this chapter we explain these. Minimizing your specimen thickness is perhaps the most critical aspect of obtaining the best spatial resolution, so we summarize the various ways you can measure your foil thickness at the analysis point, but the quality of the TEM-XEDS system is also important.

A consequence of going to higher spatial resolution is that the X-ray signal comes from a much smaller volume of the specimen. A smaller signal means that you'll find it very difficult to detect the presence of trace constituents in thin foils. Consequently, the minimum mass fraction (MMF) in TEM is not as small as many other analytical instruments which have poorer spatial resolution. This trade-off is true for any analysis technique, and so it is only sensible to discuss the ideas of spatial resolution in conjunction with analytical detection limits. We'll make this connection in the latter part of the chapter. Despite the relatively poor MMF, it is possible to detect the presence of just a few atoms of one particular element if the analyzed volume is small enough, and so the TEM actually exhibits excellent minimum detectable mass (MDM). With the latest advances in XEDS and TEM technology, particularly C_s correction, X-ray analysis with atomic-column resolution and single-atom detection is now feasible in the same instrument.

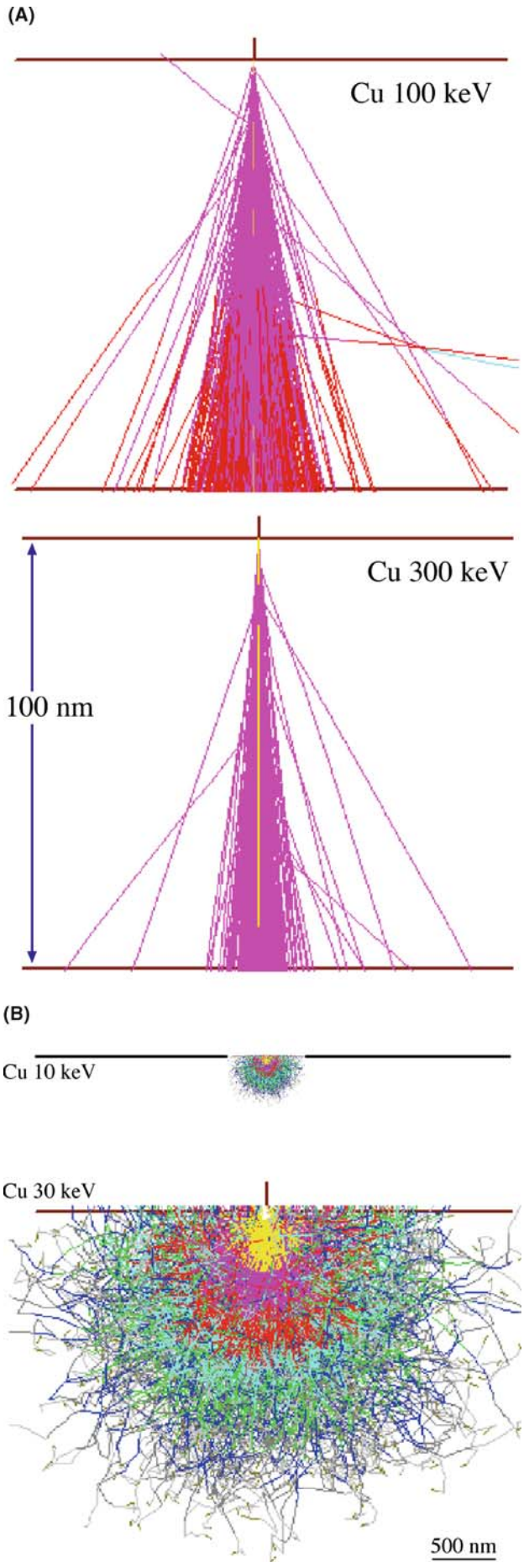
36.1 WHY IS SPATIAL RESOLUTION IMPORTANT?

As we described in the introduction to Chapter 35, the historical driving force for the development of X-ray analysis in the TEM was the improvement in spatial resolution compared with the EPMA. This improvement arises for two reasons

- We use thin specimens, so less electron scattering occurs as the beam traverses the specimen.
- The higher electron energy (>100–400 keV in the TEM compared with 5–30 keV in the EPMA) further reduces scattering.

The latter effect occurs because the mean free path for both elastic and inelastic collisions increases with the electron energy. The net result is that *increasing* the accelerating voltage when using thin specimens *decreases* the total beam-specimen interaction volume, thus giving a more localized X-ray signal source and a higher spatial resolution, which is good (see Figure 36.1A). Conversely, with bulk samples, *increasing* the voltage *increases* the interaction volume and spatial resolution is at best ~0.5–1 μm which is not so good (see Figure 36.1B). There is increasing interest in reducing the spatial resolution of SEM-X-ray analysis using very low voltage electron beams and low-energy X-ray lines. While this is challenging, there has been considerable progress and a spatial resolution <100 nm with E_0 <5 keV is feasible. Aberration correctors and bolometer detectors will help even further but, for the best spatial resolution, there is still no alternative to thinning your specimen.

Much theoretical and experimental work was carried out in the early days of AEM to define and measure the spatial resolution of XEDS in the TEM, and we'll introduce some of these concepts. The ultimate aim, of course, is to push spatial resolution to the atomic scale and detection limits to the single-atom level. Both of these goals have been attained in EELS, as we'll see in the next several chapters, but, as ever, we are limited by the small number of X-ray counts generated in thin foils and the poor collection efficiency of the XEDS. C_s correctors and SDDs are helping here, as we shall see.



36.2 DEFINITION AND MEASUREMENT OF SPATIAL RESOLUTION

It has long been recognized that the analysis volume, and hence the spatial resolution, is governed by the beam-specimen interaction volume, since the XEDS can detect X-rays generated anywhere within that volume (you'll see later that this is different to the situation in EELS). The interaction volume is a function of the incident-beam diameter (d) and the beam spreading (b) caused mainly by elastic scattering within the specimen. Therefore, the measured spatial resolution (R) is a function of your specimen and this has made it difficult to define a generally accepted measure of R. Let's look first at d and b and how we define them.

SPATIAL RESOLUTION FOR XEDS

We can define this spatial resolution as the smallest distance (R) between two volumes in the specimen from which independent analyses can be obtained. The definition of R has evolved as AEMs have improved and smaller analysis volumes have become possible.

We've already discussed how to define and measure d in TEMs and STEMs way back in Chapter 5, so you need only remind yourself that the beam diameter d is defined as the FWTM of the Gaussian electron intensity. We can measure d directly from the TEM image or indirectly by traversing the beam across a sharp edge and looking at the intensity change on the STEM screen.

This definition takes account of only 90% of the electrons entering the specimen, so it is still an approximation. Remember that the electron-intensity distribution in the incident beam is Gaussian only if you are careful in your choice (small) and alignment of the C2 aperture and you restrict the beam to paraxial conditions (go back and read Section 6.5.A to decide if you should be at the Gaussian image plane or the disk of minimum confusion for best resolution). It is a little more difficult to define and measure b, so this needs more explanation.

FIGURE 36.1. (A) Monte Carlo simulations of 10^3 electron trajectories through a 100 nm Cu foil; (upper) 100 kV; (lower) 300 kV. Note the *improved* resolution at higher kV. (B) Conversely, in a bulk sample, the interaction volume at 30 kV is much larger than that at 10 kV, thus giving *poorer* X-ray spatial resolution at higher kV. The color in both sets of simulations reflects the change in energy of the electrons. Note the relatively constant energy in the thin foil compared with the rapid energy loss in the bulk sample.

36.2.A Beam Spreading

The amount that the beam spreads (b) on its way through the specimen has been the subject of much theoretical and experimental work. While results and theories differ in minor aspects, there is a general consensus that b is governed by the beam energy (E_0), foil thickness (t), and atomic number (Z). It turns out that the simplest theory for b gives a good approximation under most analysis conditions. This theory (sometimes called the 'single-scattering' model because it assumes that each electron only undergoes one elastic scattering event as it traverses the specimen) was first given in the seminal paper by Goldstein et al. and re-defined in SI units by Jones.

$$b = 8 \times 10^{-12} \frac{Z}{E_0} (N_v)^{1/2} t^{3/2} \qquad (36.1)$$

where b and t are in m, E_0 is in keV, and N_v is the number of atoms/m^3. In the original derivation, this latter term was given as $(\rho/A)^{1/2}$ and is confusing in that the density may vary considerably from point to point in a multiphase alloy and is generally unknown anyhow. Furthermore, the atomic-weight dependence was the opposite to the atomic-number dependence which is counterintuitive. So using N_v is clearer and you can work the value out from the ratio of the number of atoms/unit cell to the volume of the unit cell, for which you need to know the lattice parameter. This definition again comprises 90% of the electrons emerging from the specimen, so it is consistent with our definition of d.

There is some question as to whether this single-scattering expression adequately describes the behavior of b for either very thin or very thick foils, but it has generally survived the test of time and its strength remains in its simplicity.

You should of course estimate/calculate b *prior* to spending an inordinate amount of time trying to do an experiment that is impossible for lack of sufficient resolution. Prior simulation of the expected resolution versus the necessary resolution to detect the phenomenon of interest can be very useful here, so let's discuss how best to do this, particularly when the specimen geometry is complex (e.g., multiple/overlapping phases) so equation 36.1 is difficult to apply.

FOR YOUR MAC/PC

We recommend that you keep this equation stored in the TEM computer (or your phone) so you can quickly estimate the expected beam spreading in your planned experiment.

When you can't apply equation 36.1, the best alternative is the Monte Carlo computer simulation, which we introduced in Section 2.5, as a way of modeling electron scattering. Such simulations are used in a wide variety of fields, including SEM and EPMA, as well as other nuclear-particle fields, as a quick search of the Web will reveal. A full description of Monte Carlo simulations is beyond the scope of this text but good reference books exist on the topic. In Joy's book, you'll find a code listing for a Monte Carlo simulation program which can be run on a PC. The public-domain Monte-Carlo programs that do the best job are WinCASINO and WinXRAY from Gauvin at McGill (see URLs #1 and #2); thin-foil versions of this software are under development. Until these are available, we recommend Joy's software. These simulations are now extremely rapid, and in a few minutes on a PC or Mac, they can provide all the information you need to estimate the beam spreading in more complex microstructures.

Basically, the Monte Carlo technique simulates, in a random manner (hence the name), a feasible set of electron paths through a defined specimen. After simulating ideally several thousand paths, an approximate value of b can be obtained by asking the computer to calculate the diameter of a disk at the exit surface of the specimen that contains 90% of the emerging electrons. This definition of b is consistent with that described at the start, and is the dimension of b given by equation 36.1. In fact, the schematic trajectories in Figure 36.1A and B are Monte Carlo simulations using Joy's software. Figure 36.2 shows Monte Carlo simulations of electron trajectories at three points across an interface between Cu and Au. Such a complex situation with elements of radically different Z cannot be easily handled by the single-scattering model estimates of b from equation 36.1.

While beam spreading is the main aspect of spatial-resolution theories, we mustn't forget that what we really want to know is the beam-specimen interaction volume, which corresponds to the size of the X-ray source. Monte Carlo simulations can help because in principle they can

- Incorporate the effects of different kVs and beam diameters
- Handle difficult specimen geometries, specimen tilt, thickness variations, and multi-phase specimens
- Automatically calculate the effect of the depth distribution of X-ray production, $\varphi(\rho t)$, on the X-ray source size
- Display the X-ray distribution generated anywhere in your specimen, as a function of all the variable parameters in equation 36.1, N_v, Z, and t. This tells you the relative contributions to your XEDS spectrum from different parts of the microstructure.

In addition to the theories of beam spreading that we've discussed, there are several more in the literature. A common feature of these theories is that they all predict a linear relationship between b and $t^{3/2}$ and an

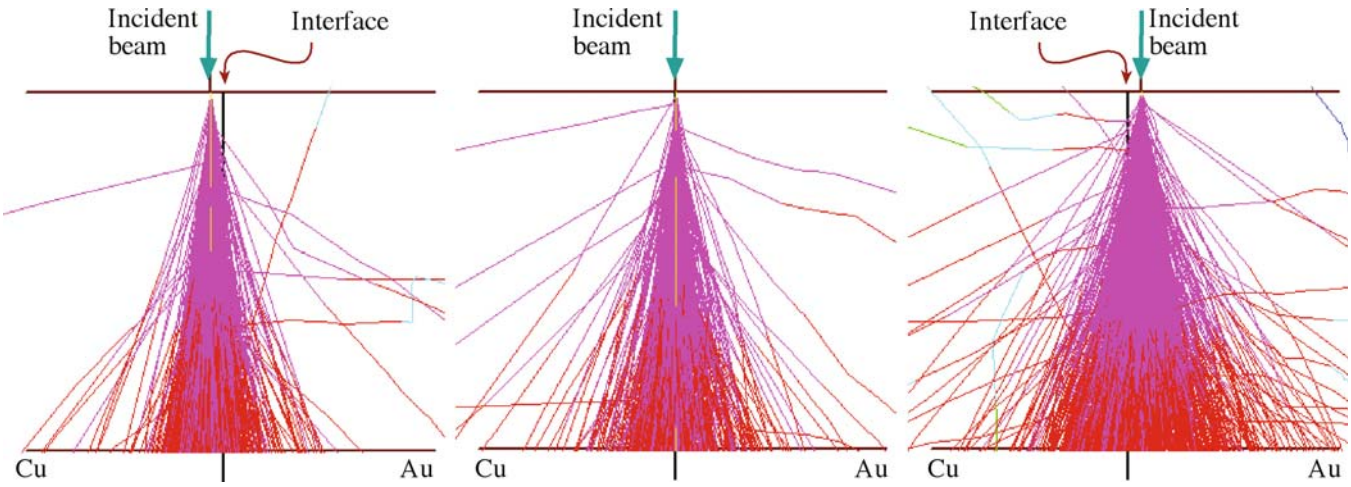


FIGURE 36.2. Monte Carlo simulation of electron trajectories across an interface between two metals of different Z, in which the scattering is very different. Note the rapid increase in the electron scattering in the higher Z region and therefore, X-rays would come from larger regions, thus lowering the local spatial resolution.

inverse relationship between b and E_0. If you're interested in the details of the various theories you'll find a discussion in the Goldstein et al. 1986 paper. However, we'll also see (look ahead to Figure 36.9 in Section 36.3.E) that there are ways to determine the spatial resolution on-line while you're doing your analyses and/or mapping and this is undoubtedly the best approach, since it combines the simple equations we'll now discuss with actual experiments rather than calculations, which make assumptions about your specimens.

36.2.B The Spatial-Resolution Equation

Now we've defined d and b, all we have to do is combine them to come up with a definition of R. If the intensity distribution of the incident beam is Gaussian, and if the beam emerging from the specimen retains a Gaussian form, it is reasonable to add b and d in quadrature (just as we did for image resolution back in Section 6.6.B) to give a value for R

$$R = \left(b^2 + d^2\right)^{\frac{1}{2}} \tag{36.2}$$

Gaussian beam-broadening models are also available, based on equation 36.1, which permit convolution of the Gaussian descriptions of d and b to come up with a definition of R. Based on the Gaussian model and experimental measurements, Michael et al. proposed that the definition of R be modified so as not to present the worst case (given by the exit-beam diameter) but to define R midway through the foil, as shown in Figure 36.3

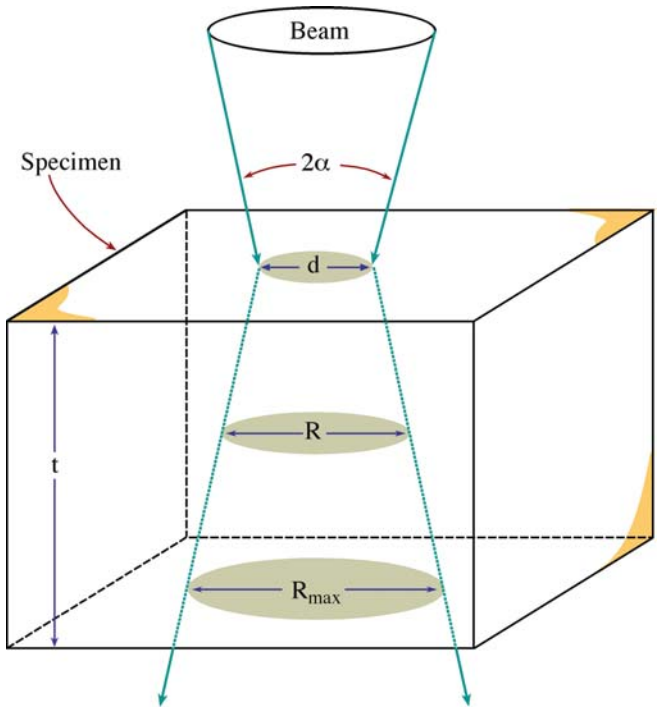


FIGURE 36.3. Schematic diagram of how the incident beam size and the beam spreading combine to degrade the exit-probe diameter to R_{max}, thus defining R.

$$R = \frac{d + R_{max}}{2} \tag{36.3}$$

where R_{max} is given by equation 36.2.

Like all definitions of spatial resolution, there is no fundamental justification for the choice of various factors, such as the FWTM diameter and the selection of the mid-plane of the foil at which to define R. Similarly,

this approach ignores any contribution of electron diffraction in crystalline specimens and beam tailing beyond the 90% limit. Nevertheless, the definition has been shown to be consistent with experimental results and sophisticated Monte Carlo simulations (Williams et al.). Finally, this definition retains the advantage of the original single-scattering model, i.e., it has a simple form and is easily amenable to calculation.

RESOLUTION IN XEDS

Equation 36.3 is the formal definition of the X-ray spatial resolution.

36.2.C Measurement of Spatial Resolution

Experimental measurements of the spatial resolution, such as composition profiles measured across atomically sharp interfaces, are very useful (go back and look at the profiles in Figure 1.4D). Several other kinds of specimens have been proposed but using interphase interfaces retains its validity since there are fewer unknowns than for the other specimens. If thermodynamic equilibrium exists on either side of the interface, the solute content of each phase is well defined. Also, interphase interfaces are common to many engineering materials, as is evident from many images of such defects throughout this text.

In order to compare experimental and calculated measurements of R, you have to understand how we relate the measured composition profile across the interface to the actual discrete profile shape, shown schematically in Figure 36.4. We do this by deconvolution of the beam shape from the measured profile. The finite beam size d and the effect of b degrade the sharp profile to a width L which is related to R by the following equation

$$R = 1.414L \tag{36.4}$$

Assuming this relationship holds, we just measure the distance L between the 2% and 98% points on the profile, as shown in Figure 36.4. This spread contains 90% of the beam electrons, consistent with our assumption of a 90% (FWTM) incident-beam diameter. In practice, you will find it difficult to measure the 2% and 98% points because of the errors in the experimental data. So you should measure the distance from the 10% to the 90% points on your profile, corresponding to the beam spread containing 50% of the electrons (FWHM), then multiply this distance by 1.8 to give the FWTM.

Nevertheless, this definition is easy to remember, relatively easy to measure, consistent with the

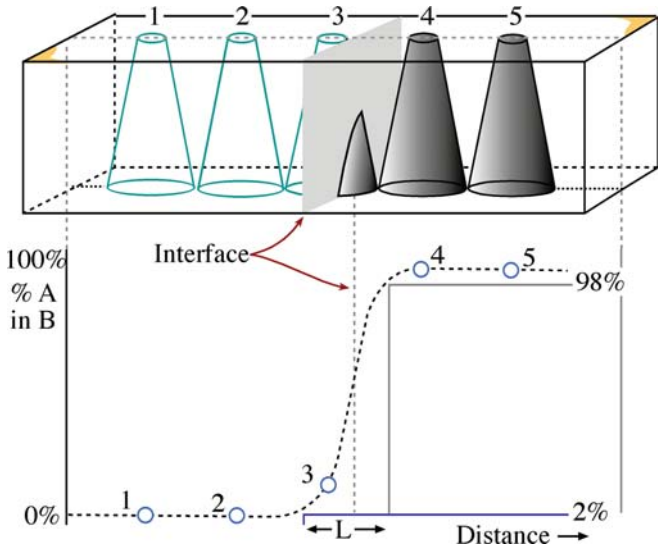


FIGURE 36.4. Schematic diagram showing a composition profile measured across an interface at which an atomically discrete composition change occurs (like the simulation in Figure 36.2). The measured spatial resolution can be defined in terms of the extent (L) of the measured profile between the 2% and 98% points.

definitions of b and d, and, most importantly, gives a number that is close to the experimentally measured degradation of discrete composition changes introduced by the beam-specimen interaction.

It is obvious from equation 36.2, that if we want to improve spatial resolution, then both d and b must be minimized. Unfortunately, if we minimize d we reduce the input beam current: for thermionic sources, if d <10 nm, count rates will become unacceptably low. However, with a FEG, sufficient current (~1 nA) can be generated in a small enough (1 nm) beam to permit quantitative analyses with high spatial resolution.

DEFINING *R, b,* AND *d*

Note that this definition of R, like the definitions of b and d that we have used, is arbitrary.

So if you have a thermionic source TEM

- Your specimen has to be thick enough that sufficient counts are generated for quantification and b will be the main contributor to R.
- Alternatively, you may have to increase the beam size such that d dominates rather than b.

A large beam is needed in that example in order to generate sufficient beam current to get a reasonable X-ray count rate at 100 kV. This is why 200–300 kV FEG TEMs are the best high-resolution analysis instruments

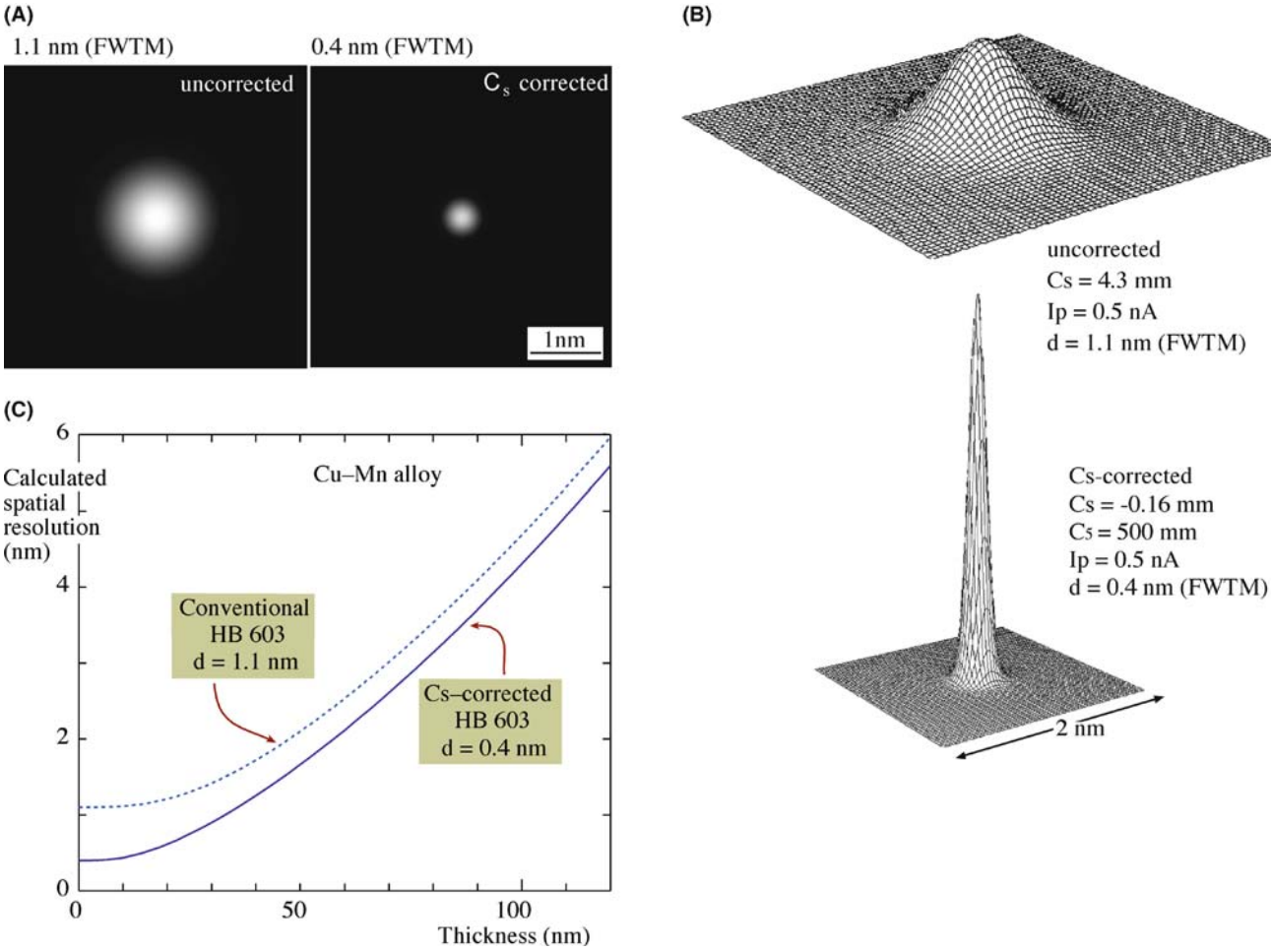


FIGURE 36.5. Simulated probe images for a VG HB-603 300-kV FEG STEM with and without C_s correction; (A) probe dimensions in plan view, (B) 3D intensity distributions. The simulations assume the same probe current (0.5 nA) and C_s correction results in a $\sim 3\times$ decrease in the FWTM probe size from ~1.1 to ~0.4 nm. (C) Calculation of the effect of C_s correction on the spatial resolution in a Cu-Mn alloy as a function of decreasing foil thickness. The resolution at zero foil thickness is improved also by $\sim 3\times$ from just >1 to ~0.4 nm. Compare Figure 36.5B with Figure 2.11 and wonder!

and C_s correction further improves the resolution (go back and compare the segregation-profile widths in Figure 35.11C and D) because you can keep the same probe current while reducing the probe size by a factor of $\sim 3\times$. New X-ray detectors with larger collection angles would also help.

There are some practical factors that can also limit your experimental spatial resolution and the most important is specimen drift. If your specimen or probe drifts for mechanical or electrical reasons, then drift-correction software should be used. If you're planning to carry out analysis at the highest spatial resolution where you're obliged to count for long times to accumulate adequate X-ray intensity, then such software is indispensable.

In summary, the spatial resolution R is a function of both the beam size and the beam spreading. You can get a good estimate of R from equation 36.3. The theories all indicate a $t^{3/2}$ dependence for b, so thin specimens are essential for the best resolution. Intermediate-voltage FEG sources, especially when augmented with C_s correctors, give sufficient beam current in sub-nm probes to generate reasonable counts even from very thin specimens and invariably give the best spatial resolution which, as you can see from the calculations in Figure 36.5, can approach atomic dimensions.

36.3 THICKNESS MEASUREMENT

Given the $t^{3/2}$ dependence of the beam spreading, you can see the importance of knowing t when estimating the spatial resolution. You already know that t is also an essential parameter in correcting for the absorption of characteristic X-rays, as we saw in Section 35.6. Furthermore, you should remember that knowledge of t is important in high-resolution phase contrast imaging and CBED. You'll also see in Chapter 39 that minimizing t is critical to obtaining the best ionization-edge spectra in EELS. So, in almost all TEM techniques, your specimen

has to be as thin as possible to get the best results (although some CBED studies and many in-situ experiments are notable exceptions to this generalization).

So let's take the opportunity here to summarize the methods available for measuring thickness. The methods are many and varied, and a full discussion of the most important techniques will be found in other parts of this book. The first point to consider is, what is t?

THE REAL THICKNESS

The thickness we are interested in is t; this is the thickness through which the beam penetrates. It is not necessarily the same as t_0.

This value of t depends both on the tilt of the specimen γ, and the true thickness at zero tilt, t_0. As shown in Figure 36.6, for a parallel-sided foil

$$t = \frac{t_0}{\cos\,\gamma} \tag{36.5}$$

If your specimen is wedge-shaped, then t and t_0 will vary in an arbitrary fashion depending on the foil shape.

36.3.A TEM Methods

In the TEM you can always make an estimate of your specimen thickness if it is wedge-shaped (and crystalline). By tilting to two-beam conditions for strong dynamical diffraction, the BF and DF images both show thickness fringes, as we saw in Section 24.2. These fringes occur at regions of constant thickness. The intensity in the BF image falls to zero at a thickness of $0.5\xi_g$ at $\mathbf{s} = 0$. Therefore, to determine t, all you have to do is look at the BF image and count the number (n) of dark fringes from the edge of the specimen to the analysis region. At that point $t = (n-0.5)\xi_g$ assuming that the thinnest part at the edge is $< 0.5\xi_g$ thick. (Be very careful with this assumption.) Remember that the value of ξ_g varies with diffracting conditions and so the $\mathbf{g}$ vector has to be specified. You can calculate ξ_g from the expression

$$\xi_g = \frac{\pi\Omega\cos\theta}{\lambda f(\theta)} \tag{36.6}$$

where Ω is the volume of the unit cell, λ is the electron wavelength, and $f(\theta)$ is the atomic scattering amplitude. Remember also that if you're not exactly at $\mathbf{s} = 0$ then the effective extinction distance ξ_{eff} must be used.

A related method relies on the presence of an inclined planar defect adjacent to the analysis region. The projected image of the defect, again under two-beam conditions, will exhibit fringes, which can be used to estimate the local thickness, or the projected width, w, of the defect image using the expression

$$t_0 = w\,\cot\,\delta \tag{36.7}$$

as shown in Figure 36.7 in which δ is the angle between the beam and the plane of the defect. Again, you have to compensate geometrically to measure t rather than t_0 if the foil isn't normal to the beam, and then

$$t = w(\cos\delta - \tan\gamma) \tag{36.8}$$

Of course, neither of these methods is applicable to non-crystalline materials, and it is not always possible to find a suitable inclined defect next to the analysis region in a crystal. Furthermore, two-beam conditions are not recommended for analysis because of the dangers of anomalous X-ray emission (see Section 35.9 on ALCHEMI for both an explanation of, and an exception to, this generalization). More insidious is the fact that oxidation, during or after specimen preparation,

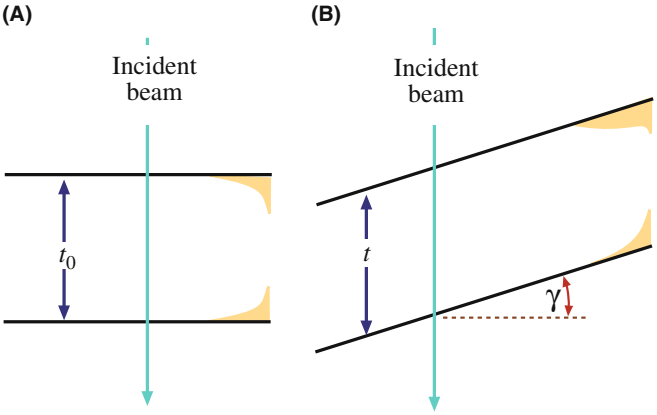


FIGURE 36.6. (A) The specimen thickness t_0 is equal to t, the distance traveled by the beam through a parallel-sided foil at zero tilt. (B) The beam travels a longer distance, t, in a specimen tilted through an angle γ and thus the beam will spread more in a tilted foil.

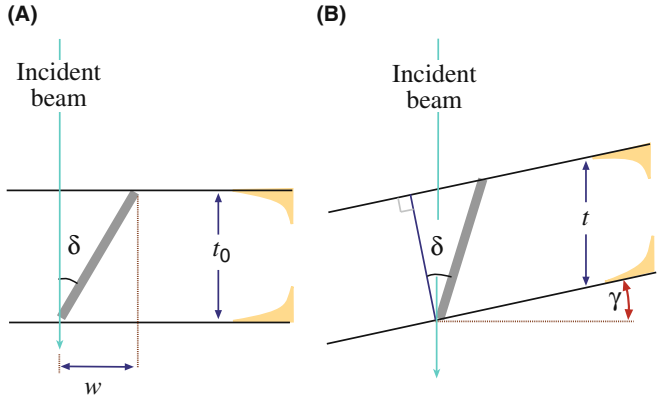


FIGURE 36.7. The parameters required to measure the specimen thickness t_0 from a planar defect (projected width, w), inclined to the incident beam by angle δ. Comparison of (A), a specimen normal to the beam, with (B) a specimen tilted through an angle γ gives some indication of the complexity of determining the appropriate thickness, t, to put into the beam-spreading equation.

means that your crystalline specimen may be coated with an amorphous layer which will not be measured by these diffraction-contrast techniques.

Another method related to the TEM-image contrast involves measurement of the relative transmission of electrons. The intensity on the TEM screen decreases with increasing thickness, all other things being equal. You can use a Faraday cup to calibrate the intensity falling on the screen and from this you can get a crude measure of relative thickness, which can be converted into an absolute measure of t if some absolute method is used for calibration. But you must be careful to make all the intensity measurements on your specimen under the same diffraction conditions and the same incident-beam current but with no objective aperture. The only advantage of this approach is that it is applicable to all materials, both amorphous and crystalline, but it is tedious and not very accurate.

36.3.B Contamination-Spot Separation Method

This method, common in old (S)TEMs, but also commonly used by makers of dirty specimens, relies on the propensity of old instruments or contaminated foils to generate carbon peaks on both top and bottom surfaces of the specimen, at the point of analysis. If you tilt your specimen by a large enough angle (γ), you can see discrete contamination spots (Figure 36.8). Their separation r, at a screen magnification M, is related to t_0 by the following expression

$$t_0 = \frac{r}{M \sin \gamma} \tag{36.9}$$

Matters get a little more complicated if the specimen itself is tilted by an angle ϵ when the contamination is deposited. Then, as in the case of tilted planar defect, you have to be careful to measure the thickness which will determine the beam spreading and, as we've taken pains to point out, this is not t_0 (the thickness at zero tilt) but t

$$t = \frac{r}{M} \frac{\cos \varepsilon}{\sin \gamma} \tag{36.10}$$

Although this method is straightforward, it relies on highly undesirable contamination, which obscures the

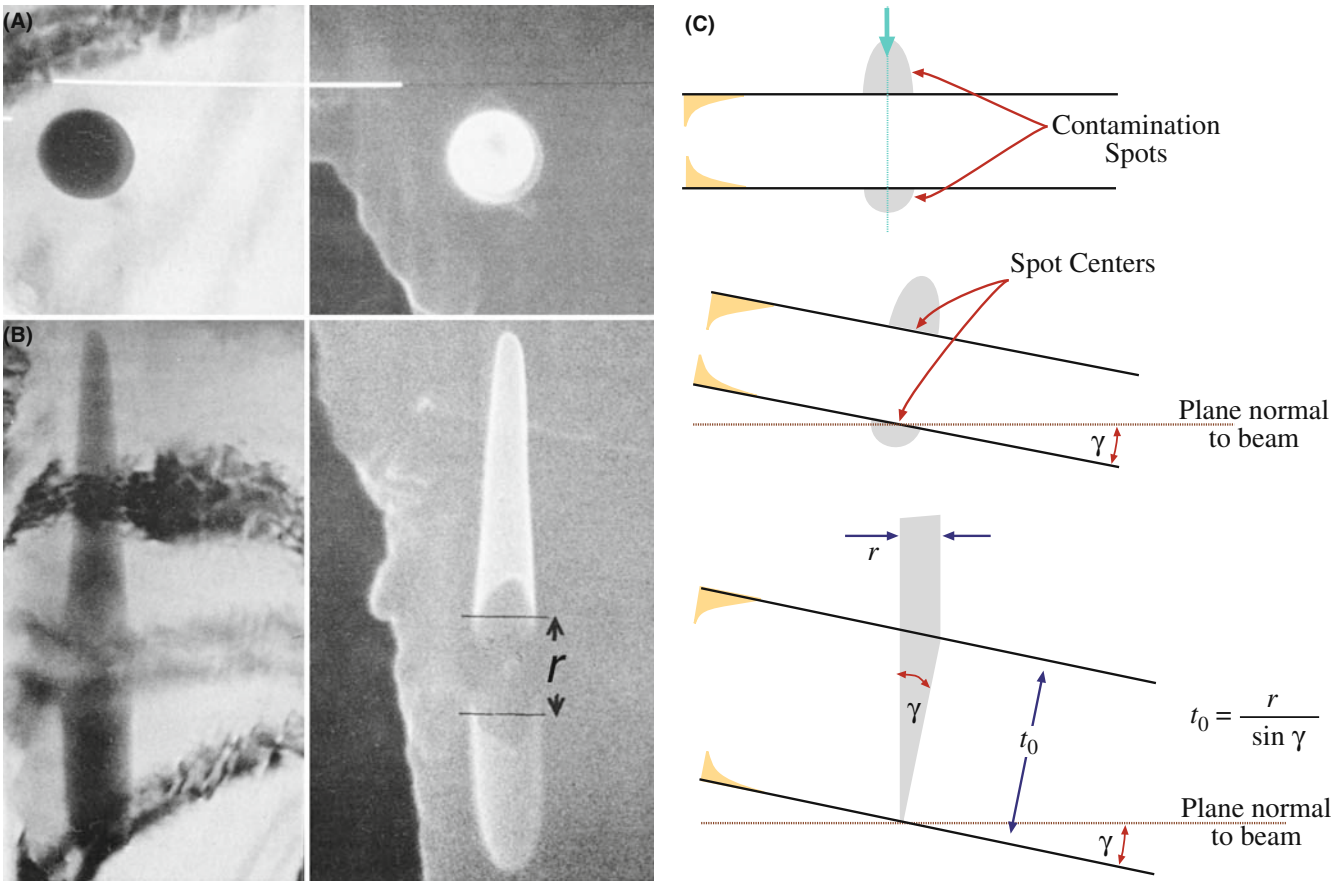


FIGURE 36.8. The contamination-spot separation method for thickness determination; (A) the contamination is deposited on both surfaces of the specimen at zero tilt and the separation (r) is only visible in (B) when the specimen is tilted sufficiently through an angle γ. STEM BF images are on the left and STEM SE images on the right; the SE mode gives the best contrast. (C) Geometrical diagrams of (A) and (B) showing how to determine t_0 from r, the projected separation of the contamination spots.

very area you're looking at. Contamination degrades the spatial resolution and increases the X-ray absorption. In fact, we spend a lot of time and effort trying to minimize contamination, so it would be perverse to propose it as a useful way of determining t. The only redeeming feature is that this method measures t exactly at the analysis point and the shape of the spots can indicate if the beam or the specimen has drifted during analysis. If you find yourself even thinking about using this method, then your TEM should not be used for analysis or you should clean up your specimen-preparation act.

36.3.C Convergent-Beam Diffraction Method

The CBED pattern which is visible on the TEM screen when a convergent beam is focused on the specimen can also be used to determine the thickness of crystalline specimens. In Section 21.2, we described the procedure to extract the thickness from the K-M fringe pattern obtained under two-beam conditions. The CBED pattern must come from a region thicker than $1\xi_g$ or else fringes will not be visible. Also the region of the foil should be relatively flat and undistorted.

Remember that for a totally clean, crystalline specimen, CBED is the way to determine t at specific points in your specimen.

36.3.D Electron Energy-Loss Spectrometry Methods

Thickness information is present in the electron energy-loss spectrum since the intensity of inelastically scattered electrons increases with specimen thickness. In essence, you have to measure the intensity under the zero-loss peak (I_0) and ratio this to the total intensity in the spectrum (I_T). The relative intensities are governed by the mean free path (λ) for energy loss. A parameterization formula for λ (Malis et al. 1988) and other EELS methods, are discussed in detail in Section 39.5.

We can apply the EELS parameterization to any specimen, amorphous or crystalline. But the main advantage is that it is possible to measure the thickness sufficiently quickly that, unlike all the methods described so far, the EELS method can also produce maps of specimen thickness. Given that we have emphasized the value of compositional mapping over point analyses or line profiles, we have to conclude that EELS is best.

EELS FOR *t*

The EELS approach is highly recommended because it is applicable over a wide range of thicknesses and you can produce thickness maps of thin foils.

36.3.E X-ray Spectrometry Method

Since we're talking about X-ray spectrometry, it's good to know that there are X-ray methods which can also determine thickness. We can categorize these approaches, which have been developed to solve the absorption-correction problem (see Section 35.6), into two types: the first is the extrapolation method, which determines the absorption correction by extrapolation of X-ray intensity ratios to zero thickness; the second uses the difference in relative X-ray absorption between two emitted X-ray lines (K and L, or L and M) from the same element. Unfortunately, the extrapolation method is not easily applicable to thin foils where compositions vary locally, since you have to obtain a series of X-ray intensities from different thickness areas (by moving the incident beam or by tilting the specimen). In the intensity-ratio method, the essential requirement of two different X-ray lines from a single element limits the application to specimens which contain elements with $Z > 20$ (Ca).

All of these problems are solved using the ζ-factor approach, as described in detail in 2006 by Watanabe and Williams and in the companion text. The general expression (equation 35.18) for ρt from the ζ-factor analysis can be modified for N different elements in the specimen, thus

$$\rho t = \sum_j^N \frac{\zeta_j I_j A_j}{D_e}, \quad C_A = \frac{\zeta_A I_A A_A}{\sum_j^N \zeta_j I_j A_j}, \cdots$$

$$C_N = \frac{\zeta_N I_N A_N}{\sum_j^N \zeta_j I_j A_j} \tag{36.11}$$

An iterative process is required to solve these equations for both composition and thickness determination. However, the iteration is straightforward and converges rapidly; ~10–15 iterations converge with < 0.001 wt% and 0.01 nm differences in composition and thickness, respectively, which are clearly far more than sufficient tolerance values for termination. Obviously, if X-ray absorption is negligible in a specific material, the initial mass-thickness and compositions are the final values and the iteration is no longer necessary. The essential point here is that in the ζ-factor method, the absorption-corrected compositions can be determined simultaneously with the specimen mass-thickness by *only using X-ray intensity data*.

This method is so quick and versatile that, like the EELS methods, it also permits direct mapping of the thickness at the same time as the composition is being mapped. Therefore, there is nothing to stop you mapping out the spatial resolution at the same time as doing your quantitative mapping, as shown in Figure 36.9. Both the ζ-factor and EELS methods can handle amorphous and crystalline specimens and Ohshima et al. compare the two methods.

In summary, there are many methods for determining t, but none is universally convenient, accurate, and

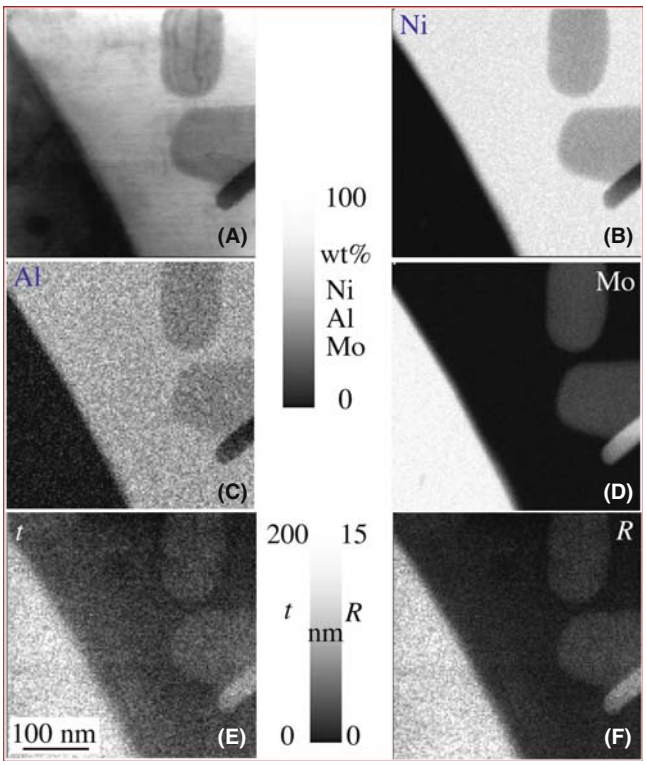


FIGURE 36.9. (A) STEM image and X-ray maps showing the quantitative distribution of (B) Ni, (C) Al, and (D) Mo in precipitates in a Ni-base superalloy. Using the ζ-factor the variation in thickness, t, across the foil can be mapped out (E). Knowing t, the spatial resolution, R, can also be mapped (F). Note the complex interaction of different atomic numbers and the variations in thickness in the resulting variations in R.

applicable. Beware; the various methods also measure different thicknesses, such as only the crystalline thickness, ignoring porosity and/or amorphous surface/oxide films, or the full thickness including porosity and surface films, or just the mass-thickness. Mitchell gives a good case study of how to handle such problems. The EELS and ζ-factor methods both have the possibility of widespread, real-time use and can produce thickness maps, so we recommend these. CBED is very useful for individual point analyses of crystals.

36.4 MINIMUM DETECTION

Minimum detection is a measure of the smallest amount of a particular element that can be detected with a defined statistical certainty. Minimum detection and spatial resolution are intimately related.

A TRUISM

It is a feature of any analysis technique that an improvement in spatial resolution is balanced by a worsening of the detection limit (all other factors being equal).

As the spatial resolution improves, the analyzed volume is smaller and, therefore, the signal intensity is reduced. This reduction in signal intensity means that the acquired spectrum will be noisier and small peaks from trace elements will be less detectable and more easily confused with artifact peaks. Accordingly, in the AEM, the price that is paid for improved spatial resolution is a relatively poor minimum detection. By way of comparison, Figure 36.10 compares the size of the analyzed volume in an EPMA, a TEM/STEM with a thermionic source, and a dedicated STEM with a FEG. The enormous reduction in the beam-specimen interaction volume explains the small signal levels that we obtain in the TEM. However, as we've noted on several occasions, C_s correction gives more current in a smaller probe so it offsets the traditional compromise. But you should now understand why we have spent so much time emphasizing the need to optimize your beam current through use of higher-brightness sources, optimizing the specimen-detector configuration, and so on.

MINIMUM DETECTION

One definition of minimum detection: the minimum mass fraction (MMF) that can be measured in the analysis volume. MMF represents the smallest concentration of an element (e.g., in wt% or ppm).

Alternatively, the minimum detectable mass (MDM) is sometimes used; the MDM describes the smallest amount of material (e.g., in mg or atoms) we can detect.

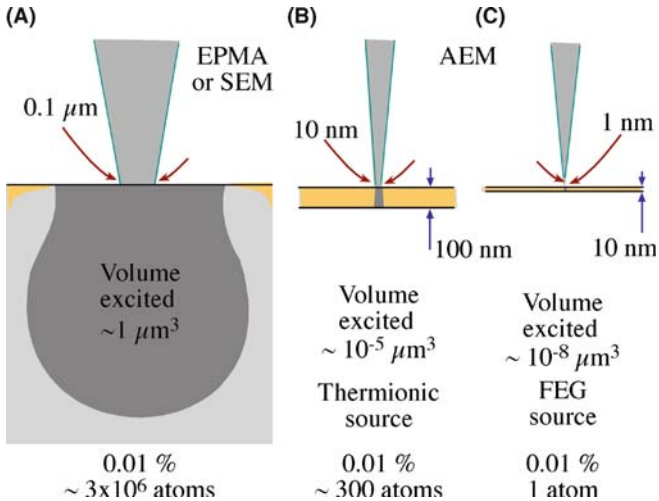


FIGURE 36.10. Comparison of the relative size of the beam-specimen interaction volumes in (A) a SEM/EPMA, (B) a thermionic source AEM, and (C) a FEG-AEM with bulk, thin, and ultra-thin specimens, respectively. The MMF (~0.01%) in each analyzed volume would correspond to ~10^7 atoms, ~300 atoms, and <1 atom, respectively.

We'll use the MMF since materials scientists are more used to thinking of composition in terms of wt% or at.%.

36.4.A Experimental Factors Affecting the MMF

We can relate the MMF to the practical aspects of analysis through the expression of Ziebold

$$\mathrm{MMF} \propto \frac{1}{\sqrt{P(P/B)n\tau}} \tag{36.12}$$

Here P is the X-ray count rate in the characteristic peak (above background) of the element of interest, P/B is the peak-to-background count-rate ratio for that peak (defined here in terms of the same width for both P and B), and τ is the analysis time for each of n analyses.

To increase P you can increase the current in the beam by increasing the probe size and/or choosing a thicker analysis region. To increase P/B you can increase the operating voltage (E_0), which is easy, and decrease instrumental contributions to the background, which is not so easy (Lyman et al.). Improvements in TEM design, such as using a high-brightness, intermediate-voltage source, a C_s corrector if possible, and a larger collection angle for the XEDS will also increase P. To increase P/B, you need a stable instrument with a clean vacuum environment to minimize or eliminate specimen damage and contamination. Improved stage design, to minimize stray electrons and bremsstrahlung radiation, both of which contribute background to the detected spectrum, will also help to increase P/B, as we discussed back in Chapter 33.

Remember that the Fiori definition of P/B is not the one used in Ziebold's equation (36.12). If you actually want to calculate the MMF, go back and check the original references.

The other variables in equation 36.12, are the time of analysis (τ) and how many analyses (n) that you do, which are entirely within your control as operator. Usually both n and τ are a direct function of your patience and the recommended coffee break is usually the maximum time for any one analysis. With computer control of the analysis procedure, however, there should really be no limit to the time available for analysis. Particularly when detection of very small amounts of material is sought, τ should be increased to very long times. As computer control and stage stability improve, acquisitions of several hours or overnight are becoming feasible. Of course, the investment of so much time in a single analysis is dangerous unless you have judiciously selected the analysis region, and you are confident that the time invested will be rewarded with a significant result. Obviously, you should minimize factors that degrade the quality of your analysis with time, such as contamination, beam damage, and specimen drift. Therefore, you should only carry out long analyses if your TEM is clean (preferably UHV) and your specimen is also clean and stable under the beam. Any specimen drift must be corrected by computer control during the analysis, unless your specimen is uniformly thin and homogeneous in composition, in which case why bother analyzing it?

36.4.B Statistical Criterion for the MMF

We can also define the MMF by a purely statistical criterion. We discussed in Section 34.5 that we can be sure a peak is present if the peak intensity is greater than three times the standard deviation of the counts in the background under the peak. From this criterion we can come up with a definition of the detection limit which, when combined with the Cliff-Lorimer equation (assuming Gaussian statistics), gives the MMF (in wt%) of element B in element A as

$$C_B(\mathrm{MMF}) = \frac{3\left(2I_B^b\right)^{1/2}C_A}{k_{AB}\left(I_A - I_A^b\right)} \tag{36.13}$$

where $I^b{}_A$ and $I^b{}_B$ are background intensities for elements A and B; I_A is the raw integrated intensity of peak A (including background); C_A is the concentration of A (in wt%); and $k_{AB}{}^{-1}$ is the reciprocal of the Cliff-Lorimer k-factor. However, if we express the Cliff-Lorimer equation as

$$\frac{C_A}{k_{AB}\left(I_A - I_A^b\right)} = \frac{C_B}{\left(I_B - I_B^b\right)} \tag{36.14}$$

and substitute it into equation 36.13, the MMF is

$$C_B(\mathrm{MMF}) = \frac{3\left(2I_B^b\right)^{1/2}C_B}{I_B - I_B^b} \tag{36.15}$$

Experimentally, low count-rates from thin specimens mean that typical values of MMF are in the range 0.1–1%, which is rather large compared with some other analytical techniques. The best compromise in terms of improving MMF while maintaining X-ray spatial resolution is to use high operating voltages (300–400 kV) and thin specimens to minimize beam broadening. The loss of X-ray intensity, P (or I), a consequence of using thin specimens, can be compensated in part by the higher voltages and/or by using an FEG where a small spot size of 1–2 nm can still be maintained. Obviously C_s-corrected TEMs will help because of their ability to put even more current into the same size probe. Figure 36.11 summarizes the classic

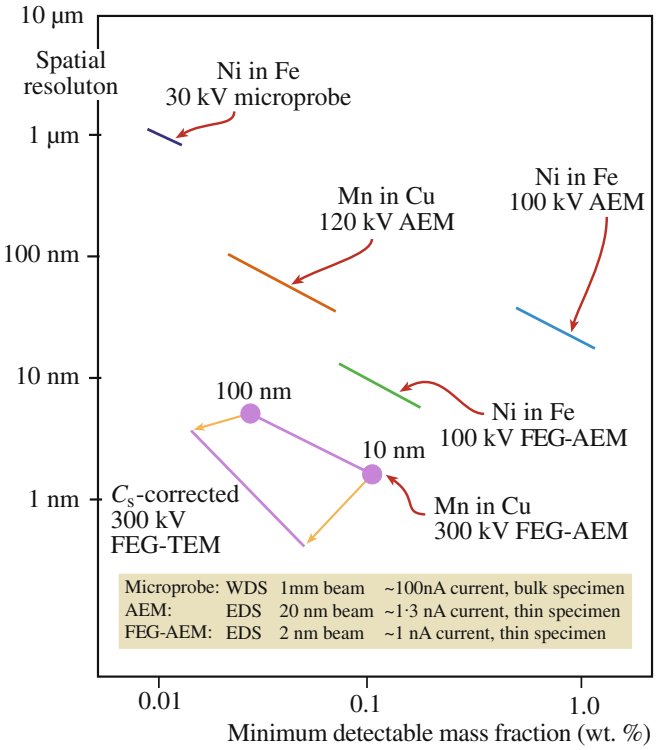


FIGURE 36.11. Calculation of the relationship between MMF and spatial resolution, R, for the EPMA and a range of AEMs. The inverse relationship between the MMF and R is clear, although it is also apparent that the high-brightness sources and high-kV electron beams in the AEM can compensate for the decreased interaction volume in a thin foil. C_s correction results in an enormous improvement in both resolution and sensitivity.

compromise between resolution and detection and how instrumentation improvements have continued to push the limits over the past few decades.

36.4.C Comparison with Other Definitions

The MMF definition is not the only way we can measure detection limits. Currie has noted at least eight definitions in the analytical-chemistry literature. Currie defined three specific limits.

- The decision limit: Do the results of your analysis indicate detection or not (L_C)?
- The detection limit: Can you rely on a specific analysis procedure to lead to detection (L_d)?
- The determination limit: Is a specific analysis procedure precise enough to yield a satisfactory quantification (L_q)?

For I_B counts from element B in a specific peak window and I_B^b in the background it can be shown that

$$L_C = 2.33\sqrt{I_B^b} \tag{36.16}$$

$$L_d = 2.71 + 4.65\sqrt{I_B^b} \tag{36.17}$$

$$L_q = 50\left\{1 + \left(1 + \frac{I_B^b}{12.5}\right)^{\frac{1}{2}}\right\} \tag{36.18}$$

If there are sufficient counts in the background

$$L_d = 4.65\sqrt{I_B^b} \quad \text{when } I_B^b > 69 \tag{36.19}$$

$$L_d = 14.1\sqrt{I_B^b} \quad \text{when } I_B^b > 2500 \tag{36.20}$$

Comparison of these definitions with the statistical criterion in the previous section shows that $C_{MMF} \approx L_d$. So, if you want to quantify an element, not just determine that it is present (L_d), then you need substantially more ($\sim 3\times$) of the element in your specimen. Rather than do the experiment yourself, it is possible to simulate spectra from small amounts of element B in A (or vice versa), using DTSA, as described in the companion text. We recommend that you simulate your analysis before embarking on a time-consuming experiment, which may be futile because the amount of the element you are seeking is below the MMF.

36.4.D Minimum-Detectable Mass

The MMF values of fraction of a percent may seem poor compared with other analytical techniques which report ppm or even ppb detection limits. However, it's a different matter if you calculate what the MMF translates to in terms of the minimum detectable mass (MDM).

Using data for the MMF of Cr in a 304L stainless steel measured in a VG HB-501 AEM with an FEG, Lyman and Michael obtained an MMF of 0.069 wt% Cr in a 164 nm foil with a spatial resolution of 44 nm and a 200 s counting time. The electron beam size was 2 nm (FWTM) with a beam current of 1.7 nA. In this analysis, an estimated 2×10^4 atoms were detected. The MDM was less than 10^{-19} g. If the counting time is increased by a factor of 10 and if the operating voltage is increased to 300 kV, the spatial resolution would improve to ~15 nm and the MMF would improve to ~0.01 wt%. Thus about 300 atoms could be detected. For a foil thickness of 16 nm (1/10th the above measured thickness), the MMF would degrade to ~0.03 wt%. However, the spatial resolution would improve to about 2 nm. For this case, about 20 atoms would be detected corresponding to less than 10^{-22} g, which is an amazing figure by any standard. Experimental verification of this was reported in 1999 by Watanabe and Williams: 2–5 atoms of Mn were detected in a 10-nm thick Cu-Mn alloy film. With the advent of C_s-correction and improved computer data analysis routines, single-atom

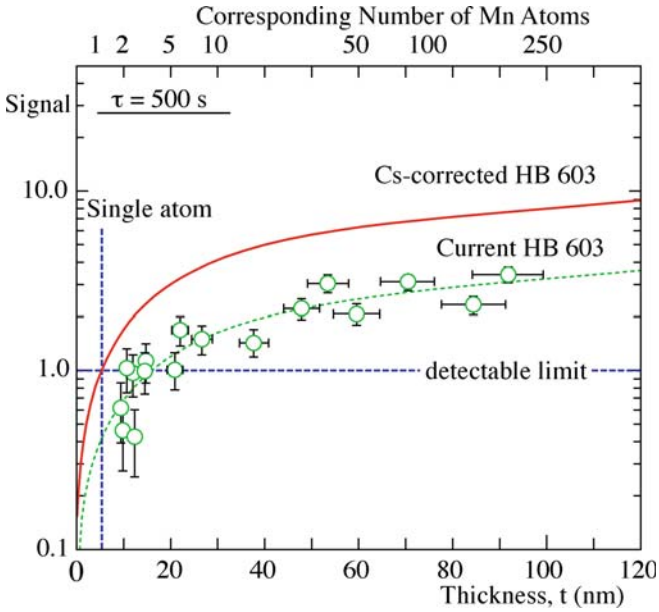


FIGURE 36.12. Calculation of the number of Mn atoms detectable in a Cu-0.1 wt% Mn foil as a function of foil thickness (dotted green line) based on experimental Mn K_α counts (green circles) in a 300-keV FEG STEM. When the Mn K_α signal is undetectable the ordinate axis value = 1 and this occurs when there are between 2 and 5 Mn atoms in the analysis volume (see top axis) which can be calculated knowing the foil thickness and bulk chemistry. A C_s corrector (red line) is calculated to improve the MDM from several atoms to ~1 atom right at the detection limit.

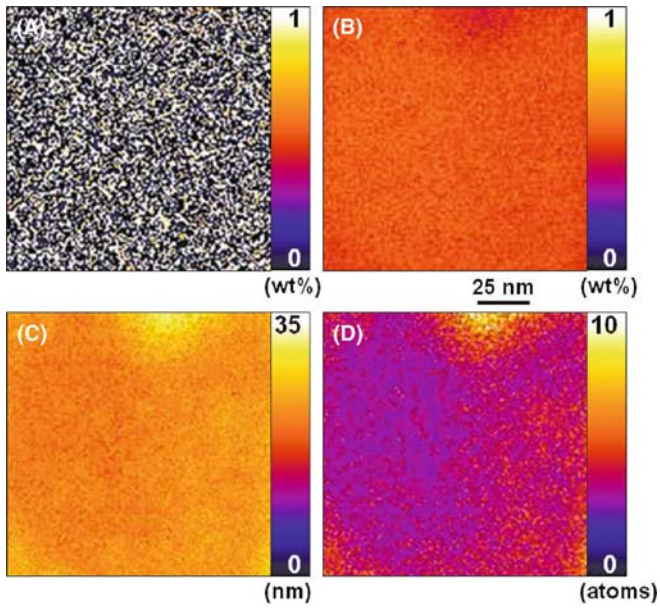


FIGURE 36.13. A series of quantitative maps obtained from a homogeneous Cu-0.5 wt% Mn foil in a C_s-corrected, 300-kV, UHV, FEG STEM. (A) Mn composition map from the original spectrum image, (B) Mn composition map from the spectrum image enhanced by MSA noise reduction, (C) thickness map, and (D) map of a number of Mn atoms. Note the look-up tables with each map. In (D) the dominating purple color corresponds to ~ 2–3 atoms. These maps were quantified by the ζ-factor method.

detection is now a distinct possibility and Figure 36.12 shows calculated improvements in detection limits for Mn atoms in solution in Cu in a C_s-corrected 300-kV FEG TEM. Figure 36.13 shows how mapping of a homogeneous solid solution can detect a few atoms at each pixel. This last figure summarizes just about everything we have discussed for AEM quantification and C_s-corrected mapping: (a) ζ-factor quantification (the image is still noisy), (b) MSA data manipulation (the image is much less noisy), (c) the importance of good thin foils (specimen thickness is very uniform and < 20 nm in most areas), and (d) MDM close to 1–2 atoms is attainable (even when mapping). Just to remind you how good this is, go back and take a look at Figure 36.10. Consider that in the EPMA with a ~1 μm^3 excitation volume and a 0.01 wt% MMF, ~3 million atoms are detected in the analysis volume. So XEDS in the best C_s-corrected, intermediate-voltage, UHV, FEG TEM has an MDM detection limit that is *several million times better* than an EPMA.

MDM

In AEM it is useful to define the MDM as the minimum number of atoms detectable in the analyzed volume.

While the best XEDS-TEM combinations are approaching atomic-level detection and sub-nm spatial resolution, it is not yet possible to detect single atoms within individual atomic columns as is achievable in EELS in similar, C_s-corrected, intermediate-voltage FEG TEMs (see Chapter 39) so there is still room for improvement, e.g., through larger collection angles and more sophisticated data processing.

CHAPTER SUMMARY

Optimizing spatial resolution and minimum detection in the same experiment is always a compromise. You must decide which of the two criteria is more important for the result you're seeking

- To get the best spatial resolution, operate with the thinnest foils and the highest energy electron beam. Use an FEG if possible and a C_s corrector if you're lucky.

- To measure the specimen thickness use the ζ-factor method or the parameterized EELS approach. If neither is possible, use CBED for a crystalline foil. If you're reduced to contamination spots, find a better TEM or make cleaner specimens.
- To get the best MMF, use the brightest electron source, the largest possible beam, and thickest specimen, and count for as long as possible with the shortest time constant.
- If you want the best resolution *and* MMF, a C_s-corrected, intermediate-voltage, UHV, FEG TEM is essential, along with a clean specimen and computer-controlled drift correction; patience is also equally essential.

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URLs

1) http://montecarlomodeling.mcgill.ca/software/winxray/contacts.html

SELF-ASSESSMENT QUESTIONS

Q36.1 Why do we spend so much time discussing the spatial resolution of XEDS?
Q36.2 Define R, b, and d.
Q36.3 Why are there so many variable definitions of the spatial resolution in the literature?
Q36.4 What's the most important factor controlling the spatial resolution?
Q36.5 Why do you sometimes have little control over this specific factor?
Q36.6 Why is it challenging to measure the spatial resolution experimentally?
Q36.7 List the various methods of determining your specimen thickness and under each method list its most important advantage and its greatest disadvantage.
Q36.8 What's the most important factor in controlling the detection limits in any experiment?
Q36.9 What's the difference between the MMF and the MDM?
Q36.10 Why is a high peak (P) intensity more important than a high P/B ratio when trying to improve the detection limit?
Q36.11 Why do we choose 90% of the exit electron distribution to define the spatial resolution? Why not choose 100%? Why not choose 50% which is commonly used when calculating probe-limited image resolution?
Q36.12 Why is an interphase interface often chosen as the ideal feature across which to measure the experimental spatial resolution of analysis?
Q36.13 Can you suggest other specimens that might offer similar advantages?
Q36.14 Why is an FEG the best electron source to use if you want the highest spatial resolution?
Q36.15 Is an FEG necessarily the best source to use if you want to obtain the highest analytical sensitivity? If not, why not?
Q36.16 What improvements might be gained in both spatial resolution and analytical sensitivity from using an aberration-corrected electron probe?
Q36.17 Why isn't it a good idea to rely on the contamination-spot method to estimate your specimen thickness?
Q36.18 Define the decision limit, the detection limit, and the determination limit.
Q36.19 If a 300-keV FEG AEM can detect 0.01 wt% of an element in a foil ~5 nm thick, estimate how many atoms this represents in the analyzed volume. State any assumptions; be brief.

TEXT-SPECIFIC QUESTIONS

T36.1 Why does a higher voltage give higher spatial resolution in a thin specimen in the AEM but lower spatial resolution in a thick, EPMA specimen as shown in Figure 36.1?
T36.2 Figure 36.1A does not take into account electron-diffraction effects; why does this not seriously compromise our estimation of spatial resolution?
T36.3 The situation in Figure 36.3 assumes that all the incident beam is confined on the entrance surface of the specimen in a circular probe of diameter b. List several factors that can make this assumption unreasonable. (Hint: go back and look at Figure 33.5.)
T36.4 Look at Figure 36.4. Is there any advantage to be gained by moving the interaction cones closer together (i.e., taking more point analyses in the profile)? (Hint: go and look at equation 36.3.)
T36.5 Estimate, from Figure 36.4, the maximum angle at which the interface could be tilted before the spatial resolution profile is degraded beyond the usual experimental limits.
T36.6 Tilting the specimen (see Figure 36.6) degrades the spatial resolution. What other disadvantages occur when the specimen is tilted, and under what analytical conditions is there an advantage to tilting the specimen?
T36.7 To a first approximation, calculate what it would take to detect a single atom of element B in the analyzed volume of element A such as in Figure 36.10. State any assumptions.
T36.8 If you compare the left and right diagrams in Figure 36.10, it is clear that if a FEG AEM is to exhibit comparable analytical performance to an EPMA, it has to be millions of times more sensitive, since the analyzed volume is smaller by such a factor. Indicate what technical differences exist between the two techniques such that this extraordinary improvement in signal detection and generation actually occurs.
T36.9 Explain clearly why the trend in Figure 36.11 is common to all microanalysis techniques, i.e., improving spatial resolution invariably results in degrading the minimum detection limit.
T36.10 Which method(s) would you use to determine the thickness of (a) SiO_2 glass, (b) SiO_2 crystal, (c) Cu-4% Al? Justify your choice of method in each case.
T36.11 Use DTSA to determine the minimum amount of P impurity detectable in a spectrum from otherwise pure Fe. Your specimen is 100 nm thick, and you are operating at 200 kV with a take-off angle of 20°. Courtesy M. Watanabe
T36.12 Using the results of the previous question (MMF of P in Fe), calculate a number of detectable P atoms in Fe (MDM) for a LaB_6-AEM (incident beam size, $d = 10$ nm) and a FEG-AEM ($d = 2$ nm). For the density and the atomic weight to calculate the beam broadening, use the values for Fe, since the detection limits of P are low enough to ignore any effects of this element (if you have answered correctly). Courtesy M. Watanabe