The XEDS–TEM Interface

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CHAPTER PREVIEW

In principle, all you have to do to create an AEM is to hang an XEDS detector on the side of a TEM. However, in practice it isn't always that simple because the TEM is designed primarily as an imaging tool, and microanalysis requires different design criteria. The AEM illumination system and specimen stage are rich sources of radiation, not all of it by any means coming from the area of interest in your specimen. So you have to take precautions to ensure that the X-ray spectrum you record comes from the area you chose and can ultimately be converted to quantitative elemental information. You therefore need to understand the problems associated with the XEDS–TEM interface and find ways to maximize the useful data. We describe several tests you should perform to ensure that the XEDS–TEM interface is optimized.

D. B. Williams et al., *Transmission Electron Microscopy*

The XEDS–TEM Interface

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33.1. THE REQUIREMENTS

The interfacing of the XEDS to the TEM is not something over which you have too much control. It has already been carried out by the manufacturers, so you purchase an AEM system of TEM and XEDS. Often you won't be able to change anything about the system, but nevertheless you should be aware of the important factors that characterize the interface between the XEDS and the TEM column and what effect these factors will have on your microanalysis experiments. Knowing these factors may help you to select the best AEM to use.

The stage of a TEM is a harsh environment. An intense beam of high-energy electrons bombards a specimen which interacts with and scatters the electrons. The specimen *and any other part of the microscope* that is hit by electrons emit both characteristic and bremsstrahlung X-rays which have energies up to that of the electron beam. X-rays of such energy can penetrate long distances into material and fluoresce characteristic X-rays from anything that they hit. Ideally, the XEDS should only "see" the X-rays from the beam–specimen interaction volume. However, as shown in Figure 33.1, it is not possible to prevent radiation from the microscope stage and other areas of the specimen from entering the detector. The X-rays from the microscope itself we will call "system X-rays." All the X-rays arising from regions of the specimen other than that chosen for analysis, we term "spurious X-rays." Your job, as an analyst, is to learn how to identify the presence of these undesirable X-rays and to minimize their effect on your microanalysis.

33.2. THE COLLIMATOR

As you can see from Figure 33.1, the XEDS has a collimator in front of the detector crystal. This collimator is the front line of defense against the entry of undesired radiation from the stage region of the microscope.

The collimator also defines the (desired) collection angle of the detector (see below) and the average take-off angle of X-rays entering the detector.

Ideally, the collimator should be constructed of a high-Z material such as W, Ta, or Pb, coated externally and internally with a low-Z material such as Al, C, or Be. The low-Z coating will minimize the production of X-rays from any backscattered electrons that happen to spiral into the collimator and the high-Z material will absorb any high-energy bremsstrahlung radiation. The inside of the collimator should also have baffles to prevent any backscattered electrons from generating X-rays that then penetrate the detector. Such a design is shown in Figure 33.2 (Nicholson *et al.* 1982), and aspects of this design are available in some commercial systems. They are strongly recommended.

33.2.A. Collection Angle

The detector collection angle (Ω) is the solid angle subtended at the analysis point on the specimen by the active area of the front face of the detector. The collection angle is shown in Figure 33.1 and is defined as

$$\Omega = \frac{A \cos \delta}{S^2} \qquad [33.1]$$

where A is the active area of the detector (usually 30 mm^2), S is the distance from the analysis point to the detector face, and δ is the angle between the normal to the detector face and a line from the detector to the specimen. In many XEDS systems, the detector crystal is tilted toward the specimen so $\delta = 0$; then $\Omega = A/S^2$. It is clear that to maximize Ω the detector should be placed as close to the specimen as possible.

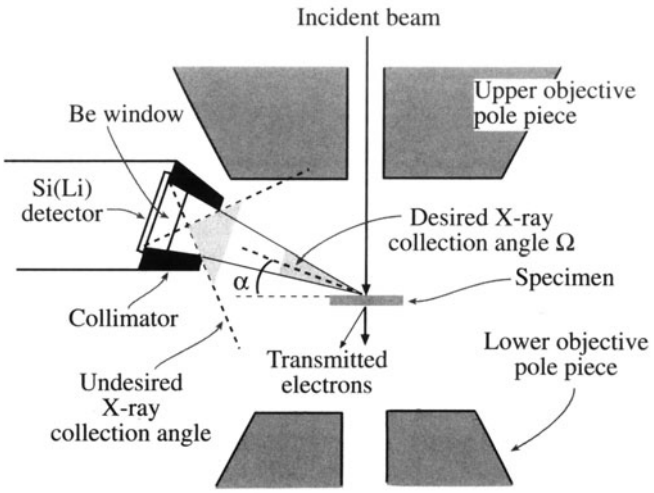


Figure 33.1. The interface between the XEDS and the AEM stage, showing how the detector can "see" undesired X-rays from regions other than the beam–specimen interaction volume. The desired collection angle Ω and take-off angle α are also shown.

The value of Ω is the most important parameter in determining the quality of your X-ray microanalysis.

In most cases, particularly with thermionic-source instruments, it is the low X-ray counts that limit the accuracy of the experiment. Now in commercial AEMs, S varies from about 10–30 mm, and as a result values of Ω lie in the range from 0.3 down to 0.03 sr. ATW detectors invariably have lower Ω values than Be window or windowless detectors, because the polymer window has to be supported on a grid (usually etched Si) which reduces the collection angle by ~20%. So, at best, Ω is a small fraction of the total solid angle of characteristic X-ray generation which is, of course, 4π sr. These values of Ω are calculated from the dimensions of the stage and the collimator. Unfortunately, there is no way you can measure this critical parameter directly, although you can compare X-ray count rates between different detector systems using a standard specimen, such as our thin Cr film, and a known beam current. A figure of merit for this parameter is given in terms of the X-ray counts per second detected from the standard, when a given beam current is used with a given detector collection angle (cps/nA/sr). Typically, for an AEM with a nominal Ω of 0.13 sr and a beam energy of 300 keV the figure of merit is >8000. For an energy of 100 keV, it is about 13,000 (Zemyan and Williams 1994). The increase at lower keV is due to the increased ionization cross section.

The magnitude of Ω is limited because the upper polepiece of the objective lens gets in the way of the collimator, thus limiting S. To avoid this limitation we could increase the polepiece gap, but doing so would lower the maximum beam current and degrade the image resolution, both of which are highly undesirable. So a compromise has to be made in the design of the stage of the AEM to ensure both adequate current in the beam and the best possible collection angle. If we move the detector too close to the specimen, it will eventually suffer direct bombardment by backscattered electrons. The other alternative we have, looking at equation 33.1, is to increase A. However, increasing the detector area results in a small decrease in energy resolution. As we noted already, there are certainly situations where increased count rate is to be preferred at the expense of a small decrease in resolution; while 50-mm^2 detectors are available, they are rarely used.

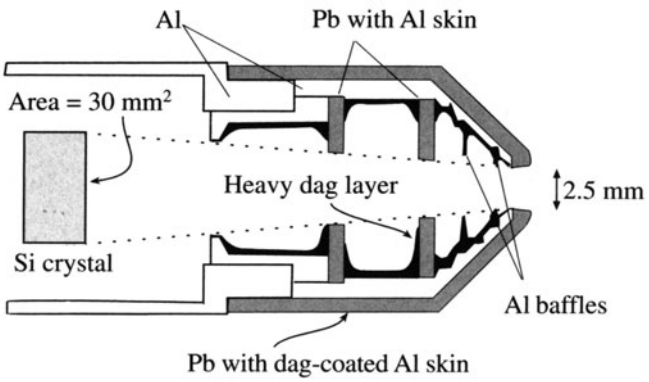


Figure 33.2. Combination high-Z (Pb) and low-Z (Al/carbon paint) collimator design to prevent high-energy bremsstrahlung from penetrating the collimator walls. Baffles are incorporated to minimize BSE entry into the detector.

33.2.B. Take-Off Angle

The take-off angle α is the angle between the specimen surface (at 0° tilt) and a line to the center of the detector, as shown in Figure 33.1. Sometimes, it is also defined as the angle between the transmitted beam and the line to the detector, which is simply (90° + α). Traditionally in the EPMA, the value of α is kept high to minimize the absorption of X-rays as they travel through bulk specimens. Unfortunately, if we maximize α the price we pay is lowering Ω. Because the detector then has to be positioned above the upper objective polepiece, it will "look" through a hole in the polepiece. Therefore, it will be much further from the specimen. In the EPMA low Ω is not a problem because there are always sufficient X-rays from a bulk specimen, but in the AEM the highest possible Ω is essential, as we've already emphasized.

We would like to optimize the take-off angle and maximize the count rate.

In AEMs where the detector "looks" through the objective polepiece giving a high take-off angle but a low Ω, the poor X-ray count rate makes quantitative analysis much more time-consuming. Keeping the detector below the polepiece restricts α to a maximum value of about 20°. In most cases you will find that such a small value of α is not a problem, because one of the major advantages of thin-specimen AEM compared to bulk EPMA is that absorption can usually be neglected. However, if absorption is a problem in your specimen then you can reduce the path length of X-rays traveling through your specimen by tilting it toward the detector, thus increasing α (see Section 35.5). Tilting may increase spurious effects, which we'll discuss later, and also generally lowers the P/B (peak-to-background) ratio in the spectrum; so tilting is always a compromise.

33.2.C. Orientation of the Detector to the Specimen

(a) Is the detector pointing on axis? The detector is inserted into a position where it is almost touching the objective polepiece, and you hope that it is "looking" at the region of your specimen that is on the optic axis when the specimen is eucentric and at zero tilt. We have to assume that the XEDS and the TEM manufacturers have collaborated closely in the design of the collimator and stage. To find out if your system is well aligned, you can make a low-magnification X-ray map from a homogeneous specimen such as a thin Cr film (Nicholson and Craven 1993). If the detector is not pointing on axis, the map will show an asymmetric intensity distribution. Alternatively, if you cannot map at low enough magnification, simply see how the Cr K_α intensity varies from area to area on the foil with the specimen traverses set at zero and different areas selected using the beam deflectors. The maximum intensity should be recorded in the middle grid square and for some distance around. It is also instructive to do the same test with the specimen moved up or down away from the eucentric plane using the *z*-control. Again, the maximum intensity should be recorded at the eucentric plane. If the intensity is asymmetric, then the detector or the collimator is not well aligned and some of your precious X-ray intensity is being shadowed from the detector, probably by the collimator; so you need to consult the manufacturer.

(b) Where is the detector with respect to the image? When you look at a TEM or STEM image to position the beam on an area for microanalysis, it is best if the detector is "looking" toward the thin region of the specimen rather than toward the thicker region, as shown in Figure 33.3A. This position minimizes the X-ray path length through the specimen and helps to ensure that any absorption is minimized. In TEM mode, the detector orientation with respect to the BF image on the screen will vary with magnification if the BF image rotates when changing magnification. In a STEM BF image there is no rotation, so the relative orientation of the detector to the image will be fixed. It is simple to find this orientation if the detector axis (*y*-axis) is normal to a principal traverse axis (*x*) of the stage. Under these circumstances, if you push in the end of the holder while the specimen is in the column, the image will move in the +*x*-direction. Then you can determine by simple geometry the direction (+*y* or –*y*) along which the detector is looking with respect to that +*x*-direction in the TEM image. In STEM, the image is sometimes rotated 180° with respect to

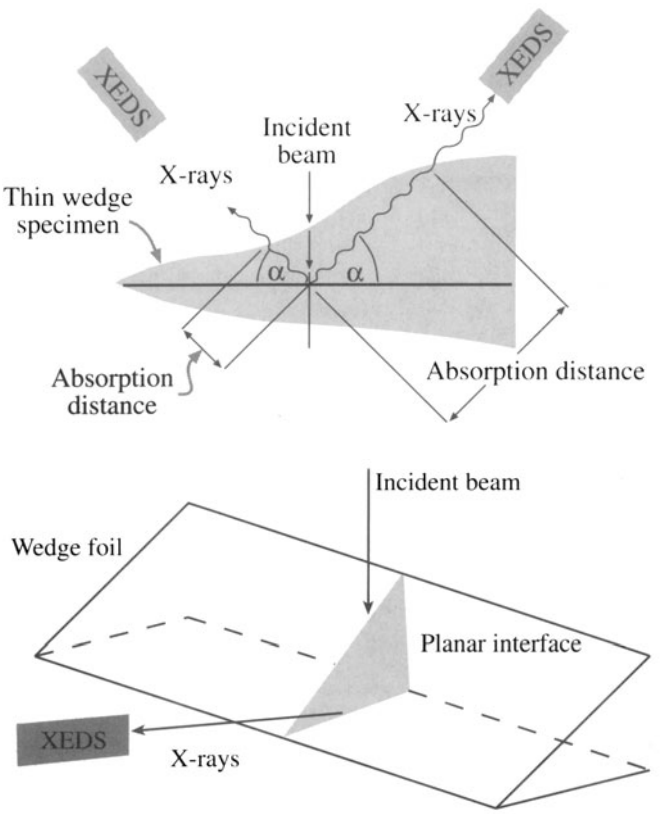


Figure 33.3. (A) The position of the XEDS detector relative to a wedge-shaped thin foil results in different X-ray path lengths. The shortest path length with the detector "looking" at the thinnest region of the foil is best. (B) The preferred orientation of the XEDS detector when analyzing a planar defect: the interface plane is parallel to the detector axis and the incident beam direction.

the TEM image, so you have to take this into account (just check TEM and STEM images of a recognizable area of your specimen).

If you're doing microanalysis across a planar interface, which is a common AEM application, then you will also need to orient your specimen such that the interface is parallel to the detector axis and the beam. A tilt-rotation holder would be ideal for this, but a low-background version is not available, so you may need to reposition your foil manually until the interface is in the right orientation (see Figure 33.3B).

> The XEDS detector must be "looking" at the thin edge of your specimen and aligned with any planar interface you are studying.

33.3. PROTECTING THE DETECTOR FROM INTENSE RADIATION

If you are not careful, the XEDS electronics can be temporarily saturated if high doses of electrons or X-rays hit the detector. The detector itself may also be damaged, particularly in intermediate voltage microscopes. These situations usually occur when you place bulk material under the beam. This can happen if you leave the objective diaphragm inserted, if you go to low magnification and expose the bulk regions of a disk to the beam, or if you are traversing around a thin specimen supported on a grid and a grid bar is hit by the beam. To avoid these problems there are various kinds of shutter systems built into XEDS detectors which automatically protect the detector crystal if the instrument is switched to low magnification or if the pulse processor detects too high a flux of radiation.

> To avoid reliance on the automatic system, it is best to have the shutter closed until you have decided which area you want to analyze, and it is thin enough that the generated X-ray flux doesn't saturate the detector.

If you don't have a shutter, then you can physically retract the detector, which lowers Ω (if it is retracted along a line of sight to the specimen) or removes the detector from out of view of the specimen. The drawback to this approach is that constant retraction and reinsertion of the detector may cause undue wear on the sliding "O"-ring seal and also you may reposition your detector slightly differently each time, unless the system is designed so that you can push the detector up to a fixed stop, thus insuring a constant collection and take-off angle. A shutter is highly recommended!

33.4. SYSTEM X-RAYS AND SPURIOUS X-RAYS

In an ideal AEM, all spectra would be characteristic only of the chosen region of your specimen. The analysis of bulk specimens in the EPMA approaches this ideal, but in the AEM several factors combine to introduce false information which can introduce serious errors into both qualitative and quantitative microanalysis unless you are aware of the dangers and take appropriate precautions to identify and minimize the problems. The factors unique to the AEM that are responsible for these problems are:

- The high accelerating voltages which generate intense doses of stray X-rays and electrons in the illumination system.
- The scattering of high-energy electrons and X-rays by the thin specimen in the limited confines of the TEM stage.

Most AEMs are now designed to minimize some of these problems. Nevertheless, when identification and quantification of small (<~5%) elemental amounts are required, you have to be wary of system and spurious X-rays, which we will now discuss in some detail. These artifacts, which are in addition to the XEDS system artifacts, can be responsible for large errors in quantification or, in the extreme, may make your microanalysis impossible.

33.4.A. Pre-Specimen Effects

Ideally, the electron beam should be the sole source of radiation incident on your specimen, and the X-rays then originate in a well-defined interaction volume. In practice, the illumination system can produce high-energy bremsstrahlung X-rays and uncollimated electrons, which may strike the specimen anywhere, producing spurious X-rays indistinguishable from those generated in the region of interest. In inhomogeneous specimens (which are usually just the kind that we want to analyze) the presence of significant amounts of spurious X-rays means that the quantification process could give the wrong answer. There are several review papers (e.g., Williams and Goldstein 1981, Allard and Blake 1982) which describe in detail how to identify and minimize these artifacts from the illumination system, so we will just describe the precautions necessary to ensure that the AEM is operating acceptably. Since these artifacts are primarily a result of the high-energy electrons interacting with column components such as diaphragms and polepieces, you must take extra care when using intermediate-voltage instruments.

The standard way to detect stray radiation from the illumination system is to position the focused electron beam down a hole in your specimen and see if you can detect an X-ray spectrum characteristic of the specimen.

> Such a spectrum, sometimes termed a "hole count," is *invariably* obtained in all AEMs if you count for long enough.

If the hole count contains more than a few percent of the characteristic intensity obtained from a thin area of your specimen under similar conditions, then we say the illumination system is not "clean."

You can easily determine whether stray electrons or X-rays are the problem, as illustrated in Figure 33.4 (Goldstein and Williams 1978). Almost invariably, the problem is caused by stray X-rays penetrating the C2 diaphragm.

> The solution to this problem is to use very thick (several mm) platinum diaphragms which have a "top-hat" shape and a slightly tapered bore to maintain good electron collimation.

These diaphragms should be a standard fixture in all AEMs (check with your manufacturer), but they are expensive, and you cannot flame-clean them in the usual way. When the thick diaphragms do contaminate, you should discard them, otherwise the contamination itself will become a source of X-rays and also deviate beam electrons by charging. Some AEMs incorporate a small diaphragm just above the upper objective lens to shadow the thicker outer regions of the specimen from stray X-rays. Other AEMs use virtual beam-defining apertures, keeping the diaphragm itself well away from the specimen, and this is ideal. Another good way to minimize the effects of the bremsstrahlung is to use an evaporated film or window-polished flake on a Be grid, rather than a self-supporting disk. If the specimen is thinner than the path length for fluorescence, spurious X-rays will not be generated. Of course, such thin specimens may not be possible to prepare, or may take a great deal of effort, while self-supporting disks are relatively easy and quick to produce; so this isn't a popular suggestion with graduate students.

For a quantitative, reproducible measure of the hole count, you should use a uniform thin specimen such as the Cr film we have described. This film should be supported on a bulk material that has a low-energy (<~3 keV) L line and a high-energy (>~15 keV) K line. A thick molybdenum or gold washer is ideal. Any high-energy bremsstrahlung X-rays penetrating through the C2 diaphragm will strongly fluoresce the Mo K or Au L line, while stray electrons will excite the Mo L or Au M lines preferentially.

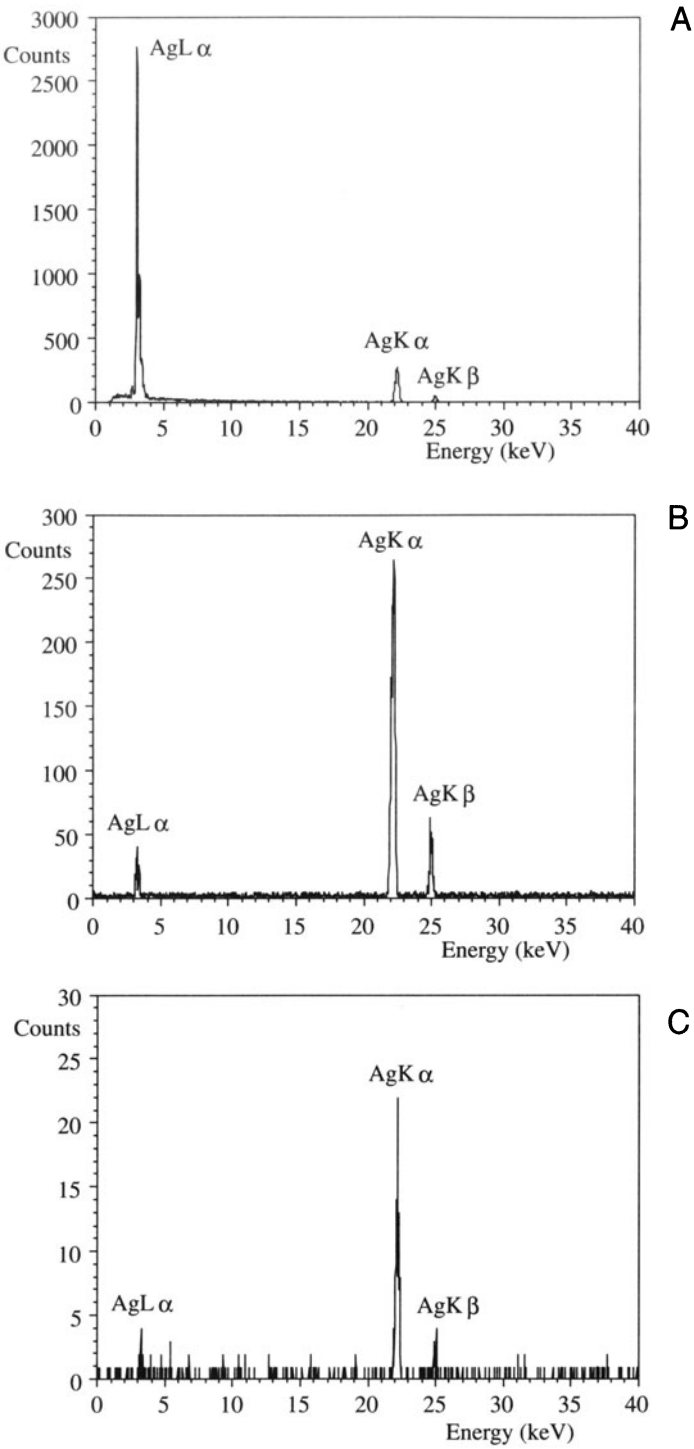
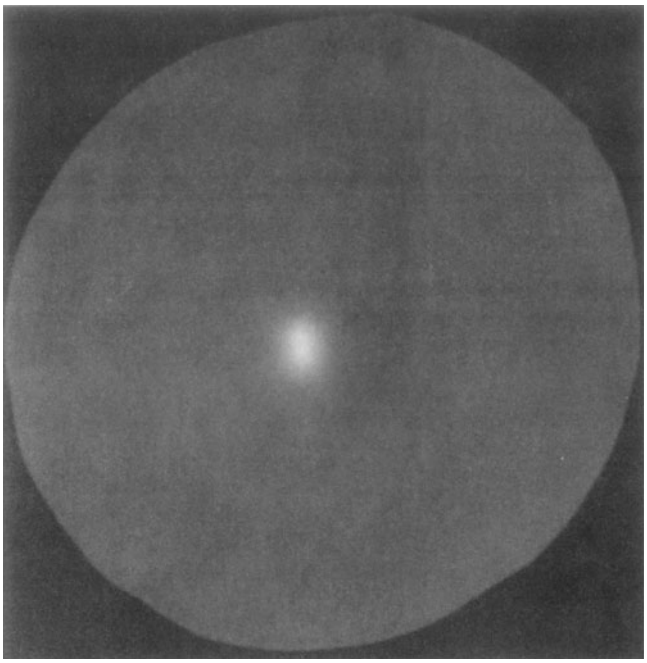


Figure 33.4. The "hole count." (A) A Ag self-supporting disk produces an electron-characteristic (high L/K ratio) spectrum when struck by the primary beam. (B) Without a thick C2 diaphragm, an intense Ag spectrum is also detected when the beam is placed down a hole in the specimen. This spectrum has a low L/K ratio, which indicates high-energy bremsstrahlung fluorescence of the K lines. Approximately 50% of the K_α line in (A) was due to these spurious X-rays. (C) Use of a thick Pt C2 diaphragm reduces the intensity of the hole count substantially. The K_α intensity in (C) is about 30 times less than in (B). (Note the scale change.)

A



B

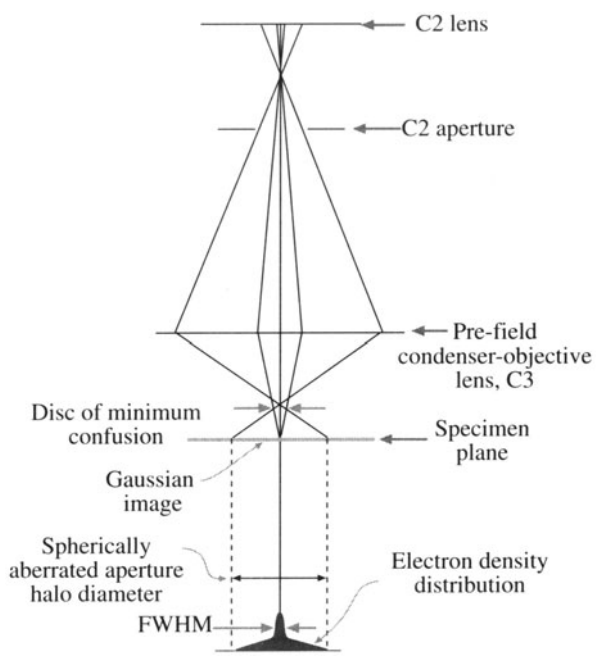


Figure 33.5. (A) The shadow of the diaphragm defines the extent of the halo which excites X-rays remote from the chosen microanalysis region. (B) Ray diagram showing how the STEM probe obtained with a large C2 aperture has a broad halo of electrons surrounding the intense Gaussian central portion. Such a halo is the major source of uncollimated electrons and arises due to spherical aberration in the C3 lens.

As a rule of thumb, the ratio of Mo K_α or Au L_α intensity detected (when the beam is down the hole) to the Cr K_α intensity obtained with the beam on the specimen should be less than 1%.

Under these conditions the remaining stray X-rays will not influence the accuracy of quantification, or introduce detectable peaks from elements not in the analysis region. For more detail on this test see Lyman and Ackland (1991). If you don't want to go to the trouble of this test, then the least you should do is measure the in-hole spectrum from your specimen and subtract it from your experimental spectrum.

In addition to stray X-rays, it is possible that all the electrons are not confined to the beam. If your microscope has a non-beam-defining spray aperture below the C2 aperture, it will eliminate such stray electrons without generating unwanted X-rays. Then the main source of poorly collimated electrons is usually the "tail" of electrons around the non-Gaussian-shaped probe that arises from spherical aberration in the C3 lens, as shown in Figure 33.5 from Cliff and Kenway (1982). The best way to minimize this effect is to image the beam on the TEM screen under the conditions that you will use for microanalysis and select the best C2 aperture, as we discussed earlier in Chapter 6. It is a simple test to move your probe closer and closer to the edge of your specimen and see when you start generating X-rays. Do this with different-size, top-hat C2 diaphragms.

In summary:

- Always operate with clean, top-hat C2 diaphragms.
- Use very thin flake specimens, if possible.
- Always image the electron beam on the TEM screen prior to microanalysis, to ensure that it is well collimated by the C2 aperture.

Under these circumstances, the primary X-ray source will be the region where you put the beam.

33.4.B. Post-Specimen Scatter

After the electrons interact with the specimen, they are scattered elastically or inelastically. It is fortunate for us that the intensity of elastic and inelastic scatter from a thin specimen is greatest in the forward direction. Most of the forward-scattered electrons are gathered by the field of the lower objective polepiece and proceed into the imaging system of the microscope. Unfortunately, some electrons are scattered through high enough angles that they strike some part of the specimen holder or the objective lens polepiece or other material in the stage of the microscope.

This effect will be severely exacerbated if the objective diaphragm is not removed during microanalysis.

It is instructive to try this experiment (just once!) to see the enormous increase in spurious and system X-rays that result. Usually, the X-ray flux is so great that the pulse-processing electronics are saturated and the dead time reaches 100%, and the automatic shutter will activate. Even when you remove the objective diaphragm, scattered electrons may create X-rays characteristic of the materials used to construct the holder, the polepiece (mainly copper and iron), and the collimator, and these X-rays could be picked up by the XEDS detector. Furthermore, the scattered electrons may travel directly into the XEDS detector, generating electron–hole pairs, or they may hit your specimen at some point remote from the area of interest and produce specimen-characteristic spurious X-rays. These possibilities are undesirable but unavoidable, because without the beam–specimen interactions that produce this scattering, we would get no information at all from the specimen. Figure 33.6 summarizes all the possible sources of spurious X-rays from post-specimen scatter.

In addition to electron scatter, there will be a flux of bremsstrahlung X-rays produced in the specimen. The intensity of these X-rays is also greatest in the forward direction (see shaded area in Figure 33.6). Since they possess a full spectrum of energy, the bremsstrahlung will fluoresce some characteristic X-rays from any material that they strike. The easiest way to discern the magnitude of this problem is to use a uniformly thin foil (such as our standard Cr film) on a copper grid. When you place the probe on the film in the middle of a grid square, many micrometers from any grid bar, the collected spectrum will invariably show a copper peak arising from the grid as a result of interactions with electrons or X-rays scattered by the specimen. An example of this effect is shown in Figure 33.7. You can remove the presence of the copper peak by using a beryllium grid, since Be K_α X-rays are not routinely detectable. However, using Be grids merely removes the observable effect, not the cause. Therefore, the post-specimen scatter will still generate specimen-characteristic X-rays remote from the area of interest, even if a Cu peak is not present.

Remember that Be oxide is highly toxic if inhaled, so if you have to handle Be grids or other Be components, use gloves and tweezers and don't breathe!

To minimize the effects of the scattered radiation, you should keep your specimen close to zero tilt (i.e., normal to the beam). Experimentally, it seems that if you tilt less than about 10°, then the background intensity is not measurably increased. Under these conditions, your specimen will undergo minimum interaction with both the forward-directed X-rays and any backscattered electrons.

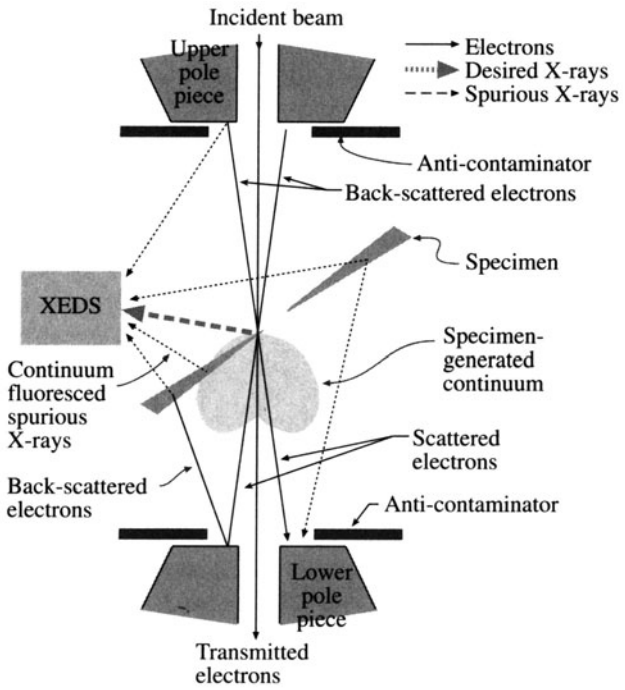


Figure 33.6. Sources of system and spurious X-rays generated when the primary beam is scattered by a tilted, wedge specimen. Note the BSEs which excite X-rays in the stage and elsewhere in the specimen and the specimen-generated bremsstrahlung which fluoresces X-rays from the specimen itself, but well away from the region chosen for analysis.

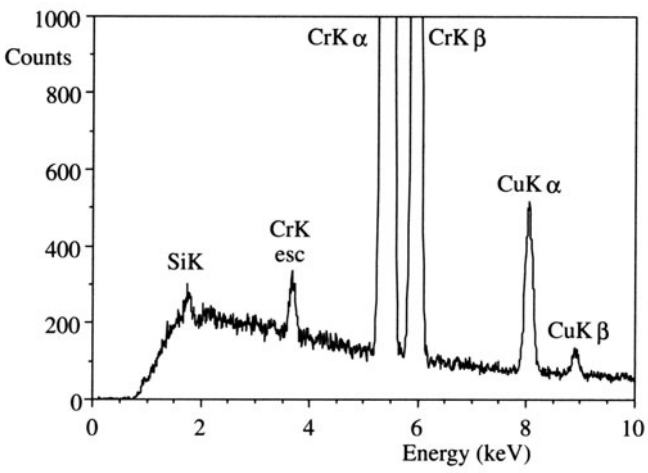


Figure 33.7. Cu peaks in a spectrum from a thin Cr film on a Cu grid. Although the beam is many micrometers from the grid, Cu X-rays are excited by electron scatter and bremsstrahlung from within the specimen and their intensity generally increases with tilt. The Cr escape peak and the Si internal fluorescence peak are also visible.

Both of these phenomena have only a small horizontal component of intensity. The effects of the specimen interacting with X-rays which it has generated will be further reduced if you use thin foils, such as evaporated films or window-polished flakes, rather than self-supporting disks, just as we suggested in the previous section. In self-supporting disks, the bulk regions will interact more strongly with the bremsstrahlung. We do not know what fraction of the post-specimen scatter consists of electrons and what fraction is X-rays, because this will vary with both specimen and microscope conditions. However, there is no evidence to suggest that this X-ray fluorescence limits the accuracy of quantitative analyses.

In addition to keeping your specimen close to zero tilt, you can further reduce the effects of post-specimen scatter by surrounding the specimen with low-atomic-number material. Use of low-Z materials will also remove from your spectrum any characteristic peaks due to the microscope constituents. Be is the best material for this purpose and, as we said right at the beginning of this part of the book, Be specimen holders in addition to Be support grids are essential for X-ray microanalysis. Ideally, all solid surfaces in the microscope stage region that could be struck by scattered radiation should also be shielded with Be. Unfortunately, such modifications are rarely available commercially. The narrow polepiece gap, required to produce high probe currents, and the cold finger, used to reduce hydrocarbon contamination of the specimen, both tend to increase the problems associated with post-specimen scatter. In the ideal AEM, the vacuum would be such that a cold finger would not be necessary and the polepiece gap would be chosen to optimize both the detected peak-to-background ratio and the probe current. When an AEM stage was substantially modified with low-Z material (Nicholson *et al.* 1982), a large reduction in bremsstrahlung intensity was reported and X-ray peak-to-background ratios were produced that are still unmatched by most commercial AEMs. We'll discuss this more in Section 33.5.

You must note, however, that whatever precautions you take, the scattered electrons and X-rays, which are invariably present, result in a specific limitation to X-ray microanalysis.

> If you are seeking small amounts (<~1–2%) of an element A in a specific region of your specimen, and that same element A is present in large amounts, either elsewhere in your specimen or in the microscope stage, then you *cannot* conclusively determine the presence of element A in the specific region of the specimen.

A small peak from A will *invariably* be present in all spectra, just as surely as the Si or Ge internal fluorescence peak will be present.

Obviously, then, you must determine the contributions to the X-ray spectrum from your microscope, and this is best achieved by inserting a low-Z specimen in the beam that generates mainly a bremsstrahlung spectrum, such as an amorphous carbon film, supported on a Be grid or a pure B foil. If a spectrum is accumulated for a substantial fraction of time (say 10–20 minutes), then in addition to the C or B peak, if your XEDS can detect it, the various instrumental contributions to the spectrum should become visible. Such an "instrument spectrum" (see Figure 33.8) should only exhibit the internal fluorescence peak and possibly the Au absorption edge from the detector. Any other peaks will be from the microscope itself, assuming the specimen is pure. These peaks will tell you which elements it is *not* possible to seek in small quantities in your specimen because of their presence in your AEM.

We can summarize the methods used to minimize the effects of post-specimen scattering quite simply:

- Always remove the objective diaphragm.
- Operate as close to zero tilt as possible.
- Use a Be specimen holder and Be grids.
- Use thin foils, flakes, or films rather than self-supporting disks.

Remember that even with these precautions you will still have to look out for artifacts in the spectrum, particularly those from the XEDS system.

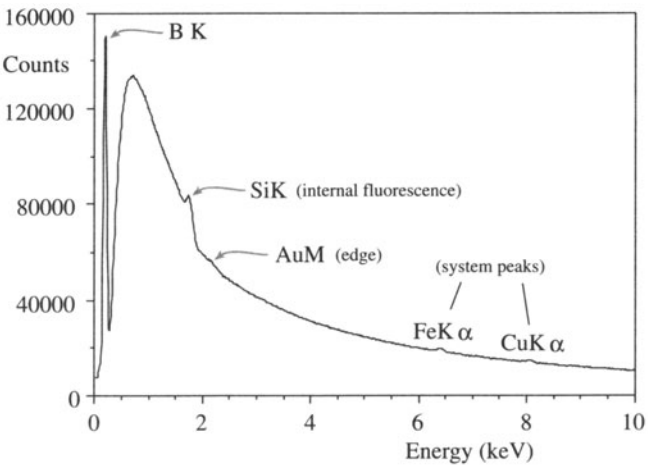


Figure 33.8. An XEDS spectrum from high-purity boron, showing system peaks. The Si K_α peak and the Au M absorption edges are detector artifacts, but the small peaks at 6.4 keV and 8 keV are Fe and Cu system peaks, respectively.

33.4.C. Coherent Bremsstrahlung

As we noted back in Chapter 4, the bremsstrahlung spectrum is sometimes referred to as the "continuum" because the intensity is assumed to be a smooth, slowly varying function of energy. This assumption is perfectly reasonable when the bremsstrahlung is generated in bulk materials by electrons with energies <~30 keV, such as in an SEM. However, in thin monocrystalline specimens illuminated by high-energy electrons, it is possible to generate a bremsstrahlung X-ray spectrum that contains small, Gaussian-shaped peaks known as "coherent bremsstrahlung" (CB). The phenomenon of CB is well known from high-energy physics experiments, but no one thought it would occur at AEM voltages until it was clearly demonstrated by Reese *et al.* (1984). Figure 33.9A shows a portion of an X-ray spectrum from a thin foil of pure copper taken at 120 keV. The primary peaks, as expected, are the Cu $K_{\alpha/\beta}$ and the L lines. In addition, the escape peak is identified. The other small peaks are the CB peaks. They arise, as shown in Figure 33.9B, by the nature of the coulomb interaction with the regularly spaced nuclei. As the beam electron proceeds through the crystal lattice, close to a row of atoms, each bremsstrahlung-producing event is similar in nature and so the resultant radiation tends to have the same energy. The regular interactions result in X-ray photons of energy E_{CB} given by

$$E_{CB} = \frac{12.4\,\beta}{L(1 - \beta\cos(90 + \alpha))} \qquad [33.2]$$

where β is the electron velocity (v) divided by the velocity of light (c), L is the real lattice spacing in the beam direction (= $1/H$ in a zone-axis orientation), and α is the detector take-off angle. More than one CB peak arises because different Laue zones give different values of L. The CB peak intensity seems greatest when the beam is close to a low-index zone axis, and these conditions should be avoided if possible. Unfortunately, you can't remove the CB effects entirely by operating far from a major zone axis, since some residual peaks are invariably detectable.

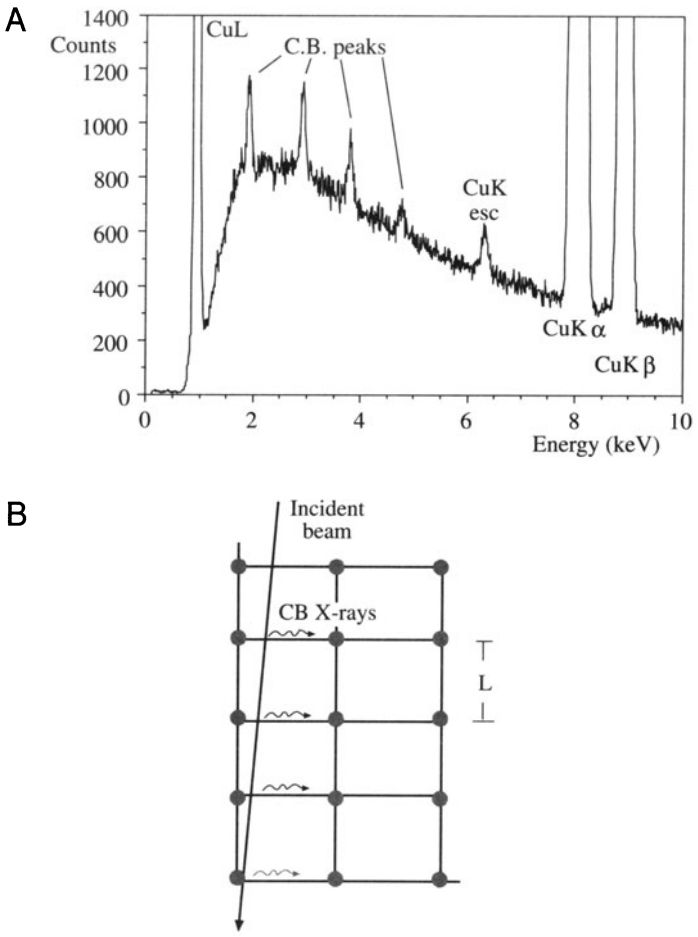


Figure 33.9. (A) CB peaks in a spectrum from pure Cu and (B) the regular generation of CB when the beam passes close to a row of atoms in the specimen.

You may mistakenly identify these CB peaks as characteristic peaks from a small amount of some element in the specimen, but fortunately, you can easily distinguish CB peaks from characteristic peaks.

As predicted by equation 33.2, the CB peaks will move depending on both the accelerating voltage (which will alter v and, hence, β) and the specimen orientation, which will change the value of L. Of course, characteristic peaks show no such behavior, and are dependent only on the elements present in the specimen. While the CB peaks are a nuisance, it may be possible to use them to advantage. There is some evidence that the true bremsstrahlung intensity is low in the regions between the CB peaks. Therefore, if you are seeking to detect a very small amount of segregant, e.g., S segregated to grain boundaries in Cu, then it is possible to "tune up" the CB peaks by careful choice of kV and orientation to ensure that the S K_{α} line will appear between two CB peaks and not be masked by them.

33.5. PEAK-TO-BACKGROUND RATIO

The best test of how well your XEDS is interfaced to your TEM is to measure the peak-to-background (P/B) ratio in a standard specimen (the 100-nm Cr film). There are several

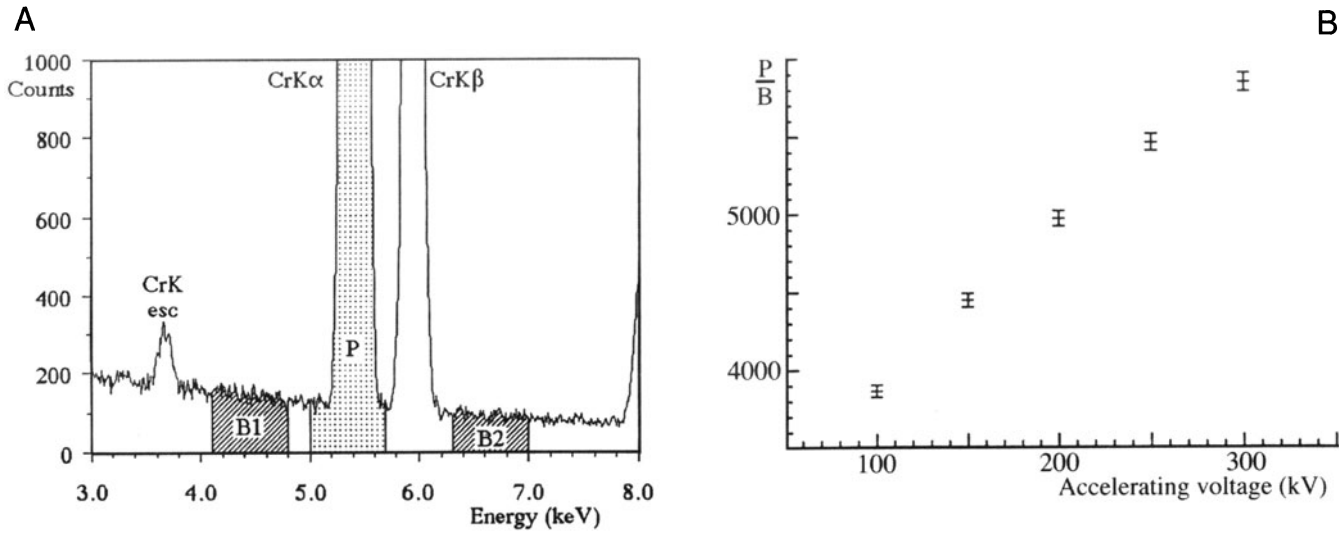


Figure 33.10. (A) The Fiori definition of the peak to background ratio for Cr. The total CrK_α peak intensity *P* is integrated from 5.0 to 5.7 keV. The background windows B1 and B2 are integrated over seventy 10-eV channels from 4.1 to 4.8 keV and from 6.3 to 7.0 keV, respectively. The average of the two windows [(B1 + B2)/2] is B(avg). This B(avg) is divided by 70 to give the background in a single 10-eV channel [B(10 eV)]. The Fiori definition is given by P/B = [P – B(avg)]/[B(10 eV)]. (B) The increase of the Fiori P/B with accelerating voltage in a well-behaved 300-keV IVEM.

definitions of P/B ratio, but the best one (termed the "Fiori" definition, Fiori *et al.* 1982) is shown in Figure 33.10A. For the Cr K_α peak, you should integrate the peak intensity from 5.0 keV to 5.7 keV and divide this by the average background intensity in a 10-eV channel, as shown in Figure 33.10A. In a well-behaved AEM, the P/B ratio will increase with keV. Recommended P/B values, as shown in Figure 33.10B (Zemyan and Williams 1994), should be close to 4000 at 100 keV, rising to almost 6000 at 300 keV.

CHAPTER SUMMARY

The (S)TEM is not well designed for unambiguous X-ray analysis because X-rays are generated and detected from many sources other than the region of your specimen where you put the beam. Nevertheless, there are well-defined precautions you can take so that you are sure that the spectrum is primarily from your specimen and your interpretation and quantification are not compromised. There are also several standard tests you can carry out to compare your AEM system performance with other instruments.

You must always:

- Ensure the XEDS is pointing toward the thin edge of any wedge specimen.
- Have the shutter closed until you know the area you want to analyze.
- Operate with clean, top-hat C2 diaphragms.
- Use thin foils, flakes, or films rather than self-supporting disks.
- Image the electron beam on the TEM screen to ensure that it is Gaussian.
- Remove the objective diaphragm.
- Operate as close to zero tilt as possible.

Check that:

- The hole count is <1%.
- You know your system peaks and other artifacts.

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