CHAPTER 4

PRINCIPLES OF X-RAY ENERGY-DISPERSIVE SPECTROMETRY IN THE ANALYTICAL ELECTRON MICROSCOPE

D. B. Williams and J. I. Goldstein

Department of Materials Science and Engineering
Lehigh University, Bethlehem, Pennsylvania

C. E. Fiori

National Institutes of Health
Bethesda, Maryland

I. INSTRUMENTATION

1. The Energy-Dispersive Spectrometer

The solid state x-ray detector or energy-dispersive spectrometer (EDS) was developed in the late 1960s and rapidly found use on electron-beam instruments (Fitzgerald et al., 1968) because of its speed in collecting and simultaneously displaying x-ray data from a wide energy range. Its small size, but relatively large collection angle
also gives it significant advantages over the traditional crystal or so-called wavelength-dispersive spectrometer (WDS), enabling it to interface easily to an AEM despite the severe space constraints of modern TEM stages. The drawbacks to the conventional EDS are its relatively poor energy resolution (~150 eV) and its inability to detect x-rays from elements below Na (Z = 11) in the periodic table. These limitations, however, are not major practical handicaps in most analyses, and no modern AEM (since the EMMA series in about 1970) has had a crystal spectrometer interfaced to the column. Hence, we will consider the EDS only.

The physics of the x-ray detection process are shown in Figure 1. X-ray photons generated by inner-shell ionizations in the specimen enter the detector, where they create electron-hole pairs in the lithium-drifted silicon crystal. The charge pulse thus created is proportional to the energy of the incoming x-ray. The charge is amplified and discriminated according to its energy, and a signal corresponding to the energy is processed into the appropriate channel of a multi-channel analyzer (MCA). The detector is enclosed in a high-vacuum tube protected from the atmosphere and stage environment by a thin (nominally 7.5 μm) beryllium sheet or "window." The whole assembly is cooled to liquid nitrogen temperatures to minimize electronic noise. This accounts for the large dewar attached to every EDS system and shown schematically in Figure 2.

Typical EDS spectra obtained from an AEM at ~100 keV are shown in Figure 3. The spectrum is a histogram of x-ray intensity versus energy and consists of several approximately Gaussian-shaped peaks characteristic of the elements present in the analyzed volume. The characteristic peaks are superimposed on a background or continuum intensity that rises from ~0.8 keV, peaks at ~1.5 keV, and then decreases slowly, with increasing energy, reaching zero at the incident-beam voltage (~100 keV).

Figure 1  X-ray detection process in the Si(Li) detector (Goldstein et al., 1981).
The characteristic peaks are due to x-rays emitted when ionized atoms return to the ground state; therefore, they contain the elemental information sought. The background is due to bremsstrahlung x-rays produced when electrons are slowed down by inelastic interactions with the nuclei in the specimen. Quantification of the spectrum involves removal of the background and determination of the true relative intensities of the characteristic peaks. This subject is addressed principally in the subsequent chapter. The rest of this chapter deals mainly with the precautions necessary to ensure that the resultant quantification is as accurate and precise as possible.

B. Interfacing the EDS to the AEM

The EDS is inserted into the stage of the AEM, usually in an orthogonal position with respect to the tilt axis, although this varies with manufacturer. While it is not essential to have the EDS in this configuration, it is important to know the position of the detector with respect to the region of the specimen from which microanalysis data are required. This position can be deduced from the stage geometry and a knowledge of the specimen traverse directions. The orthogonal position therefore has a geometrical advantage. The major variables of concern are those of the detector take-off angle, the solid angle of collection, and the resolution of the detector.

The x-ray take-off angle, \( \alpha \), is the angle between the plane of the specimen and the detector axis. If the detector sits in the plane of, and orthogonal to, the specimen holder (which then has to be tilted to permit detection of x-rays), the goniometer tilt angle is the take-off angle. However, the ideal configuration is a positive take-off angle.

![Schematic of EDS system](image-url)
Figure 3  Typical EDS spectra from an AEM operated at ~100 keV: (a) Fe-10 wt% Ni alloy, spectrum displayed from 5.97 to 8.53 keV; (b) Fe-50 wt% Ni alloy, spectrum displayed from 0.0 to 10.24 keV.
such that the x-rays can be detected with the specimen at 0° tilt (i.e., normal to the beam). The specific value of $\alpha$ can clearly be changed by tilting the specimen, changing the specimen height, or retracting the detector. The exact value of $\alpha$ is critical for x-ray absorption corrections (Williams and Goldstein, 1981a), but rapid and accurate experimental determination is not straightforward, and reliance has to be placed on the manufacturer's estimate.

It has been shown by Zaluzec et al. (1981) that a take-off angle of 20° is a reasonable compromise position. Lower take-off angles introduce large path-length corrections for x-ray absorption (Chapter 5), and line-of-sight problems mean the specimen will probably have to be tilted away from 0° anyway. To go to higher take-off angles usually means that the detector has to avoid the upper objective polepiece. By suitable retraction of the detector and redesign of the polepiece, values of $\alpha \approx 70°$ are available. Because of the retraction, however, the detector collection efficiency drops markedly since the solid angle it subtends at the specimen decreases as the square of the distance away from the specimen. In fact, the collection angle of the detector $\Omega$ (in steradians) is given by the approximation

$$\Omega \approx \frac{A}{S^2}$$

(1)

where

$A = \text{active area of detector}$

$S = \text{distance from specimen to detector (not the collimator)}$

For example, with a detector of $\sim 30 \text{ mm}^2$ active area, $\sim 15 \text{ mm}$ from the specimen, $\Omega \approx 0.13 \text{ sr}$. (This approximate equation may be modified if the detector is in the plane of the specimen and not orthogonal to the specimen holder. See Zaluzec, 1981, for a full discussion of all the geometrical considerations.)

Any adjustment of the detector position will lower the value of $\Omega$ since $\sim 15 \text{ mm}$ is usually the closest distance of approach possible, without contact being made with the upper objective polepiece.

There are two detector variables that require calibration. First, the resolution and second, the Be window thickness. The resolution is customarily defined as the full width at half-maximum (FWHM) of the MnK$_\alpha$ peak (5.898 keV) and may be measured directly from the MCA output on a Mn specimen. The discrete nature of the MCA output leaves room for error since the chosen channels may not contain exactly half the counts in the maximum channel. Consequently, the MCA system often contains a program to calculate the effective resolution at the time of operation. Manufacturers' quoted resolutions vary from $\sim 142 \text{ eV}$ to $\sim 155 \text{ eV}$, although in practice, a value of $\sim 160 \text{ eV}$ is reasonable to expect during routine EDS analysis.

As noted previously, the Be window thickness is usually assumed to be $\sim 7.5 \mu\text{m}$ (0.3 mil), but recent difficulty in obtaining such thin Be sheet means that $\sim 12 \mu\text{m}$ is being used more often. It is certain that the Be sheet is not perfectly parallel, nor is it perfectly flat, since SEM studies show it to contain pores (Freund et al., 1972; Statham, 1981). Also, it may change with time because of interaction with high-keV electrons and/or strain induced by constant vacuum cycling or thermal cycling if the detector is warmed up. This latter step is particularly deleterious to the window integrity (because of thermal stresses at the seal with the detector); it should be carried out only when essential, and with the approval of the manufacturer.
Generally it is safe to assume that the window is not thinner than 7.5 μm, and a value of >10 μm is likely to be closer to the true figure. But the occasions when an accurate value is needed are few. In those circumstances (e.g., calculation of k factors and absorption corrections; Williams and Goldstein, 1981a), errors resulting from other factors usually outweigh the error in Be window thickness (Chapter 5).

C. Collimators

The collimator is the front portion of the detector assembly that limits the acceptance angle of radiation entering the detector. Little attention has been paid to the design and constituents of collimators, despite their important role. The fact that the collimators must invariably interact with high-energy electrons and x-rays means that care should be taken to ensure that this interaction does not affect the detected spectrum in any significant way. Nicholson et al. (1982) have described a carbon-coated Pb collimator containing Pb and Al baffles. The carbon-coated Pb design minimizes transmission of x-rays generated by radiation incident on the outside of the collimator. The Al baffles restrict the direct entry of backscattered electrons into the detector because the bending of the backscattered electron trajectories by the magnetic field of the objective lens can be used to ensure that a scattered electron following a path in the magnetic field will intercept the collimator wall or the baffles, which are lined with a low-atomic-number material. The exact design of such a collimator will depend on the particular instrument and detector configuration and may require a trial-and-error approach. Undoubtedly a heavy metal collimator is essential to limit the penetration of high-energy bremsstrahlung x-rays into the detector, and these are slowly becoming available commercially.

D. Windowless Ultra-Thin Window (UTW) EDS

A major limitation of EDS is that the Be window is the primary absorber of low-energy x-rays in the system. This fact accounts in part for the drop-off in intensity of the spectral background below ~1.5 keV and the inability to detect characteristic peaks of energy below ~1 keV (NaK). As mentioned, the Be window is required to protect the cooled detector from the vagaries of the vacuum in the microscope stage. Removal of the window is possible only in an ultraclean environment; otherwise, contaminants will form on the cold detector and degrade the performance. In modern AEMs, the vacuum approaches acceptable levels of cleanliness, and windowless detectors have been placed in AEMs successfully, for short periods of time.

It is generally accepted, however, that so-called “ultra-thin window” (UTW) detectors are a better compromise. These use a gold-coated Formvar film, a few tens of nanometers thick, which protects the detector but absorbs fewer low-energy x-rays than the conventional Be window and thus permits detection of x-rays from boron (Z = 5) and higher-atomic-number materials. The drawback to these detectors is that the window cannot maintain the internal detector vacuum against atmospheric pressure; therefore, there has to be an airlock system to protect the window when the microscope goes to air. The airlock mechanism and the magnetic electron “traps” required to stop backscattered electrons from entering the detector prevent the placement of the EDS detector close to the specimen. Therefore, the collection efficiency is decreased. Also, the general detection efficiency of the spectrometer falls rapidly below ~1 keV. The fluorescence yield of the characteristic x-rays is low absorption corrections are almost always required for the light-element x-rays, and...
overlap with the L lines of the transition metals often occurs. For example, the V \( L_\alpha \) line is at 0.510 keV, and O \( K_\alpha \) is 0.523 keV. These problems all mean that sophisticated data handling, background subtraction, and peak stripping routines are essential if light-element x-rays are to be detected and quantified by using windowless or UTW detectors. But such detectors do provide an alternative to electron energy-loss spectroscopy as a means of detecting the presence of low-Z elements (Thomas, 1980, 1984), and their increasing use is reflected in several papers on the subject presented at the 1984 AEM conference (Williams and Joy, 1984). An example of a spectrum obtained using a UTW detector is shown in Figure 4.

II. ANALYSIS PRECAUTIONS

Before analyzing the EDS spectrum, several precautions have to be taken to ensure that (a) the detected x-rays come only from the region of interest and (b) the region of interest in the thin specimen is compositionally unchanged from that of the bulk by the specimen-thinning procedure. We will discuss these two problems separately.

A. Instrumental Artifacts

This topic is of concern because instrumental effects may produce spurious x-rays that, although apparently from the specimen, may not have originated from the analysis point. Any such effect would reduce the accuracy of quantification and restrict

![Figure 4](Figure 4 EDS spectrum of clinopyroxene taken with a UTW x-ray detector on an HB-501 STEM. The unprocessed spectrum shows an energy resolution of ~100 eV (FWHM) for oxygen K x-rays (spectrum courtesy of L. E. Thomas, Westinghouse Hanford, Richland, Washington).)
the minimum mass fraction that is detectable. In particular, under these circumstances, unambiguous detection of small amounts of one element of interest in a matrix of another is impossible if the element of interest is also present elsewhere in the specimen or the AEM stage region in large amounts. AEM instrumental problems arise because of prespecimen illumination system effects and postspecimen effects in the AEM stage region. In addition, we must consider any artifacts resulting from the EDS system itself.

1. Illumination System Artifacts

Because the EDS detector is some distance from the specimen, the collimator has a wide angular view of the specimen and its surrounds. Therefore, generated x-rays should be confined to the region of interest if quantification is to be meaningful. However, this may not be the case in an AEM, either because uncollimated 100-keV primary electrons hit the specimen away from the point of interest, or more probably because bremsstrahlung radiation from the illumination system floods the specimen, fluorescing it, as shown in Figure 5. These two sources are instrument-dependent since illumination systems differ.

![Diagram of AEM illumination system and artifacts](image)

**Figure 5** Sources of AEM illumination system artifacts: hard x-rays and uncollimated electrons. Hard x-rays that penetrate the C₂ aperture can fluoresce the specimen. Also, stray electrons that are poorly collimated or travel around the final C₂ aperture can generate spurious x-rays.
The existence of this type of artifact is easy to determine. By placing the primary beam down a hole in the specimen, a specimen-characteristic spectrum (often termed the "hole-count") will still be detected, as shown in Figure 6. Using a specimen with an EDS spectrum containing a low-energy L line (<5 keV) and a high-energy K line (>20 keV), the source of the spurious x-rays can be distinguished since a high L/K ratio is usually the result of electron excitation and a low L/K ratio, of x-ray excitation (Goldstein and Williams, 1978). In practice, the problem is usually due to high-energy bremsstrahlung generated in the illumination system (although stray electrons have been reported in early AEMs).

This problem has been recognized for a long time, and several reviews detail the solutions (Bentley et al., 1979; Williams and Goldstein, 1981b; Allard and Blake, 1982). By now all manufacturers of modern AEMs minimize the effects by offering extra-thick, beam-defining apertures and/or nonbeam-defining "spray" apertures as options. These options are essential if the AEM is to be used for quantitative x-ray microanalysis; with their use, the illumination-system problem can be effectively solved (Figure 6). If the illumination-system bremsstrahlung remains a problem in any specific instrument, it is worth noting that thin-flake specimens (supported on Be grids), where the whole sample is electron-transparent or nearly so, can minimize the problem since the analyzed region is thinner than the average path length for fluorescence (~1 to 2 μm). Therefore, the amount of spurious x-rays generated is much smaller than for a disc specimen, where most of the specimen is relatively thick.

2. Postspecimen Effects

Assuming that the illumination-system problems are removed, it is still not certain that all the detected characteristic x-rays are generated solely from the point of interest. The primary reason for this is that the thin specimens allow both transmission of high-keV electrons and scatter of electrons in both the forward and backward directions.

These major "postspecimen interaction" sources may be summarized as follows (Figure 7):

(a) Incident high-energy electrons are backscattered into the microscope specimen chamber and generate x-rays from this region (e.g., cold trap, upper polepiece, EDS collimator). If the specimen is tilted away from 0°, interaction with the specimen is also possible since the electrons will be spiraling back up the column under the influence of the objective lens prefield. The possibility of direct backscatter into the EDS itself also cannot be discounted, although the strong prefield of the upper objective polepiece in the STEM mode helps to reduce this effect (Figure 7(a)).

(b) Incident high-energy electrons are transmitted, scattered, or diffracted into the specimen chamber (or specimen support grid if it is very close to the region of interest) (Figure 7(b)) and generate (i) characteristic and continuum x-rays and (ii) backscattered electrons from, e.g., the lower objective polepiece or objective aperture drive (which should never be inserted during microanalysis).

(c) Characteristic x-rays and high-energy bremsstrahlung from the point of interest on the specimen fluoresce the specimen environment. If the specimen is a disc and is tilted to some nonhorizontal orientation to permit detection of the characteristic x-rays, the possibility of self-fluorescence exists (i.e., fluorescence induced by the continuum radiation generated in the sample) (Figure 7(a)). This of course depends on the specimen shape, thickness, and microstructure,
Figure 6 Hole-count on a Ag specimen: (a) Left-hand side: Ag spectrum down the hole in a Ag specimen using a conventional Pt C2 aperture. Energy range 0 to 40.96 keV. AgK\textsubscript{α}, AgK\textsubscript{β}, and L\textsubscript{α} x-rays are present. Right-hand side: Ag spectrum down the hole at the same intensity and energy scale (0 to 40.96 keV) after minimizing illumination system artifacts by use of an ultra-thick C\textsubscript{2} aperture. Small AgK\textsubscript{α} and AgK\textsubscript{β} peaks are still observed. (b) The two spectra of Figure 6(a) are superimposed. Scale: 0 to 40.96 keV.
Figure 7  Postspecimen interactions: (a) current situation—disc specimen; (b) current situation—thin-film specimen supported on suitable grid bars (Cu or Be); (c) ideal situation to minimize postspecimen interactions.
and the actual energy and intensity distribution of the bremsstrahlung x-rays. If a specimen support grid is used, this radiation will fluoresce the grid (Figure 7(b)). A low-atomic-number cover for the lower polepiece and anticontaminator and the use of a low specimen tilt angle will minimize postspecimen interactions (Figure 7(c)).

Some combination of sources (b) and (c) probably accounts for the well-known observation of copper peaks in otherwise “clean” AEM systems when a copper support grid is used (Figure 8). Similarly, if a specimen on a Cu grid must be tilted because an image defect has to be aligned with respect to the beam, or if specific diffracting conditions have to be avoided, an increased Cu peak intensity will be noted, consistent with the increased interaction of the grid with postspecimen radiation.

Close examination of the background in the CuKα/Kβ region in Figure 8 reveals the presence of a copper absorption edge. The mass thickness of a typical thin film is not sufficient and does not produce enough absorption for an absorption edge to be observed. The copper absorption edge results from the fact that the grid has sufficient mass thickness to behave as a bulk target. Therefore, the copper is most probably excited by electrons that are elastically scattered from the grid and rescattered from the microscope surfaces below the specimen, rather than by specimen-generated bremsstrahlung.

This scattering is essentially unavoidable, although it can be minimized by using low-atomic-number materials for the microscope surfaces (Nicholson et al., 1982). Grids of low-atomic-number materials can eliminate the presence of anomalous characteristic peaks in the spectrum, but it must be recognized that a significant contribution to the bremsstrahlung can still be made by the low-Z grid and that specimen-characteristic x-rays will still be excited away from the point of interest. The spectrum thus measured should always be viewed as a possible composite of the spectrum of the specimen and of the surroundings. This is especially important in quantitative analysis since most methods depend on measurements of the peak and background for corrections. It should also be noted that some copper grids can contain several percent of elements such as Mn, Co, Fe, and Ni. The characteristic x-ray lines of these elements might then appear in the spectra.

Figure 8  EDS spectrum obtained at 15 keV from a Au thin film supported on a Cu grid. The Cu absorption edge can be readily observed.
The use of “window”-polished foil fragments rather than self-supporting disc specimens will also reduce the possibility of specimen self-fluorescence. Furthermore, the use of high-take-off-angle detectors (standard on some AEMs and being developed on others) is an essential step since at zero tilt, specimen interaction with its own bremsstrahlung or its own backscattered electrons is minimized. In this configuration, however, increased backscatter directly into the detector is possible, further emphasizing the need for improved design of collimators.

B. Spectral Artifacts Caused by Operation at High Beam Energies

1. Processing High-Energy Pulses in the EDS

In addition to the well-known spectral artifacts such as the escape peak, sum peak (Goldstein et al., 1981), and incomplete charge collection (Nicholson et al., 1984), the very act of capturing a high-energy (e.g., $E > 20$ keV) photon in the EDS can introduce artifacts into the spectrum. The pulses that appear in the amplifier while processing low-energy photons are shown schematically in Figure 9. A pulse from a low-energy photon rises to a maximum and decreases smoothly to the baseline. However, when a high-energy photon is processed, the amplifier response is saturated. Saturation is the condition in which a further increase in the input to the amplifier does not result in an increase in the amplifier output. The return to the baseline from the saturated condition may not be smooth because of “ringing” or transient oscillations of the amplifier. These transients can disturb the electronic circuitry that first measures the voltage of the pulse and then classifies the photon in the appropriate channel of the MCA.

Processing saturated pulses can result in degradation of the detector resolution by as much as 5 eV or more (at MnK$_{\alpha}$). Transient oscillations can disturb the dead time correction circuitry, resulting in incorrect spectral accumulation times. Another effect of transient oscillations is to disturb the return to the baseline. Moreover, the extreme width of the high-energy pulse relative to the pulses associated with low-energy photons increases the probability that a low-energy photon pulse will enter the detector before the amplifier has returned to the baseline. The low-energy photon pulse will thus be measured with apparently higher energy than normal, which will result in a significant deviation from the usual Gaussian shape on the high-energy side of the peak. The distortion of characteristic peak shapes varies as a function of peak energy, becoming more pronounced at low peak energies, since the influence of the tail of the high-energy pulse represents a larger fraction of a low-energy pulse.

Figure 9 Schematic diagram of main amplifier response to normal and saturated pulses associated with low-energy and high-energy radiation.
2. Compton Scattering

The passage of high-energy x-rays through the detector introduces a new category of unavoidable artifacts not observed in the low-beam-energy EDS such as practiced in the SEM. The high-energy x-ray photons can scatter inelastically in the detector by means of the Compton effect, in which the photon interacts with a loosely bound electron, transferring energy to it. Energy is deposited in the silicon of the detector, in the form of the Compton recoil electron, while the x-ray photon, now of lower energy, escapes the detector. The detector will therefore register an apparent x-ray count because of the Compton electron.

The energy transferred to the recoil electron is \(~10\) keV or less, so that the apparent x-ray event will be recorded in the low-energy spectral range, which is usually the region of interest. These Compton events distort the shape of the spectrum from that which would be expected simply from window absorption of the generated spectrum. As shown in Figure 10, the cross sections for the photoelectric and

![Figure 10 Cross sections for photoelectric and Compton (incoherent) effects in Si as a function of energy (keV).](image)
Compton (incoherent) effects change rapidly at high energies, with Compton scattering becoming the dominant interaction process in the Si(Li) detector at photon energies above \(\sim 60\) keV.

In considering sources of high-energy photons that can undergo Compton scattering in the detector, it is important to realize that the detector is vulnerable to other sources in addition to the x-rays generated in the specimen. The transmission of x-rays through the collimator of the detector becomes significant above 40 keV. Thus, electrons scattered in the microscope at the level of the detector or above can produce x-rays that can penetrate the wall of the collimator. In this region between the condenser and objective lenses, the electron flux may be quite high because of apertures that intercept the beam and cause scattering off all surfaces of the microscope. As we have seen, however, appropriate attention to collimator design may reduce any effects, and one way to do so is to install a heavy-element shroud around all parts of the detector housing. Note that this shroud should be used in addition to any heavy-element column liners and thick apertures that serve to protect the specimen from stray radiation in the illumination system. In fact, the very act of reducing the "in-hole" spectrum may actually increase the flux of hard radiation striking the detector through the walls as a result of placing efficient high-Z scattering materials above the specimen.

3. Electron Penetration

Penetration of high-energy-beam electrons through the beryllium window into the detector can occur above an electron energy of 20 to 25 keV. When an energetic electron strikes the silicon detector, it generates a voltage pulse through the production of electron-hole pairs in a manner similar to the process of x-ray detection. In penetrating the beryllium window, the energetic electron will lose \(\sim 20\) keV of energy because of inelastic scattering. In the environment of the AEM, there will be a significant number of high-energy backscattered electrons with an energy range up to the accelerating voltage. Even with the loss of 20 keV in penetrating the beryllium window, these electrons can influence the measured spectrum over the full analytical range of interest, e.g., \(\sim 1\) to 20 keV. Often, the influence of these backscattered electrons can go unnoticed unless the maximum energy range examined is increased to 40 or 80 keV or even greater.

An example of the distortion of the spectrum by electron penetration is shown in Figure 11, which was prepared from a bulk arsenic target bombarded with 40-keV electrons. In the situation shown in Figure 11, the energy loss of the electrons restricts their influence to the range 0 to 25 keV. Above 25 keV in this spectrum, the spectral intensity is due entirely to bremsstrahlung x-rays. By fitting this bremsstrahlung intensity distribution with a physical model, the bremsstrahlung contribution below 25 keV can be calculated, revealing directly the strong influence of the high-energy electrons entering the detector.

The influence of scattered electrons upon x-ray spectra measured in an AEM is difficult to predict because of the interaction of the electrons with the strong magnetic field of the upper objective polepiece. Therefore, the magnitude of the problem will vary with the instrument configuration and even with sample position in a particular instrument. Figure 12 shows two x-ray spectra of an aluminum-iron target obtained under constant-beam conditions but with the specimen at two different positions separated by \(\sim 3\) mm in height. The intensity of the iron K\(_\alpha\) peak is similar in both spectra.
Figure 11  EDS spectrum of arsenic excited by a 40-keV electron beam, showing an anomalous background below 25 keV caused by direct entry of electrons scattered from the specimen into the detector. The x-ray continuum was fitted from the high-energy end of the spectrum (Goldstein et al., 1981).

Figure 12  Effect of backscattered electrons on background shape. EDS spectra (0 to 80 keV) from an aluminum-iron specimen, with the specimen at two different heights in the instrument. The spectrum labeled "4" was obtained in the normal operating position and shows the effects of high-energy electron scatter.
The spectrum obtained in the lower sample position, labeled "1" in Figure 12, has a nearly ideal background shape, arising almost exclusively from bremsstrahlung x-rays. The spectrum labeled "4," obtained in the upper (normal operating) position, shows an anomalous background, with significant deviation above 30 keV caused by the entrance of high-keV electrons into the detector. A broad electron "hump" centered about 60 keV can be seen. Although the spectra in Figure 12 represent two different sample positions, similar scattered electron effects could be encountered at the same sample position if the spectra were recorded from different regions of the sample where the atomic number or mass thickness varied.

Upon initial examination of Figure 12, it appears that the spectrum in the analytical energy range of 1 to 20 keV is unperturbed by the electron effects above 30 keV. As we have noted, however, the high-energy electrons affect the analytical energy range in two deleterious ways. First, the system dead time correction may be adversely affected. Although the total live time may not be perturbed if the dead time correction circuit is functioning properly, the amount of collection time available for the 1- to 20-keV analytical energy range is necessarily reduced because of the number and length of the high-energy pulses from scattered electrons. If the spectra in Figure 12 represented low- and high-atomic-number regions of the same specimen, there would be an anomalous reduction of ~25% in the live time available for x-ray counting in the analytical energy range of the spectrum as a result of the increased number of high-keV electrons entering the detector from the high-atomic-number region.

The second adverse effect of the scattered electrons is the perturbation of the characteristic x-ray peak shapes caused by the baseline restoration problem discussed previously. While high-energy x-ray pulses can also cause baseline restoration problems, the flux of electrons into the detector can be the dominant feature of the high-energy end of the spectrum, as shown in Figure 12.

Figure 13 shows an aluminum Kα x-ray peak obtained under the conditions shown in Figure 12 for the spectrum labeled "4," containing significant scattered electron effects. To quantify the data (Chapter 5), the peak is modeled with a procedure constrained to use a Gaussian function to describe the peak. Because the peak deviates significantly from a Gaussian shape, the "best fit" Gaussian would be substantially broader than the real peak. When the fitted peak is subtracted from the real peak, the resulting residuals, also shown in Figure 13, indicate a severe deviation from the

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**Figure 13** EDS spectrum of AlKα peak from an aluminum-iron specimen obtained with a scattered electron component in the spectrum (position 4). The effect of the scattered electrons is to introduce strong deviations from the expected Gaussian profile (upper curve). These deviations are indicated by the residuals from the Gaussian peak-fitting operation.
expected Gaussian profile. The deviation from the Gaussian peak profile caused by the high-energy electrons leads to substantial errors in extracting intensities from the spectrum by any peak-fitting procedures used to solve spectral overlaps and may therefore influence quantification.

4. Detector Degradation

The operation of Si(Li) detectors in the AEM environment has resulted in a noticeable rate of detector failure. Detectors are often observed to undergo temporary or apparently permanent failure following exposure to high fluxes of electrons and x-rays when operating in the conventional TEM mode or during lens transitions from the STEM to conventional TEM modes. The detector malfunction may involve loss of resolution, generation of a “low-energy” noise peak, or even result in total failure, requiring return to the manufacturer. The mechanism of these problems is poorly understood at present.

When this phenomenon occurs, however, it is not necessarily indicative of permanent damage. For one detector system within the authors’ experience, the following behavior was noted. After accidental exposure to a large radiation dose in the conventional TEM mode, the detector was found to be inoperative. After 72 hours in a quiescent state, the detector was found to be operating normally, with a slight degradation in resolution. Subsequent high-dose episodes produced failures with rapidly diminishing resolution periods. After about one month of exposure, the detector reached a condition in which it recovered within a few seconds after high-dose conditions associated with a STEM/TEM transient. The resolution degradation was \( \sim 10 \text{ eV} \) as a result of this sequence. The explanation for this behavior is currently unknown.

This experience suggests that when similar phenomena are observed, it would be wise to allow a recovery period including, perhaps, a brief excursion to room temperature before returning the detector to the manufacturer.

C. Unusual Sources of Interference

EDS detectors have been in extensive use in the field for more than 10 years. One would like to think that all of the artifacts arising from improper interfacing to the various instruments would have been identified by now, but sadly this is not the case. New artifacts are occasionally observed, and this will be especially true as EDS detectors are applied to high-voltage electron microscopes, high-energy proton microprobes, synchrotrons, etc. One example of a bizarre artifact encountered in a 200-keV AEM is illustrated in Figure 14. This artifact took the form of a peak with an apparent energy that varied in the range 0.5 to 2 keV, depending on the magnification of the STEM image!

In Figure 14(a), the three peaks were obtained by recording the spectrum for equal lengths of time at three different settings of the STEM magnification control, with the highest energy peak corresponding to the lowest magnification. This peak could also be caused to shift by altering the scan rate, with the peak disappearing at the slow photographic scan rate. No electrons struck the sample during the accumulation of this spectrum. The origin of this artifact is illustrated in Figure 14(b). Electromagnetic coupling occurs between the alternating current passing through the scan coils and the EDS detector assembly. This coupling produces a periodic signal in the EDS signal chain that is interpreted as a false x-ray pulse.
The problem is more likely to be observed in high-voltage scanning instruments for two reasons: (1) Larger currents are necessary to scan the beam as compared to an SEM operating at a beam energy of 20 keV. (2) A “top looking” detector in the AEM is normally located close to the scan coils and lens and is thus immersed in the electromagnetic field, whereas in the SEM the detector is located in the virtually field-free region of the sample chamber.

D. Specimen-Preparation Artifacts

The preparation of thin-foil TEM specimens has long been considered an art rather than an exact science. Because of the drastic measures (chemical attack, electropolishing, ion-beam thinning) used to generate electron-transparent specimens, much debate has occurred as to whether or not the thin-film microstructure is characteristic of the bulk. More recently, a similar debate has arisen concerning the chemistry of the thin film. The problem was first mentioned by Thompson et al. (1977), who reported composition variations with thickness in Al-Cu specimens that could not be explained by absorption, but were apparently due to redeposition of a thin layer of Cu on the foil surface during electropolishing. Morris et al. (1977) showed SEM image evidence for deposition of particles on the surface of Al-4% Cu and reported similar effects in Al-Zn and Al-Ag. The effect was present whether electropolishing or conventional ion-beam thinning was used and could only be removed by sputtering in an ultra-high-vacuum system. More recently, Pouyat and Loretto (1980) observed the effect in electropolished Cu-Al by using Auger electron spectroscopy but reported that hand-polished specimens did not show preferential solute deposition on the surface. A review of the problem has been given by Fraser and McCarthy (1982).

This problem is clearly alloy-dependent and varies with specimen preparation technique. It can easily be detected by first observing nominally homogeneous thin-foil specimens and measuring x-ray intensity ratios as a function of thickness. Data such as those in Figure 15 indicate that surface-layer problems exist. Under these
circumstances, alternative preparation techniques should be pursued, or a suitable surface-cleaning method should be found. Under the same circumstances, however, it is worth varying the preparation conditions to see the effect on surface-layer deposition. For example, in studies of Al-16% Ag (Merchant, 1982), severe surface-layer problems were found only if the electrolyte (nitric acid/methanol) was used on several occasions. Use of fresh electrolyte produced no detectable surface layers. Similarly, cleaning the thin foil with benzene removed any detected deposits very rapidly.

These data are contradictory to other reported results in Al-Ag (Morris et al., 1977), but this serves only to emphasize variabilities inherent in the specimen-preparation process. Clearly, each specimen should be examined for such effects and analysis proceeded with or not, accordingly. There is always the possibility of proceeding to thicker areas of the foil where the surface-layer effect is too small to affect the bulk concentration. In Al-Cu, for example, this occurs at ~300 nm (Thompson et al., 1977). The drawback to this, obviously, is that spatial resolution deteriorates probably to unacceptable levels. It has recently been proposed that ultramicrotomy be reexamined as a specimen-preparation technique for materials (Ball and Furneaux, 1982; Ball et al., 1984). This technique is clearly unsuitable if the defect substructure is also to be studied. Otherwise, it might be a way around the chemical redistribution that apparently occurs in many specimens.

Extraction replication is another specimen preparation technique that is having somewhat of a resurgence due to the advent of AEM. This technique permits the removal of second-phase particles from the surrounding matrix, in principle allowing unambiguous phase identification. It is not yet known, however, whether the particles are unaffected by the vigorous chemical attack that is part of the process or whether, for example, a thin matrix film is left on the particle. These artifacts would limit use of this process in quantitative microanalysis.

III. SELECTION OF EXPERIMENTAL PARAMETERS

Prior to quantitative x-ray analysis in the AEM, a number of instrumental variables can be optimized to ensure that, for example, quantification is accurate or that the best conditions exist for detecting small amounts of a particular trace element or segregant. In these latter situations, x-ray counting statistics may be the limiting factor in quantification. Therefore, it is essential to maximize both the total counts and the count rate of the characteristic x-rays of interest. The time to acquire the
x-ray counts must also be short enough, however, to ensure that specimen drift or contamination does not degrade the desired spatial resolution. As described in Chapter 5, spatial resolution is optimized by small probes and thin specimens, and these conditions are exactly the opposite of those required to generate high count rates. Therefore, under the situations where count rate is a limiting factor, a compromise experimental setup is often required whereby reasonably accurate quantification ($\pm 5\%$ relative accuracy) can be achieved at a reasonable spatial resolution ($\sim 10$ to $30$ nm). In situations where x-ray counting statistics are good, the accuracy of quantification or the spatial resolution can be improved accordingly.

As we shall see, the quantification process requires acquisition of the maximum characteristic x-ray intensity above the continuum background. Therefore, the peak-to-background ratio (P/B) should be maximized along with the absolute count rate. As a rule of thumb, the total x-ray count rate over the whole of the energy spectrum (up to $E_o$ the accelerating voltage) should not exceed $\sim 3000$ counts per second, since the x-ray detector resolution may then be impaired. Even in typical thin-foil specimens using small ($<10$-nm) probes, this count rate can often be achieved in modern AEMs, so caution is required. However, even under these circumstances, the count rate in a small peak may be so low that long times (300 to 500 s) may be required to accumulate sufficient counts for quantification. Then spatial resolution may be lost, and it is more than ever essential to ensure that the AEM is optimized for x-ray analysis. The relevant instrumental variables over which the operator has control will now be discussed.

A. Choice of Accelerating Voltage

Several theoretical treatments (e.g., Joy and Maher, 1977) predict that P/B increases with keV, but until recently there was a lack of conclusive experimental evidence for this because of the increase in background x-rays from extraneous sources as the accelerating voltage increases. (Nicholson et al., 1982, have reported increasing P/B in pure Co with increasing keV in a suitably “cleaned-up” AEM.) Given that this can be achieved in most AEMs, in combination with the fact that gun brightness increases and beam spreading decreases with increasing keV, there is a strong argument for invariably operating at maximum keV.

B. Choice of Probe Parameters

As well as emission current, which is a function of the gun, the operator has a choice of the probe size ($C_1$ lens strength) and the probe convergence angle, $2\alpha$, ($C_2$ aperture size). As shown in Figure 16, the current in the probe at the specimen can be varied over two orders of magnitude depending on the probe size (Williams, 1984). If spatial resolution is a secondary consideration, a large probe size will minimize any x-ray count problems. Similarly, increasing the value of $2\alpha$ increases the probe current (Figure 17) for a fixed probe size. In theory, probe size is independent of $2\alpha$, but in practice, spherical aberration at very high ($>10^{-2}$ rad) $2\alpha$ values and small ($<4$-nm) probe sizes may result in loss of resolution (Cliff and Kenway, 1982).

C. EDS Variables

The EDS detector itself has a fixed geometry with respect to active area ($\sim 30$ mm$^2$) and take-off angle (0º, 20º, or $\sim 70$º, depending on the specific instrument). The solid angle is usually maximized, again to maximize the number of detected x-ray
photons, by placing the detector as close (~15 mm) to the specimen as possible. The
detector can be backed off mechanically if the count rate is too high or if it is
considered that extraneous radiation (e.g., backscattered electrons or hard x-rays from
the illumination system) is penetrating the collimator.

Attention should be given to the choice of spectral display variables, in particular,
the energy range of the display on the MCA and the experimental counting time. The
former should always be as large as possible (at least 40 keV) in the case of an
unknown specimen where the existence of K and L lines at >10 keV may be essential
in initial qualitative analysis. For example, as shown in Figure 18, it is possible to
distinguish between MoL and SK, overlap at 2.3 keV (Figure 18(b)) by observation of
the MoK line at 17.5 keV (Figure 18(a)). Selection of the desired energy range for
analysis should then maximize the resolution of the display to ~5 to 10 eV/channel if
all the peaks of interest can still be displayed in the available channels. If the
specimen is known, the appropriate energy range can, of course, be selected
immediately.

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

Figure 16 Variation of electron probe current in TEM or STEM modes
with focused probe or spot size (courtesy Philips Electron
Optics Publishing Group).
D. Choice of Electron Gun

The choice for the average user is between a conventional W hairpin filament and a LaB₆ gun. The latter is brighter by a factor of ~10 times at 100 kV but substantially more expensive. However, if properly operated and maintained, a single LaB₆ source will operate for many months, which is significantly longer than the life of a W hairpin. The relatively poor brightness of the W gun can be offset partially by the fact that operation at emission currents of 100 μA or more is not unreasonable for short periods of time if a reduced filament life is acceptable. However, operating a LaB₆ gun much above 10-μA emission may result in premature breakdown. This difference in emission current does not totally offset the inherent brightness difference since the probe diameter formed by a LaB₆ source is at most half that from a W source. The field-emission gun as an alternative source is expensive, requires ultrahigh-vacuum conditions, and is available in very few laboratories. But, in situations where the highest spatial resolution in both images and microanalysis is demanded and minimum detectability problems are encountered, it is the best electron source to use.
Figure 18 Identification of the presence of Mo in a NiCrFe weld metal: (a) EDS spectrum of NiCrFe weld metal, 0 to 20.48 keV. The major peaks are CrKα/Kα, FeKα/Kα, and NiKα. A MoKα peak is observed at 17.5 keV. (b) EDS spectrum of NiCrMo weld metal, 0 to 10.24 keV. The x-ray peak at 2.3 keV is MoLα and not SKα (see 0 to 20.48-keV spectrum in (a)).
IV. IMAGING AND DIFFRACTION CONDITIONS DURING ANALYSIS

The image and diffraction conditions for thin-foil crystalline specimens may affect the x-ray data because of the so-called "Borrman effect," in which anomalously high electron penetration occurs when the specimen is close to the Bragg diffraction position ($\theta \approx 0$). Since this corresponds to the dynamical imaging conditions used in the TEM for maximum diffraction contrast ($\theta$ small and positive), care should be taken not to perform x-ray microanalysis under the optimum imaging conditions.

This problem has been studied by several investigators, notably Chern et al. (1973), using an EMMA 4, and more recently by Bourdillon (1982), using a modern AEM. Both studies concluded that the maximum x-ray generation anomalies occur near strong, low-index Bragg conditions, and a bend-center is the least desirable place from which to obtain x-ray data. However, by operating under kinematical conditions ($\theta \gg 0$, i.e., well away from strong Bragg diffraction), the effect can be eliminated. Bourdillon also points out that using large probe-convergence angles ($2\alpha$) such as exist in STEM mode also reduces the effect. Similarly, if a ratio of intensities is used, as is almost always the case, the problem disappears.

However, the best approach experimentally is to observe the defect structure in TEM or STEM under appropriate dynamical conditions, but tilt slightly away from the Bragg condition before carrying out microanalysis. Although diffraction contrast will be reduced, it is usually possible to maintain enough contrast to localize the probe on the precipitate, defect, or other area of interest that is being analyzed. This problem does not exist in amorphous specimens.

It is worth noting, however, that under certain circumstances the variation of x-ray emission with orientation can be used to determine crystallographic site occupancy (Spence and Tafto, 1983). This is discussed in Chapter 5.

V. COHERENT BREMSSTRAHLUNG

Recently, a new phenomenon has been discovered in EDS spectra from thin crystalline specimens in the AEM that may give rise to errors in the interpretation of small intensity peaks from limited amounts (~1 to 3 wt%) of material. The phenomenon, termed "coherent bremsstrahlung" (CB), is not an artifact in the spectrum but the result of the regular crystal structure of a thin foil sample causing bremsstrahlung production in a regular, coherent manner rather than in random fashion. The net result is that, superimposed on the classical (random) bremsstrahlung background, are small Gaussian peaks at positions that depend on the beam energy and the specimen orientation.

The effect, discussed in detail by Spence et al. (1983) and Reese et al. (1984), can be predicted using the equation

\[ E(\text{keV}) = 12.4 \frac{\beta}{L} (1 - \beta \cos (90 + \Omega)) \]  

where

- $E$ = energy of the CB peak
- $\beta$ = electron velocity/velocity of light
- $L$ = atomic plane spacing in the beam direction
- $\Omega$ = take-off angle as defined in Eq. (1).

$L$ can be determined from convergent-beam diffraction patterns.
The main reason for concern about the presence of CB peaks is that they may mask or be misinterpreted as genuine x-ray peaks from small amounts of a particular element in the specimen. For common accelerating voltages used in AEMs (~100 keV) and at atomic spacings (~0.3 nm) typical of many important materials, CI peaks occur at energies from ~1 to 8 keV. Often the CB peaks could be confused with the Si internal fluorescence peak, “impurity” peaks such as Cl and Ar from various specimen preparation techniques, or escape peaks/sum peaks. These facts may explain why it took so long to recognize the presence of CB peaks.

Typical examples of CB peaks from Cu over a range of accelerating voltages and Fe over a range of orientations are shown in Figures 19(a) and (b). The integers above the peaks correspond to the Laue zones in the crystal from which they originate. Vecchio (1985) has indicated methods by which CB peaks can be discriminated from elemental peaks for the specific purpose of detecting segregants in Cu and Fe. Basically, the effect of CB in overlapping elemental peaks can be minimized by careful choice of keV and orientation, using Eq. (2). If analysis is performed >10° away from a major zone axis, then CB peak intensities are lower (Figure 19(c)), although the general bremsstrahlung intensity appears to increase.

VI. MEASUREMENT OF X-RAY PEAK AND BACKGROUND INTENSITIES

When all the above precautions have been taken and the instrument optimized for the particular microanalysis problem at hand, acquiring the necessary x-ray spectra and identifying the characteristic peaks are straightforward matters since modern MC systems are computerized and carry out most of the operations automatically.

The only experimental information that is required for quantification of the ED spectrum is the characteristic peak intensities I_A, I_B, etc., of the elements of interest. As discussed in Chapter 5, these can then be converted directly into values of the wt% of each element C_A, C_B, or corrected for absorption, etc., where necessary. We will outline briefly the various options available to extract peak intensities. The subject is in general, beyond the scope of this chapter, and we refer the reader to the literature for a more detailed explanation (Goldstein et al., 1981; Heinrich et al., 1981; and Fic and Swyt, 1981).

The determination of the characteristic intensity requires first that the continuum background, or bremsstrahlung radiation contribution to the peak, be removed. Methods that separate characteristic x-ray peaks from the background can be classified into one of two categories: background modeling and background filtering.

Background modeling consists of calculating or measuring a continuum energy distribution and combining it with a mathematical description of the detector response function. The resulting function is then used to calculate an average background spectrum that can be subtracted from the observed spectral distribution. Background filtering ignores the physics of x-ray production, emission, and detection; the background is viewed as an undesirable signal to be removed by modification of the frequency distribution of the spectrum. Examples are digital filtering and Fourier analysis.

A method that does not require an explicit model of the background radiation is clearly advantageous for applications in the electron microscope operating in the energy range above 50 keV. One can, in principle, calculate background from
The presence of CB peaks in spectra from thin crystal specimens: (a) pure Cu (L, K, K\textsubscript{\alpha}, escape peaks identified) showing CB from Laue zones 2 – 5 which move as a function of keV; (b) pure Fe (L, K, K\textsubscript{\alpha} escape peaks identified) showing the variation of CB peak position with different orientations; and (c) pure Cu showing the decrease in CB peak intensity with deviation from the exact (114) orientation (courtesy K. S. Vecchio).
continuum model. In practice, however, it is extremely difficult and often impossible to make such a prediction since a significant proportion of the background does not originate from the impact point of the primary electron beam but from grid bars or the specimen holder. Furthermore, Compton recoil electrons generated in the active volume of the silicon detector from high-energy x-rays (above 80 keV) further distort the expected shape of the background. Consequently, the following background filtering procedure is highly recommended for applications in the AEM.

The “top-hat” digital filter was first applied to energy-dispersive x-ray spectra by Schamber (1977). The algorithm is both simple and elegant. Briefly stated, counts in a group of adjacent channels of a spectrum are averaged and the average assigned to a channel equivalent to the center channel of the filter; the procedure is repeated as the filter is stepped through the spectrum and a new, filtered spectrum is created. The original spectrum is retained unaltered. One may describe the averaging by the following equation, using the notation of Statham (1977)

$$y'_i = \frac{1}{2M + 1} \sum_{j=-M}^{M} y_j - \frac{1}{2N} \left[ \sum_{j=-M-N}^{-M+1} y_j + \sum_{j=M+1}^{M+N} y_j \right]$$  \hspace{1cm} (3)

where $y'_i$ is the content of the $i^{th}$ channel of the filtered spectrum and $y_j$ is the content of the $j^{th}$ channel of the original spectrum.

The filter is divided into three sections: a positive, central section consisting of $2M + 1$ channels and two side sections each containing $N$ channels. The grand average of the side sections is subtracted from the grand average of the central section.

The effect of this particular averaging procedure is as follows: If the original spectrum is straight, across the width of the filter, then the average is zero. If the original spectrum is curved concave upward, across the width of the filter, the average is negative; if curved convex upward, the average is positive. The greater the curvature, the larger the average.

For the filter to respond with the greatest measure to the curvature found in spectral peaks, and with the least measure to the curvature found in the spectral background, the width of the filter must be carefully chosen. For a detailed treatment of the subject, see Schamber (1977) and Statham (1977). In general, the width of the filter for any given spectrometer system is chosen to be twice the FWHM of the MnKα peak, with the number of channels in the central section equal to, or slightly more than, the combined number of channels in the side sections.

To measure the intensity of an x-ray peak in a spectrum, we must not only separate the peak from the average effect of the continuum but from the average effects of other peaks as well. If a spectral peak stands clear of other peaks in the spectrum, it is, of course, a trivial matter to sum a group of adjacent channels that straddle the peak and provide a measure of the peak intensity. The greatest peak-to-continuum ratio is obtained when the channels containing only the top half of the peak are summed. When peaks from other elements in the specimen or standard overlap the measured peak, we must consider ways to remove the average effects of the other peaks by some sort of mathematical procedure. Procedures that address themselves to the solution of this problem have a variety of names, such as curve fitting, deconvolution, peak stripping, peak unraveling, multiple linear least-squares curve fitting, etc. The essence of these procedures is as follows.
We start with a partial spectrum obtained from the multichannel analyzer. This partial spectrum is a group of adjacent channels fully encompassing the peak we wish to measure and all peaks that overlap this peak. We will call this partial spectrum our "data" spectrum. We next consider a second but corresponding spectrum that we will call a "calculated" spectrum. This spectrum can be created in several ways. One way is to use a mathematical model to describe each peak in the spectrum separately. At each channel in the calculated spectrum, the effects of all the peaks at that channel are summed together. This process is called convolution, and it is by this process that we can "generate" a spectrum. The mathematical model used to describe the shape of each peak has a minimum of three parameters—one to specify the amplitude of the peak, one to specify its position (energy), and one to specify its width. The Gaussian (normal) profile is the model most often used.

An alternative method of "calculating" the second spectrum is to add together simpler measured spectra (i.e., spectra obtained from standards that contain very few elements or are, preferably, pure elements). Each of these spectra is referred to as a "reference" spectrum.

Regardless of which method we use to create the "calculated" spectrum, we compare it to the data spectrum and adjust the parameters of the calculated spectrum until we obtain the "best" agreement between the two. This procedure provides us with a knowledge of the height of each individual peak, which, when added together will be the "data" spectrum.

The procedure by which the parameters in the "calculated" spectrum are adjusted is mainly responsible for the properties of a particular fitting procedure and, mainly therefore, its name. There are two major classifications: linear and nonlinear. In the linear procedures, only the amplitudes of the peaks in the "calculated" spectrum are adjusted, whereas in the nonlinear procedure, one can adjust also the width and position of each peak in the overlapped bundle. Each of the two methods has its advantages and disadvantages, but we must refer the interested reader to the references at the beginning of this section. A sufficiently detailed description is beyond the scope of this chapter.

VII. SUMMARY

In this chapter we have discussed the use of the energy-dispersive spectrometer to obtain characteristic x-ray intensities \( I_A \), \( I_B \), etc., of elements A, B, etc., present in a given specimen. These intensities are necessary for the measurement of chemical composition in thin-film specimens. Various factors that have been discussed include:

- Interfacing the EDS detector to the AEM
- Effect of collimators
- Special precautions necessary because of instrumental artifacts and of operation at high electron-beam energies
- Effect of specimen-preparation artifacts and imaging and diffraction conditions during analysis
- Selection of experimental parameters to maximize the quality of the x-ray data
- Coherent bremsstrahlung phenomena
- Method(s) to extract the desired characteristic x-ray intensities from the continuum background and from overlapping peaks

It appears that with sufficient attention to the EDS problems discussed in this chapter, pertinent characteristic intensity data can be obtained from specific specimen analysis areas when using the AEM.
TABLE OF CHAPTER VARIABLES

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>Active area of EDS detector</td>
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<tr>
<td>eV</td>
<td>Electron volts</td>
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<tr>
<td>E</td>
<td>Energy of coherent bremsstrahlung x-rays</td>
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<tr>
<td>E_a</td>
<td>Accelerating voltage</td>
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<tr>
<td>I_A</td>
<td>Characteristic x-ray intensity (above background) from element A</td>
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<tr>
<td>L</td>
<td>Atomic plane spacing in electron beam direction</td>
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<tr>
<td>mm</td>
<td>Millimeters</td>
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<tr>
<td>M, N</td>
<td>Number of channels in “top-hat” digital filter (M positive N negative)</td>
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<tr>
<td>nm</td>
<td>Nanometers</td>
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<tr>
<td>rad</td>
<td>Radians</td>
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<tr>
<td>s</td>
<td>Seconds</td>
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<tr>
<td>s_A</td>
<td>Deviation parameter in electron diffraction pattern</td>
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<tr>
<td>S</td>
<td>Distance from specimen to detector</td>
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<tr>
<td>y_i</td>
<td>Content (counts) in i_th channel in filtered spectrum</td>
</tr>
<tr>
<td>y_j</td>
<td>Content (counts) in j_th channel of original spectrum</td>
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<tr>
<td>Z</td>
<td>Atomic number</td>
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α: X-ray take-off angle
α_s: Electron probe convergence semiangle
β: v/c = electron velocity/velocity of light
µm: Micrometers
Ω: X-ray detector collection angle

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