32

X-ray Spectrometry

CHAPTER PREVIEW

To make use of the X-rays generated when the beam strikes the specimen, we have to detect them and identify from which element they originated. This is accomplished by X-ray spectrometry, which is one way to transform the TEM into a far more powerful instrument, called an analytical electron microscope (AEM). Currently, the only commercial spectrometer that we use on the TEM is an X-ray energy-dispersive spectrometer (XEDS), which uses a Si semiconductor detector or sometimes a Ge detector. New detector technologies are emerging, which we'll describe briefly. While some of these may render the Si detector obsolete, we'll nevertheless emphasize this particular detector.

The XEDS is a sophisticated instrument that utilizes the fast processing speeds made possible by modern semiconductors. The detector generates voltage pulses that are proportional to the X-ray energy. Electronic processing of the pulses translates the X-ray energy into a signal in a specific channel in a computer-controlled storage system. The counts in the energy channels are then displayed as a spectrum or, more usefully, transformed into a quantitative compositional profile or, better still, a compositional image or 'map.'

COUNTS
We'll see over and over again that maximizing the number of X-ray counts is paramount.

The Si detector is compact enough to fit in the confined region of the TEM stage and, in one form or another, is sensitive enough to detect all the elements above Li in the periodic table. We'll start with the basic physics you need to understand how the detectors work and give you a brief overview of the processing electronics. We then describe a few simple tests you can perform to confirm that your XEDS is working correctly and the choices you have to make due to the way the XEDS is interfaced to the AEM column.

It is really most important from a practical point of view that you know the limitations of your XEDS and understand the spectrum. Therefore, we'll describe these limitations in detail, especially the unavoidable artifacts (Chapter 33). In Chapter 34, we'll show how the spectra can easily give a qualitative elemental analysis of any chosen feature in your image and, in just a little more time (Chapter 35), a full quantitative analysis. In Chapter 36, we'll show that this information can be obtained with a spatial resolution approaching a nanometer or below and offers detection limits close to a single atom. So '*micro*analysis' is not a good term; 'nanoanalysis' is more accurate but sounds worse. 'Analysis' is how we'll describe it.

32.1 X-RAY ANALYSIS: WHY BOTHER?

The limitations of only using TEM imaging should, by now, be obvious to you. Our eyes are accustomed to the interpretation of 3D, reflected-light images. However, as we have seen in great detail in Part 3, the TEM gives 2D projected images of thin 3D specimens and you, the operator, need substantial experience to interpret these images correctly. For example, Figure 32.1 shows six images, taken with light and electron microscopes (can you distinguish which images are from which kind of microscope?). The scale of the images varies over 6 orders of magnitude from nanometers to millimeters and yet they all appear similar. Without any prior knowledge it would not be possible, even for an experienced microscopist, to identify the nature of these specimens simply from the images.

Now if you look at Figure 32.2, you can see six X-ray spectra, one from each of the specimens in Figure 32.1. The spectra are plots of X-ray *counts* (imprecisely

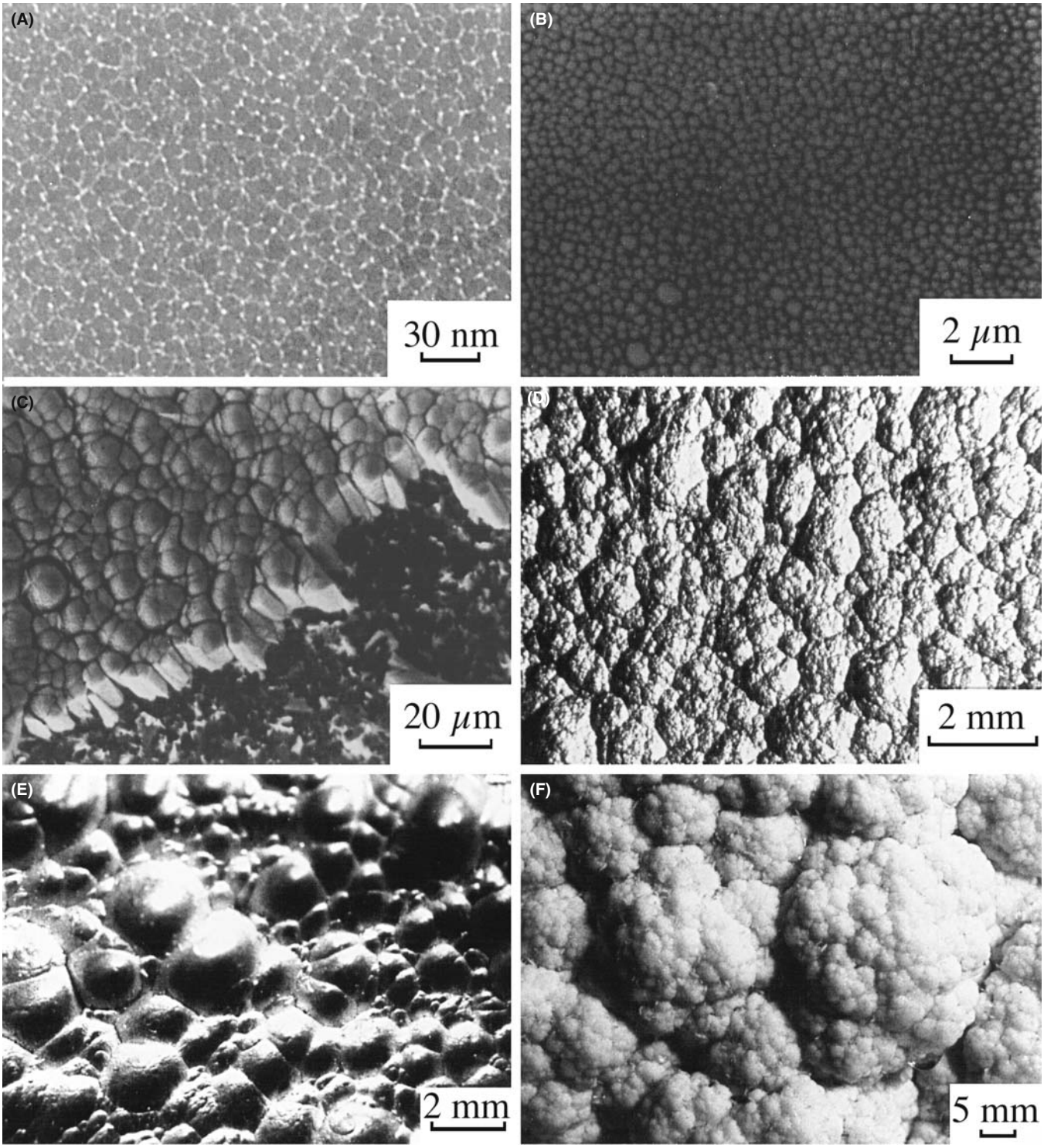

FIGURE 32.1. Six images of various specimens, spanning the dimensional range from nanometers to millimeters. The images were taken with TEMs, SEMs, and light microscopes, but the characteristic structures are very similar, and it is not possible, without prior knowledge, to identify the specimens.

termed 'intensity') versus X-ray *energy* and basically consist of Gaussian-shaped peaks on a slowly changing background. From Chapter 4 you already know that the peaks are characteristic of the elements in the specimen and the background is also called the bremsstrahlung. But even with no knowledge of XEDS, you can easily see that each specimen gives a different spectrum.

Different characteristic peaks mean different elemental constituents; it is possible to obtain this information in a matter of minutes or even seconds.

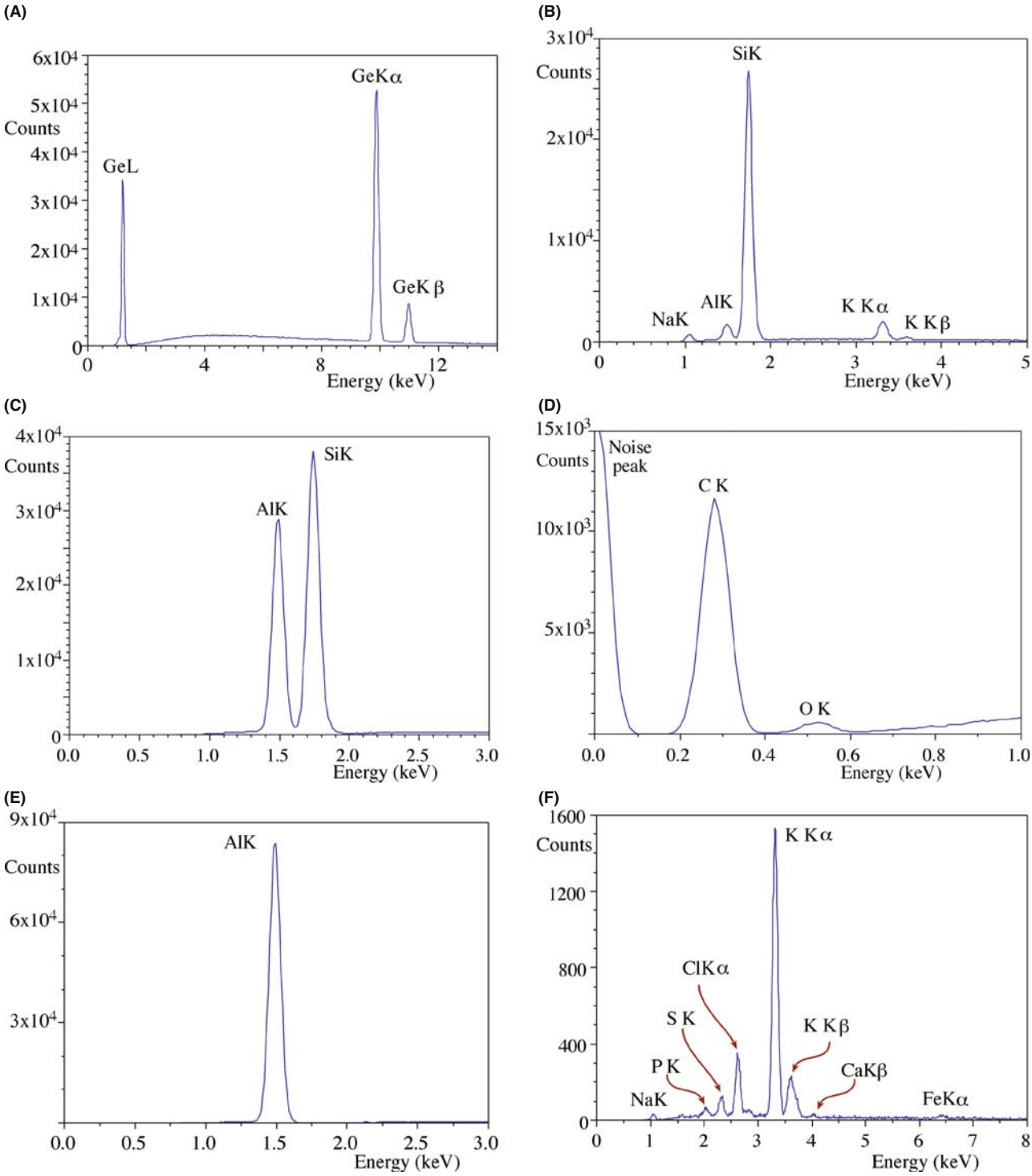

FIGURE 32.2. XEDS spectra from the six specimens in Figure 32.1. Each spectrum is clearly different from the others, and helps to identify the specimens as (A) pure Ge, (B) silica glass, (C) Al evaporated on a Si substrate, (D) pyrolitic graphite, (E) pure Al, and (F) a cauliflower.

When you have such elemental information, any subsequent image and/or diffraction analysis is greatly facilitated. For your interest, the identity of each specimen is given in the caption to Figure 32.2. While Figure 32.2A–E is from common inorganic materials, Figure 32.2F is from a cauliflower which, once you get it into the electron microscope, provides a very distinctive spectrum, albeit from a somewhat carbonized relic of the original vegetable. The familiar morphology of this specimen, now obvious in Figure 32.1F, also accounts for the generic term 'cauliflower structure' which is given to these and similar microstructures.

The main message you should get from this illustration is that the combination of imaging and spectroscopy transforms a TEM into the much more powerful AEM.

32.2 BASIC OPERATIONAL MODE

To produce spectra such as those in Figure 32.2, you first obtain a TEM or STEM image of the area you wish to analyze. In TEM mode, you then have to condense the beam to an appropriate size for analysis. This means exciting the C1 lens more strongly, decreasing the C2 aperture size and adjusting the C2 lens strength. These steps will misalign the illumination system and it can be tedious to move between TEM-image and focused-spot analysis modes, unless you are driving a fully computer-controlled (S)TEM. So, we recommend that you operate in STEM mode. First, create your STEM image as we described back in Section 9.4. Then simply stop the scanning probe and position it on the feature you wish to analyze and switch on the XEDS. In STEM mode, digital software can also check for specimen drift during your analysis.

STEM MODE

Use STEM for AEM. It makes it easier to change from image to analysis mode, easy to form compositional images, and easier to compensate for drift.

In this 'spot' mode you can simply move the beam around the specimen and get a sense of the elemental chemistry of different features you select. However, this approach is very limited from a statistical sampling standpoint and highly biased toward what you think looks interesting in the image. It is now feasible to gather not merely a spectrum from a feature in your specimen, as in Figure 32.2, but a spectrum at *every pixel* in a digital STEM image. From such 'spectrum images' we can extract maps showing the distribution of each element in the specimen and its relationship to the features in the electron image, thus adding another dimension (literally) to the power of the AEM (go back and check the X-ray map in Figure 1.4). We'll talk more about this in Chapter 33 and discuss both qualitative and quantitative maps in Chapters 34 and 35.

For reasons that we'll describe in detail later, you should *always* perform XEDS with your specimen in a low-background (Be) holder. Unless you have an UHV AEM, the holder should be cooled to liquid-N_2 temperature to minimize contamination, and we recommend a double-tilt version, so you can simultaneously carry out diffraction and/or imaging along with your analysis.

32.3 THE ENERGY-DISPERSIVE SPECTROMETER

The XEDS was developed in the late 1960s and by the mid-1970s was an option on many TEMs and even more widespread on the SEM. This rapid spread testifies to the fact that the XEDS is really quite a remarkable instrument, embodying many of the most advanced features of semiconductor technology. It is compact, stable, robust, easy to use, and you can quickly interpret the readout. Several books have been devoted to XEDS on electron-beam instruments and these are listed in the general references. Figure 32.3A shows a schematic diagram of the complete XEDS system and we'll deal with each of the major components as we go through this chapter.

The computer controls all three parts. First, it controls whether the detector is on or off. Ideally, we only want to process one incoming X-ray photon at one time. So the detector is switched off when an X-ray photon is detected and switched on again after that signal is processed (notice we use the particle description of an X-ray here; other detectors work in ways that assume the X-ray is a wave). Second, the computer controls the processing electronics, assigning the signal to the correct energy channel in the storage system. Third, the computer calibrates the spectrum display and tells you the conditions under which you acquired the spectrum, the peak identity, the number of X-rays in a specific channel

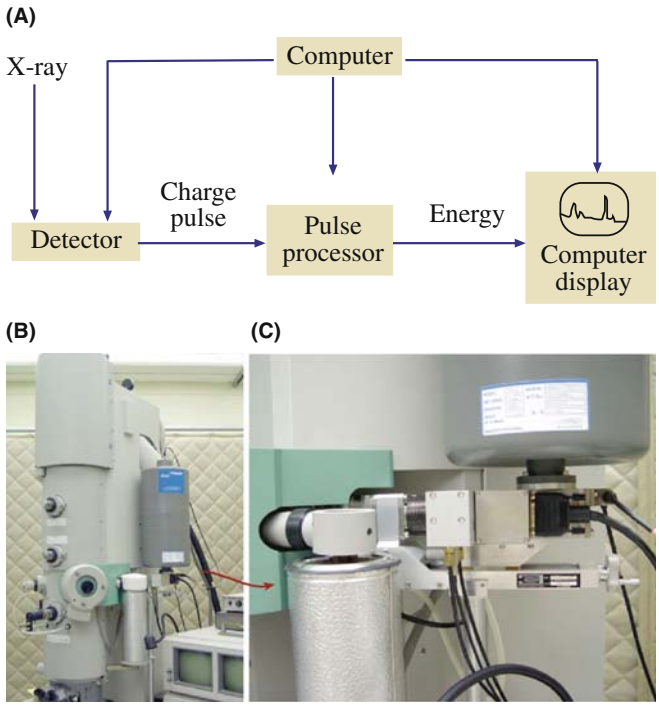

FIGURE 32.3. (A) Schematic diagram of the principle of XEDS; the computer controls the detector, the processing electronics and the display. (B) An XEDS system interfaced to the stage of an AEM. Even in close-up (inset), all that is visible is the large liquid-N_2 dewar attached to the side of the column.

or 'window' of several channels, etc. Any subsequent data processing is also carried out using the computer.

3 COMPONENTS

The three main parts of an XEDS system are
(i) the detector
(ii) the processing electronics
(iii) the computer

We can summarize the working of the XEDS as follows

- The detector generates a charge pulse proportional to the X-ray energy.
- This pulse is first converted to a voltage.
- The voltage is amplified through a field-effect transistor (FET), isolated from other pulses, further amplified, then identified electronically as resulting from an X-ray of specific energy.
- A digitized signal is stored in the channel assigned to that energy in the computer display.

The speed of this process is such that the spectrum appears to be generated in parallel with the full range of X-ray energies detected simultaneously, but the process actually involves very rapid serial processing of individual X-ray signals. Thus, the XEDS both detects X-rays and separates (*disperses*) them into a spectrum according to their *energy*; hence the name of the spectrometer.

Figure 32.3B shows an XEDS interfaced to an AEM. In fact, you can't see the processing electronics, the display, or even the detector itself because it sits close to the specimen within the column. The only feature that you can see is the dewar containing liquid-N_2 to cool the detector and even this is disappearing from the latest detectors.

32.4 SEMICONDUCTOR DETECTORS

The Si detector in an XEDS is a reverse-biased p-i-n diode and since this is still, by far, the most common detector, we will take this as our model. Later in this section we'll discuss the role of other semiconductor detectors, such as intrinsic-Ge (IG) and Si-drift detectors (SDDs).

32.4.A How Does an XEDS Work?

While you don't need to know precisely how the detector works in order to use it, a basic understanding will help you optimize your system and it will also become obvious why certain experimental procedures and precautions are necessary.

When X-rays deposit energy in a semiconductor, electrons are transferred from the valence band to the conduction band, creating electron-hole pairs, as we saw back in Section 4.4. The energy required for this transfer in Si is ~3.8 eV at liquid-N_2 temperature. (This energy is a statistical quantity, so don't try to link it directly to the band gap.) Since characteristic X-rays typically have energies well above 1 keV, thousands of electron-hole pairs can be generated by a single X-ray. The number of electrons or holes created is directly proportional to the energy of the X-ray photon. Even though all the X-ray energy is not, in fact, converted to electron-hole pairs, enough are created for us to collect sufficient signal to distinguish most elements in the periodic table, with good statistical precision. Figure 32.4 is a schematic

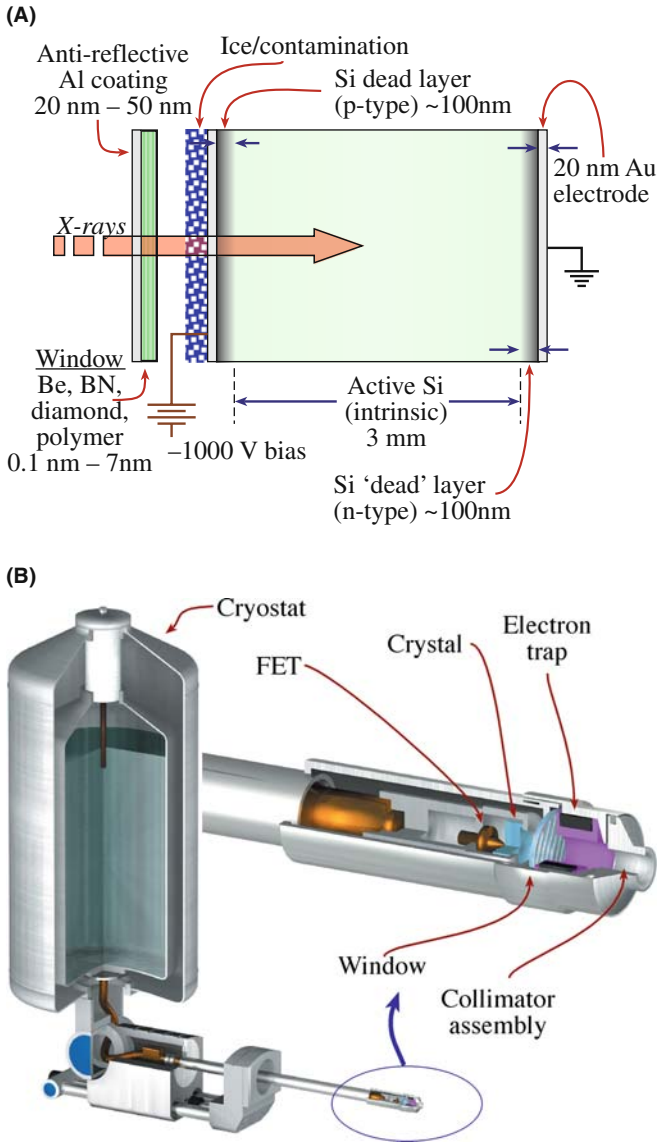

FIGURE 32.4. (A) Cross section of a Si(Li) detector with dimensions indicated (not to scale). In the intrinsic Si region the incoming X-rays generate electron-hole pairs which are separated by an applied bias. A positive bias attracts the electrons to the rear ohmic contact and this charge pulse is amplified by an FET. (B) Exploded diagram of how the individual parts fit together.

diagram of a Si detector and it is similar to the semiconductor electron detectors we discussed back in Chapter 7.

Electron detectors separate the electrons and holes by an internal reverse bias across a very narrow p-n junction, but we need a much thicker detector for X-rays to generate electron-hole pairs since X-rays penetrate matter much more easily than electrons.

Even the purest commercial Si contains acceptor impurities and exhibits p-type behavior. So we compensate for the impurities, which would aid recombination of electron-hole pairs by 'filling' any recombination sites with Li, thus creating intrinsic Si in which the electrons and holes can be separated. Henceforth, we'll refer to Si(Li) (often pronounced "silly") detectors.

The thousands of electrons and holes generated by an X-ray still constitute a very small charge pulse ($\sim 10^{-16}$ C), and so we apply a 0.5–1 keV bias between evaporated Au or Ni ohmic contacts to separate most of the charge. The metal film on the front face creates a p-type region and the back of the crystal is doped to produce n-type Si under a thicker rear contact. So the whole crystal is now a p-i-n device, with shallow junctions on either side of an intrinsic region.

THE ENERGY OF A PULSE

Remember that the magnitude of the charge pulse is proportional to the energy of the X-ray that generated the electron-hole pairs.

When a reverse bias is applied (i.e., a negative charge is placed on the p-type region and a positive charge on the n-type), the electrons and holes are separated and an electron pulse can be measured at the rear contact.

In the p and n regions at either end of the detector, the Li compensation is not completely effective. These regions are effectively unresponsive to the X-ray because most of the electron-hole pairs recombine, and don't contribute to the pulse. These so-called 'dead layers' are an inevitable result of the fabrication process and reduce the detector efficiency. In practice, it is the p-type dead layer at the entrance surface that is most important since the X-rays must traverse it to be detected and we will refer to this as *the* dead layer.

DEAD ACTIVE

The p and n regions are called 'dead layers'; the intrinsic region between them is referred to as the 'active layer.'

The dead layer has become thinner as the detector technology has improved and its effects on the spectrum continue to be reduced (although not to zero, as we shall see).

32.4.B Cool Detectors

Why do we have to cool the detector? Well, if the detector were at room temperature, three highly undesirable effects would occur

- Thermal energy would activate electron-hole pairs, giving a noise level that would swamp the X-ray signals we want to detect.
- The Li atoms would diffuse under the bias, destroying the intrinsic nature of the detector.
- The noise level in the FET would mask signals from low-energy X-rays.

So the detector and the FET are usually cooled with liquid N_2, hence the characteristic dewar shown in Figure 32.3B. The weight of the dewar and the need for constant filling with liquid N_2 are major drawbacks. While the majority of XEDS systems on AEMs still use liquid-N_2 cooled Si(Li) detectors, alternatives are available, such as compact dewars (which use much less N_2), cryo-cooling, compressor-based devices which attain liquid-N_2 temperature mechanically, non-compressive technologies and Peltier-cooled systems, which cool sufficiently (and very rapidly) to deliver reasonable energy resolution with fewer problems. Liquid-N_2 cooling has other drawbacks. Residual hydrocarbons and water vapor in the column form carbon contamination or ice films on the cold detector surface, causing absorption of low-energy X-rays. There are obvious solutions to this problem. We can either isolate the detector from the vacuum, or remove hydrocarbons and water vapor from the column. The latter is a more desirable solution but the former is far easier and much less expensive.

THE XEDS DEWAR

The cylinder hanging on the side of the AEM is the dewar holding liquid N_2 that quietly boils away.

32.4.C Different Kinds of Windows

Liquid-N_2 cooled detectors are usually isolated from the AEM stage in a pre-pumped tube with a sealed 'window' which allows most X-rays through into the detector. There are three kinds of detector; those with a Be window, those with an ultra-thin window and those without a protective window.

Let's examine the pros and cons of each window; a good review has been given by Lund.

Beryllium-window detectors use a thin Be sheet. The best foil is $\sim$7 μm which is transparent to most X-rays, and can withstand atmospheric pressure when the stage

is vented to air. But 7 μm Be is expensive (~$3 M/pound!), rare, and slightly porous, so a thicker sheet (~12–25 μm) is more commonly used. Rolling such a thin Be sheet is a remarkable metallurgical achievement but it still absorbs X-rays with energies < ~1 keV. Therefore, we cannot detect K_α X-rays from elements below about Na ($Z = 11$) in the periodic table, preventing analysis of B, C, N, and O, which are important in the materials, biological, and geological sciences. Other factors such as the low fluorescence yield and increased absorption within the specimen make light-element X-ray analysis somewhat of a challenge, and EELS is often preferable (see Chapters 38 and 39).

KLM TIME

Remind yourself now of the energies involved for K, L, and M for different elements.

Ultra-thin window (UTW) detectors use <100 nm polymer films, diamond, boron nitride, or silicon nitride, all of which can withstand atmospheric pressure while transmitting 192-eV boron K X-rays and the best UTW windows can even analyze Be K X-rays (110 eV). Early polymer UTWs would break if you accidentally vented the column to air without withdrawing the detector and window behind a valve. This problem was overcome by strengthening the polymers with Al films and this accounts for the term 'atmospheric thin window' (ATW) which you may hear. You should remember that different window materials absorb light-element X-rays differently, so you need to know the characteristics of your window. For example, carbon-containing windows absorb nitrogen K_α X-rays very strongly, nitrogen absorbs oxygen, etc.

Windowless detectors only make sense in UHV AEMs such as old VG instruments and Nion dedicated STEMs which minimize hydrocarbons and keep the partial pressure of water vapor by operating with a stage vacuum < ~10^{-8} Pa. Windowless systems routinely detect Be K X-rays as shown in Figure 32.5, which is a remarkable feat of electronics technology.

The relative performance of the various windows is summarized in Figure 32.6. Here we plot the detector efficiency as a function of X-ray energy. You can clearly see the rapid drop in efficiency at low energies and the improved performance of windowless/UTW systems. In fact, Si(Li) detectors absorb (i.e., detect) X-rays with almost 100% efficiency over the range from ~2 to 20 keV, as shown in Figure 32.7. Within this range are X-rays from all the elements in the periodic table above P. This uniform high efficiency is a major advantage of the XEDS detector. Table 32.1 is a concise summary of the pros and cons of each kind of window.

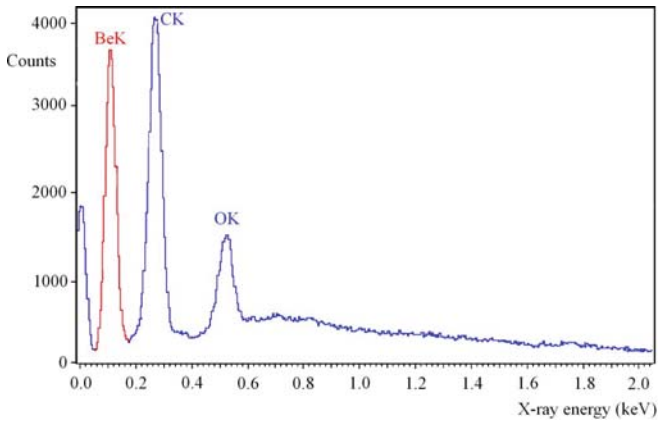

FIGURE 32.5. XEDS spectrum showing the detection of Be in an oxidized Be foil in an SEM at 10 keV. The Be K_α line is not quite resolved from the noise peak.

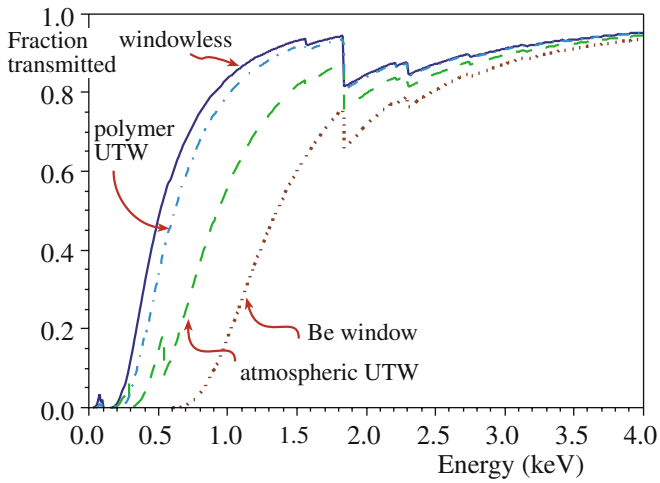

FIGURE 32.6. Low-energy efficiency calculated for a windowless detector, an UTW (1-μm Mylar coated with 20 nm of Al) detector, an ATW detector, and a 13-μm Be-window detector. Note that the efficiency is measured in terms of the percentage of X-rays *transmitted* by the window.

3.8 eV

It takes ~3.8 eV to generate an electron-hole pair in Si, so a Be K_α X-ray will create at most ~29 electron-hole pairs, giving a charge pulse of ~5×10^{-18} C!

32.4.D Intrinsic-Germanium Detectors

You can also see in Figure 32.7 that Si(Li) detectors show a drop in efficiency >~20 keV. This is because such high-energy X-rays can pass through the detector without creating electron-hole pairs. This effect limits the use of Si(Li) in 300–400 keV AEMS in

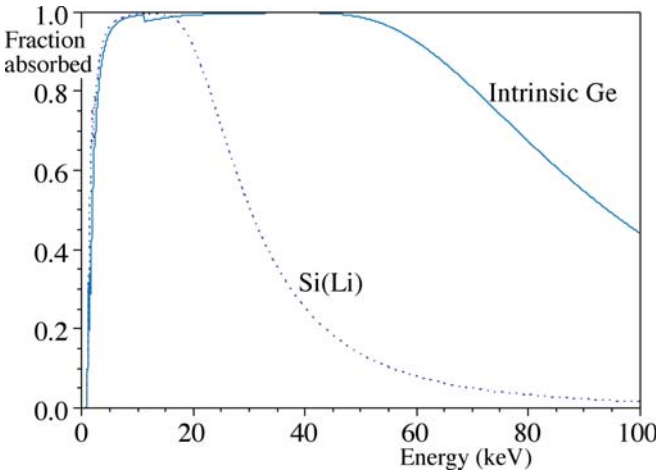

FIGURE 32.7. High-energy efficiency up to 100-keV X-ray energy calculated for Si(Li) and IG detectors, assuming a detector thickness of 3 mm in each case. Note the effect of the Ge absorption edge at about 11 keV. In contrast to Figure 32.6, the efficiency is measured by the percentage of X-rays *absorbed* within the detector.

which we can generate K_α X-rays from all the high-Z elements, e.g., 75 keV Pb K_α X-rays are easily formed at 300 keV. As we'll see in Chapter 35, there are advantages to using the K lines for quantification rather than the lower-energy L or M lines and with a Si(Li) detector, the K lines from elements above Ag ($Z = 47$) are barely detectable. One possible solution is to use an intrinsic Ge (IG) detector which more strongly absorbs high-energy X-rays, as detailed by Sareen.

We can manufacture Ge of higher purity than Si and such Ge is inherently intrinsic, so, Li compensation is not necessary. IGs are more robust and can be warmed up repeatedly which, as we'll see, can solve certain detector problems.

PROTECT YOUR DETECTOR

The intense doses of high-energy electrons or X-rays which can easily be generated in an AEM (e.g., when the beam hits a grid bar) can destroy the Li compensation in a Si(Li) detector, but there is no such problem in an IG crystal.

Furthermore, the intrinsic region can easily be made ~5 μm thick, giving 100% detection of Pb K_α X-rays. Figure 32.7 compares the efficiency of Si(Li) and IG detectors up to 100 keV. There is an even more fundamental advantage to IG detectors. Since it takes only ~2.9 eV to create an electron-hole pair in Ge, compared with 3.8 eV in Si, a given X-ray produces more electron-hole pairs in Ge, and so the energy resolution and signal to noise are better. The only drawback is that the ionization cross sections for high-energy K X-ray excitations are very small for 300–400 keV electrons, so the peak intensities are low. So, why aren't we all using IG detectors? Well, there's no good technical answer but the facts that Si(Li) detectors are easier to manufacture and have a long history of dependable operation are sound commercial reasons why IG detectors have never seriously penetrated the market.

32.4.E. Silicon-Drift Detectors

Si-drift detectors (SDD) may eventually displace traditional Si(Li) detectors; although relatively new, they are already the detector of choice in the much larger SEM and XRF markets. The SDD is basically a CCD (go back and look at Figure 7.3) consisting of concentric rings of p-doped Si implanted on a single crystal of n-Si across which a high voltage is applied to pick up the electrons generated as X-rays enter the side opposite the p-doped rings (Figure 32.8A–C). Applying a voltage from inside to outside the detector (rather than front to back as in a Si(Li)) permits collection of the electrons generated in the n-Si with a 4× lower voltage. Because the central anode in the middle of the p-doped rings has a much smaller capacitance than the large anode at the rear face of a Si(Li) detector (Figure 32.3A–C), a very high throughput of counts is possible, peaking at output rates of many hundred of kcps (Figure 32.8D and look ahead to Figure 32.12B)). If we could in fact generate such enormous count rates in an AEM, we could reduce quantification errors (see Chapter 35), increase analytical sensitivity (see Chapter 36), and seriously improve the statistics of X-ray mapping (see Chapters 33 and 35). In addition to a high throughput, the SDD can operate with no cooling or minimal thermoelectric (Peltier) cooling, while maintaining energy resolutions competitive with Si(Li) detectors (see Section 32.8). This is possible because modern Si-processing technology has reduced thermal-electron generation to extremely low values.

TABLE 32.1. Comparison of Windows

Type	Name	Thickness	Material	Advantage	Disadvantage
Be	Beryllium	~7 μm	Be	Robust	Absorption
UTW	Ultra-thin window	300 nm	Polymer	Low absorption	Breaks easily
ATW	Atmospheric thin window	300 nm	Polymer on grid	Low absorption, robust	Less effective area
None	Windowless	0 nm	None	No absorption	Contamination, light transmitted, need UHV

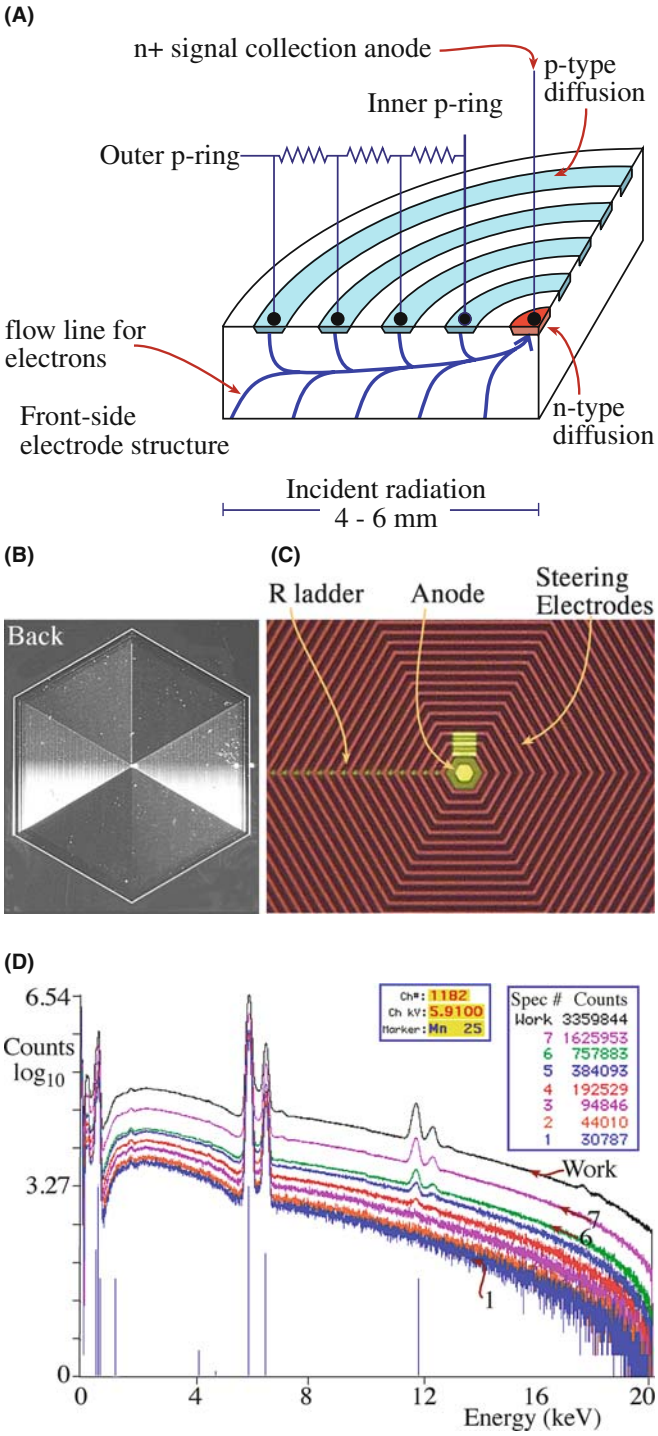

FIGURE 32.8. (A) Schematic diagram showing the back of a quadrant of an SDD consisting of concentric rings of p-type Si on a single crystal of n-type Si. The FET is integrated onto the back of the detector and the bias is applied between the outside p-type ring and the anode inside the inner ring giving electron paths inside the detector as shown in blue. (B) Low-magnification and (C) high-magnification image of the electrode structure on the back of the SDD. (D) SDD spectra from a bulk Mn sample showing no degradation in resolution with increasing output count rates. Be careful: the counts are displayed on a log scale which distorts the usual linear vertical counts scale. The maximum counts are in the Mn Ka peak at 5.91 keV. The black spectrum has over 3.3×10^6 counts in a single channel at that energy. The colored spectra have less counts down to the blue one with 30×10^3 counts in the same channel. But all spectra display the same shape. A Si(Li) spectrometer cannot handle such count rates.

The only problem here is that, as we discuss at length throughout the subsequent chapters, the use of small probes and thin specimens means that total X-ray count rates in AEMs are usually small, negating a principal advantage of SDDs. However, all is not lost and with the advent of intermediate-voltage FEGs and, more recently, C_s correctors, we can create electron probes of < 0.2 nm with > 1 nA of current. If you are prepared to sacrifice spatial resolution by increasing the size of the probe-limiting aperture, then several nA can be generated in probes of a few nm. If you are prepared to sacrifice spatial resolution still further by using thicker specimens, then it is easy to reach the current signal-processing limits (see next section) of Si(Li) electronics (>50 kcps), in which case SDDs might become attractive alternatives. But the jury is still out.

Because an SDD is made up of arrays of individual cells, each one like Figure 32.8A, it is also feasible to consider designing specially shaped SDDs that conform to the inside of the AEM stage. Thus, we could increase the collection angle well beyond typical flat Si(Li) collection angles of a few tens of mrads, and overcome the count-rate limitation (see Section 32.9.A). Count rates are, of course, no problem in SEM-based, bulk-specimen, X-ray microanalysis, which explains the rapid increase of SDDs on those instruments. If you want to learn more, Newbury gives a thorough analysis of the pros and cons of SDDs for mapping in the SEM.

32.5 DETECTORS WITH HIGH-ENERGY RESOLUTION

The poor energy resolution (typically ~135±10 eV) is a fundamental limitation of any of the semiconductor detectors. This limitation arises because, as we discuss in Section 32.7, the detection and processing steps are statistical processes. This poor resolution gives rise to significant peak overlaps (see Section 34.4) and fundamentally limits the sensitivity (detection limits) of analyses (see Section 36.4). However, there are X-ray spectrometers available with significantly better resolution than EDS (<1–10 eV), which may provide better options in the future, so it is worth noting these potential technologies.

32.6 WAVELENGTH-DISPERSIVE SPECTROMETERS

32.6.A Crystal WDS

Before the invention of the XEDS, the wavelength-dispersive (WDS) or crystal spectrometer was widely used. The WDS uses crystals of known interplanar

spacing which (see Part 2) disperse X-rays of wavelength (λ) through different angles (θ) according to Bragg's law ($n\lambda = 2d \sin\theta$). So a WDS treats electrons as waves and this gives considerable advantages over XEDS

- Better energy resolution (~5–10 eV) to minimize peak overlaps.
- Higher peak to background (P/B) ratio to improve detection limits.
- Better detection of light elements (minimum $Z = 4$, Be) by careful choice of analyzing crystal rather than solely through a dependence upon electronics, as in the XEDS.
- No artifacts in the spectrum from the detection and signal processing, except for higher-order lines from fundamental reflections (when $n \geq 2$ in the Bragg equation).
- Higher throughput count rate using a gas-flow proportional counter.

So why don't we have WDS systems on our AEMs? Well, as you'll see in Chapter 35, the forerunner of the AEM, back in the 1960s and early 1970s, was the electron microscope micro-analyzer (EMMA), which did indeed use WDS. However, the WDS was a large and inefficient addition to the TEM, and never attained general acceptance by TEM users for two reasons

- The crystal has to be moved to a precise angle where it collects a tiny fraction of the X-rays from the specimen, whereas the XEDS detector subtends a relatively large solid angle.
- The WDS collects a single λ at any time while the XEDS detects X-rays over a large range of energies. WDS is a very slow, serial collector; XEDS is a fast, effectively parallel, collector.

The geometrical advantage of XEDS (remember, we need to maximize X-ray counts) combined with rapid detection over a wide energy range, without the mechanical motion of the WDS, accounts for the dominance of Si(Li) XEDS systems in all AEMs. Two alternative approaches to overcoming the poor energy resolution of XEDS are being explored. One is a development of the traditional WDS and the other is a totally new approach to X-ray detection.

32.6.B CCD-Based WDS

In an attempt to detect ultra-soft (i.e., very low energy) X-rays, Terauchi and Kawana have designed a WDS using an aberration-corrected, concave, diffraction grating (instead of the usual bent crystal) with a CCD detector in place of the proportional counter. The

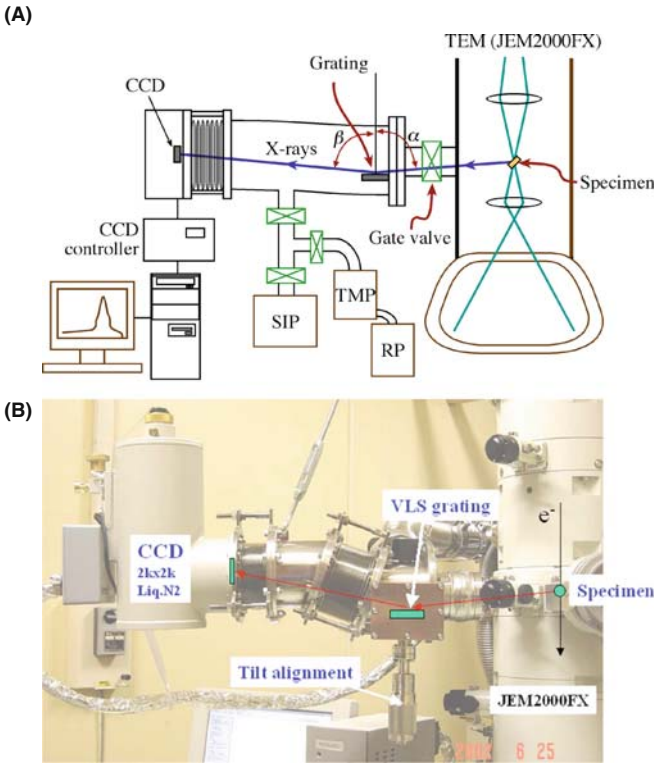

FIGURE 32.9. High-energy resolution X-ray spectrometry; (A) schematic diagram and (B) image of the diffraction-grating WDS system fixed to a TEM column. (C) High-resolution X-ray spectra from hexagonal, cubic, and wurtzite forms of BN showing differences in the B K_α peak shapes due to differences in bonding. (D) Comparison of Si(Li) and bolometer spectra obtained in an SEM illustrating the tremendous difference in energy resolution.

detector is much more compact than a standard WDS, as shown in Figure 32.9A and B, and delivers an energy resolution of 0.6 eV, which is 200× better than a typical EDS resolution and sufficient to resolve intensity variations in the characteristic peaks that arise due to changes in the density of states (DOS) of the valence band (see Figure 32.9C). Study of the DOS and related bonding effects is usually the role of EELS (see Chapter 40), so CCD-WDS is a real breakthrough for X-ray spectrometry. The energy resolution would improve further if the CCD pixel size were decreased, and the grating dispersion increased. Unfortunately, the count rate is very low and to get the spectra shown in Figure 32.9C, a probe size of ~1 μm was used. A larger CCD would permit smaller probes and these will become available via digital-camera technology. Also, recent developments in capillary optics may increase the WDS collection angle, so the technology is worth watching.

32.6.C Bolometers/Microcalorimeters

A totally different approach to detecting X-rays is to measure the heat emitted when an X-ray is absorbed. At first sight this might appear ridiculous, but the

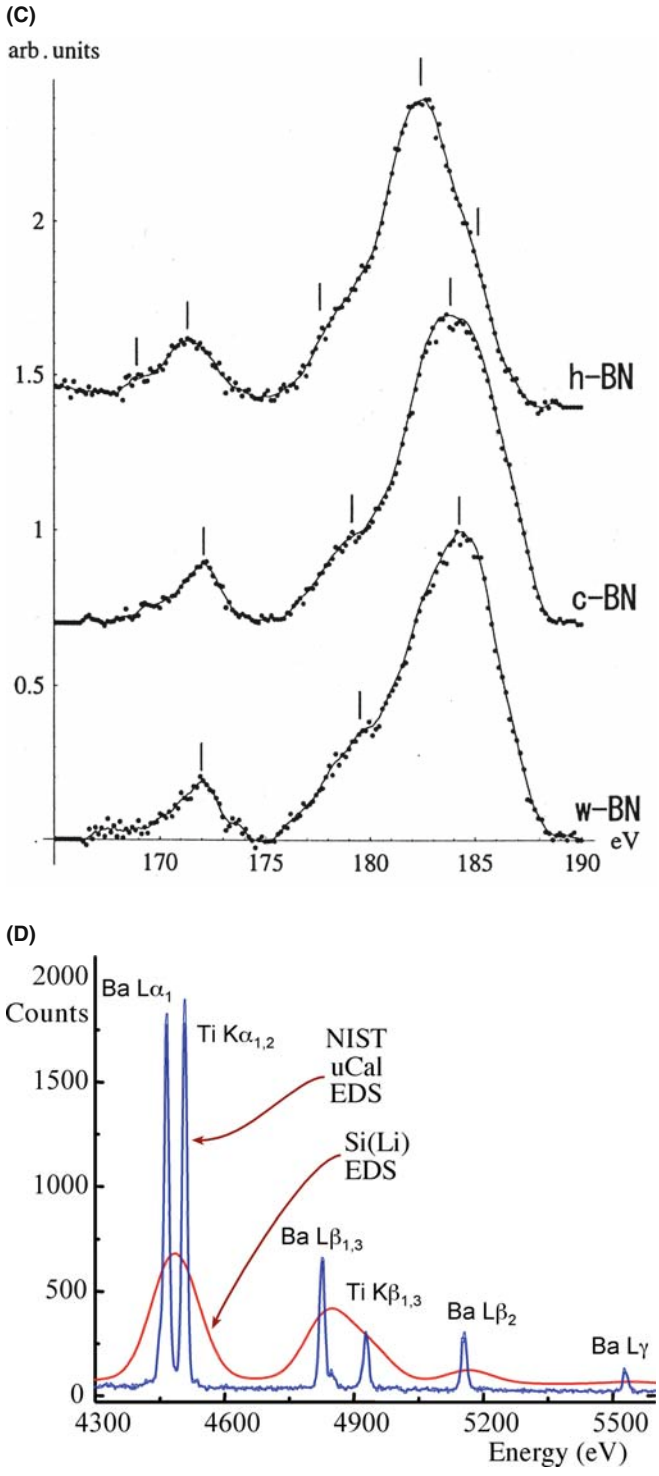

FIGURE 32.9. (Continued).

concept has been demonstrated (Wollman et al.) by creating a microcalorimeter or bolometer (i.e., a sensitive thermometer). As with WDS, the bolometer is limited by its small area, so the solid angle is small and the count rate correspondingly low, but it delivers a resolution comparable with WDS (~5–10 eV), while offering the effectively parallel-collection aspects of XEDS (see Figure 32.9D). Bolometers have been installed on SEMs where their small area is offset by the large count rate. Despite initial enthusiasm, bolometers are not commercially available because they have to be cooled to a few mK with liquid He, which increases the cost close to that of a new SEM and their size to the point where attaching one to a TEM is a major mechanical-engineering feat. The technology to create bolometer arrays is available but until compact, large collection angle WDS or cheap bolometer systems are available, we'll have to live with the poor resolution and other limitations of Si(Li) detectors, to which we'll devote the rest of the chapter.

Table 32.2 below summarizes much of the preceding and following discussion.

32.7 TURNING X-RAYS INTO SPECTRA

The electronics attached to a Si(Li) or SDD convert the charge pulse created by the incoming X-ray into a voltage pulse, which is stored in the appropriate energy channel of the computer display (which used to be called a multi-channel analyzer or MCA). The pulse-processing electronics must maintain good energy resolution across the spectrum without peak shift or distortion, even at high count rates. To accomplish this, all the electronic components beyond the detector crystal must have low-noise characteristics and employ some means of handling pulses that arrive in rapid succession. This whole process used to rely on analog pulse processing, but many of the problems inherent in the analog process have been solved by digital techniques (Mott and Friel), and all current XEDS systems process the charge pulses digitally.

Let's consider first of all what happens if a single, isolated X-ray enters the detector and the electron-hole pairs are separated and captured to create a charge pulse.

- The charge enters the FET preamplifier and is converted into a voltage pulse.
- The pulse is digitized and the X-ray energy that generated the pulse is computed.
- The computer assigns the signal to the appropriate energy channel on the display.

The accumulation of pulses or counts entering each channel at various rates produces a histogram of counts versus energy that is a digital representation of the X-ray spectrum. The computer display offers multiples of 1024 channels in which to display the spectrum and various energy ranges can be

TABLE 32. 2. Comparison of X-ray Spectrometers

Characteristic	IG	Si(Li)	SDD	WDS	Bolometer
Energy resolution (typical/on column)	135 eV	150 eV	140 eV	10 eV	10 eV
Energy resolution (best)	114 eV	128 eV	127 eV	5 eV	5 eV
Energy to form electron-hole pairs (77 K)	2.9 eV	3.8 eV	3.8 eV	n.a.	n.a.
Band gap energy (indirect)	0.67 eV	1.1 eV	1.1 eV	n.a.	n.a.
Cooling required	LN_2 or thermoelectric	LN_2/thermoelectric	None/ thermoelectric	None	100 mK
Detector active area	10–≥50 mm^2	10–≥50 mm^2	≥50 mm^2	n.a.	1 mm^2
Detector arrays available	No	No	Yes	No	Yes
Typical output rates	5–10 kcps	5–20 kcps	1000 kcps	50 kcps	1 kcps
Time to collect full spectrum	~1 min	~1 min	few secs	~30 min	~30 min
Collection angle (sr)	0.03–0.20	0.03–0.30	0.3	10^{-4}–10^{-3}	10^{-4}–10^{-3}
Take-off angle	0°/20°/72°	0°/20°/72°	20°	40°–60°	40°–60°
Artifacts	Escape, sum peaks Ge K/L peaks	Escape, sum peaks Si K peak	Multiple sum peaks	High-order lines	

Data in this table come from the Web sites of the leading XEDS manufactures. For the latest information, check the URLs listed in the reference section.

assigned to these channels. For example, a 10-, 20-, or 40-keV energy range can be used (or even 80 keV for an IG detector on an intermediate-voltage AEM). The display resolution chosen depends on the number of channels available.

A typical energy range that you might select for a Si(Li) and SDD detector is 10 or 20 keV and in 2048 channels this gives you a display resolution of 5 or 10 eV per channel.

DISPLAY RESOLUTION

You should keep the resolution at 10 eV per channel or better. Smaller values use more memory, but memory is cheap. Larger values mean fewer channels for each characteristic peak, giving the peak a serrated step-like appearance rather than a smooth Gaussian shape.

Details of the pulse-processing electronics are not important except for two variables over which you have control. These are the time constant and the dead time. The time constant (τ) is important only if you have an old analog system; it is the time (~5–100 μs) allowed for the analog processor to evaluate the magnitude of the charge pulse.

- Choosing the shortest τ (typically, a few μs) will allow more counts per second (cps) to be processed but with a greater error in the assignment of a specific energy to the pulse, and so the energy resolution (see Section 32.8 below) will be poorer.
- Choosing a longer τ will give you better resolution but the count rate will be lower.

LONG OR SHORT τ?

For most routine thin-foil analyses, you should maximize the count rate (shortest τ), unless there is a specific reason why you want to get the best possible energy resolution (longest τ).

With an analog system you can't have a high count rate and good resolution, so for most routine thin-foil analyses you should maximize the count rate (shortest τ), unless there is a specific reason why you want to get the best possible energy resolution (longest τ). This recommendation is based on a detailed argument presented by Statham.

If you have a digital system, the individual pulses are monitored and τ is varied for each pulse, depending on how close they are together. We call this 'adaptive pulse processing'; it gives a continuous variation of output count rate with input rate rather than a discrete range for each value of τ.

Now, in reality, there are many X-rays entering the detector but, because of the speed of modern electronics, the system can usually discriminate between the arrival of two, almost simultaneous, X-rays. You can find details of the electronics in Goldstein et al. When the electronic circuitry detects the arrival of a pulse, it takes less than a μs before the detector is effectively switched off for a period of time called the dead time, while the pulse processor analyzes that pulse. The dead time is clearly closely related to τ, and is so short that you should expect your XEDS system to process outputs up to 10 kcps quite easily (if it is a later analog system) and 30 kcps or more for a digital system. Even higher outputs (up to 70–100 kcps) need to be handled with an SDD (but in AEMs the beam current and/or specimen thickness is rarely great enough). The dead time increases as more X-rays enter your detector, because it shuts down more often. The dead time can be defined in several ways. If you take the ratio of the output count rate (R_{out}) to the input count rate (R_{in}), which you can usually measure, then

$$\text{Dead time in } \% = \left(1 - \frac{R_{out}}{R_{in}}\right) \times 100\% \qquad (32.1a)$$

An alternative definition is

$$\text{Dead time in } \% = \frac{(\text{clock time} - \text{live time})}{\text{clock time}} \times 100\% \quad (32.1b)$$

These different 'times' can be confusing, but it helps to think of equation 32.1b as follows: if you ask the computer to collect a spectrum for a live time of 100s, then the detector must be live and receiving X-rays for this amount of time. If the detector is actually dead for 20s because it is processing X-rays, it will actually take 120s of 'clock time' to accumulate a spectrum, so the dead time (from equation 32.1b) will be 20/120 = 16.7%. As the input count rate increases, the output count rate will drop and the clock time will increase accordingly. Dead times in excess of 50–60% (or as little as 30% in very old systems) mean that your detector is saturated with X-rays and collection becomes increasingly inefficient. Then you should turn down the beam current or move to a thinner area of the specimen to lower the count rate; but this is a rare situation for a thin-foil analyst to face. Just remember these times.

- Dead time is when the detector is not counting X-rays but processing the previous photon.
- Live time is when the detector is ready to detect an X-ray and not processing any signal.
- Clock time is what it says.

32.8 ENERGY RESOLUTION

The natural line width of the emitted X-rays is only a few eV but the measured widths are usually >> 100 eV. The electronic noise in the XEDS system is a major source of the difference between the practical and theoretical energy resolutions and the width of the electronic noise is described as the 'point-spread function' of the detector. Since the poor energy resolution of XEDS is a major limitation, we need to examine this concept more closely.

We can define the energy resolution R of the detector as

$$R^2 = P^2 + I^2 + X^2 \quad (32.2)$$

where P is a measure of the quality of the processing electronics, defined as the full width at half maximum (FWHM) of a randomized electronic-pulse generator. X is the FWHM-equivalent attributable to detector leakage current and incomplete charge collection (see Section 32.9.A). I is the intrinsic line width of the detector which is controlled by fluctuations in the numbers of electron-hole pairs created by a given X-ray and is given by

$$I = 2.35(F\varepsilon E)^{1/2} \quad (32.3)$$

Here F is the Fano factor of the distribution of X-ray counts from Poisson statistics, ϵ is the energy to create an electron-hole pair in the detector, and E is the energy of the X-ray line. Because of these two factors, the experimental resolution can only be defined under standard analysis conditions defined by the IEEE.

THE IEEE STANDARD FOR *R*

This is the FWHM of the Mn K_α peak, generated (not in the microscope) by an Fe^{55} source which produces 10^3 cps with an 8 μs pulse-processor time constant.

Rather than using IEEE-required radioactive Fe^{55} we recommend measuring the R on your AEM column! Now since Mn is not a common specimen to have lying around, you will find it useful to keep a thin NiO specimen (Egerton and Cheng) to check the resolution when the detector is on the column. You can also use the O K peak to measure the low-energy resolution of your detector. Suitable NiO films < 50 nm thick are available from commercial companies that provide supplies for EM laboratories. Ni is close enough to Mn in the periodic table that you can get good measure of resolution (although it will be slightly worse than that at Mn since resolution degrades with increasing X-ray energy). Others have used thin Cr films instead of NiO. You should be more concerned with changes in R over time than the absolute value since changes indicate that the detector is responding differently to the X-ray flux.

COUNT-RATE EFFECT

All detectors lose resolution as their temperature increases and the count rate increases, although digital electronics handle higher count rates better.

Your computer system will have software that calculates R rather than directly measuring the FWHM of the Mn or Ni peak. It's good to measure the FWHM yourself and you do this by determining the energy width between the channels either side of the peak that contain half the maximum counts in the central (peak) channel, as shown in Figure 32.10.

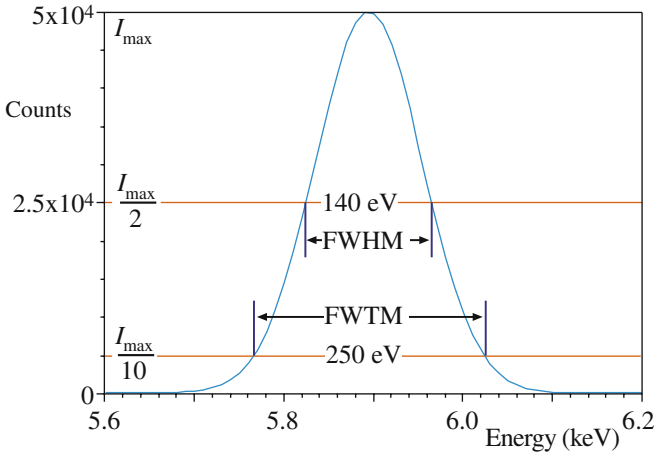

FIGURE 32.10. Measurement of the energy resolution of an XEDS detector by determining the number of channels that encompass the FWHM of the Mn K_α peak. The number of channels multiplied by the eV/channel gives the resolution which, typically, should be about 130–140 eV on the column. You can also measure the FWTM to give an indication of the degree of the ICC which distorts the low-energy side of the peak. The FWTM should be ~1.83× the FWHM if ICC is insignificant.

DETECTOR RESOLUTION

Typically, Si(Li) detectors have a resolution of ~140 eV at Mn K_α with the best being <130 eV. The best reported IG resolution is 114 eV. SDDs offer about 140 eV but can get down to ~130 eV with Peltier cooling.

Because the value of ϵ is lower for Ge (2.9 eV) than for Si (3.8 eV), IG detectors have higher R than Si(Li). The resolution is also a function of the detector area, and the best values we just gave are for 10 mm^2 detectors. The 30 mm^2 or 50 mm^2 detectors, which are typically installed on AEMs to increase the count rate, have resolutions ~5–10 eV worse than the figures just mentioned. So you should be aware that, when you measure R on your AEM, there will be a further degradation in resolution. It is rare to find a 30 mm^2 Si(Li) detector delivering a resolution <~140 eV on the AEM column, even though quoted values are typically ~10 eV less.

How close are XEDS detectors to their theoretical resolution limit? If we assume that there is no leakage and the electronics produce no noise, then $P = X = 0$ in equation 32.2, so $R = I$. For Si, $F = 0.1$, $\varepsilon = 3.8$ eV, and the Mn K_α line occurs at 5.9 keV, which gives R = 111 eV. So it seems that there is not much more room for improvement. The resolution of semiconductor detectors won't approach that of crystal spectrometers or bolometers (< 1 to ~10 eV). However, because of the dependence of I on X-ray energy, light-element K lines do have FWHMs well below 100 eV. We'll see in Section 34.5 that there are signal-processing methods to improve the resolution.

32.9 WHAT YOU SHOULD KNOW ABOUT YOUR XEDS

There are several fundamental parameters which you can specify, measure, and monitor to ensure that your XEDS is performing acceptably. Many of these tests are standard procedures (e.g., see the XEDS laboratories described by Lyman et al.) and are summarized by Zemyan and Williams. In an SEM, which is relatively well behaved, Si(Li) detectors have been known to last 10 years or more before requiring service or replacement. In contrast, an AEM is a hostile environment and the life of a detector can be considerably shortened unless there is a protective shutter (see Section 32.11), which should *always* be closed unless you are acquiring a spectrum. If you analyze a thick portion of your specimen (a waste of time), traverse a grid bar across the field of view (easy to do), or accidentally insert the objective diaphragm while the shutter is open (in which case you should be sentenced to memorize this chapter) you can 'flood' the detector and close down the electronics. If this happens, ask for help, but be prepared to wait a while because the system takes time to recover. If it happens too often, you can permanently damage your detector.

DAMAGING THE DETECTOR

High X-ray or electron fluxes can damage the detector; it is particularly important to monitor the detector performance on your AEM, so that quantitative analyses you make at different times may be compared in a valid manner.

You need to know the operating specifications for your own XEDS, and how to measure them. We can break these specifications down into detector variables and signal-processing variables.

For all of the tests/actions that we describe below, you must discuss the procedure with the instrument technician/laboratory manager **before** doing anything because it is easy to damage the detector if you don't do it right.

32.9.A Detector Characteristics

The *detector resolution* that we just defined may degrade for a variety of reasons. Two are particularly common

- Damage to the intrinsic region by high-energy fluxes of radiation.
- Bubbling in the liquid-N_2 dewar due to ice crystals building up.

We've just told you how to avoid the first problem. If part of your responsibility in the lab is to

top up the liquid N_2 then it should be filtered before putting it into the dewar and *never* re-cycled. If the N_2 is bubbling, you must ask that the problem be corrected and you can suggest warming up the detector.

Or you can suggest that the AEM needs a detector cooled by means other than liquid N_2!

A WARNING ON WARMING

Warming the detector to room temperature should only happen after consultation with the manufacturer, and after turning off the applied bias. (Think what happens to the Li otherwise.)

Incomplete-charge collection (ICC): because of the dead layer, the X-ray peak will not be a perfect Gaussian shape. Usually the peak will have a low-energy tail, because some X-ray energy will be deposited in the dead layer and will not create electron-hole pairs in the intrinsic region. You can measure this ICC effect from the ratio of the full width at tenth maximum (FWTM) to the FWHM of the displayed peak, as shown schematically in Figure 32.10.

In Si(Li) detectors, the phosphorus K_α peak shows the worst ICC effects because this X-ray fluoresces Si very efficiently. ICC will also occur if the Si has a large number of defects arising, for example, from damage via a high flux of backscattered electrons. The crystal defects act as recombination sites, but they can be annealed by warming the detector, as we just described. An IG detector should meet the same FWTM/FWHM criterion as a Si(Li) detector. If the ratio is higher than 2 for the Ni K_α peak there is something seriously wrong with the detector and it needs to be replaced. An SDD has an extremely thin dead layer, so ICC should be minimal.

Detector contamination: over a period of time, even in a UHV STEM, ice and/or hydrocarbons will eventually build up on the detector surface, or the window. When contamination occurs, it reduces the detection efficiency for low-energy X-rays. Ultimately, any detector will contaminate because of residual water vapor in the detector vacuum or because the window may be slightly porous. In all cases, the problem is insidious because the effects develop over time and you might not notice the degradation of your spectrum quality until differences in light-element quantification occur in the same specimen analyzed at different times. Therefore, you should regularly monitor the quality of the low-energy spectrum. The ratio of the Ni K_α/Ni L_α can be used (as described by Michael) as a signal to warn of icing/contamination.

IDEAL GAUSSIAN

An ideal Gaussian shape gives a ratio FWTM/FWHM of 1.82 (Mn K_α or Ni K_α) but this will be larger for lower-energy X-rays that are more strongly absorbed by the detector.

The K/L ratio will differ for different dead layers, different UTWs or ATWs, and different specimen thicknesses, so we can't define an acceptable figure of merit. The best you can do is to measure the ratio (ideally when you first use your detector) and monitor any changes, being aware that, as the ratio increases, quantification of low-energy X-ray lines becomes increasingly unreliable. When the ratio become unacceptable, the detector should be warmed up. Automatic, in situ, heating devices which raise the detector temperature sufficiently to sublime off the ice, without warming the dewar up to ambient temperature, make this process routine. If your detector doesn't have such a device then you should again ask that it be warmed. An SDD doesn't have icing problems if operated at ambient temperatures and, even if Peltier cooling is used, it is still nowhere as cold as liquid N_2.

ICE ON THE DETECTOR

If contamination or ice builds up on the detector, the K_α/L_α ratio rises; the ice selectively absorbs the lower-energy L line.

In summary, you should measure and continually monitor changes in

- *The detector resolution* on the column using the Mn or Ni K_α line (typically 150 eV for Si(Li) and 140 eV for an IG or SDD).
- *The ICC* defined by the FWTM/FWHM ratio of the Ni K_α line (ideally 1.82).
- *The ice/contamination build-up* reflected in the Ni K_α/L_α ratio.

If any of these figures of merit get significantly larger than *your* baseline values, then warming up the detector, if necessary to room temperature, may help.

In summary, you must be very careful with your XEDS.

- DO NOT generate high fluxes of X-rays or backscattered electrons unless your detector is shuttered.
- DO NOT ever warm up the detector yourself; get help. But make sure that the bias is turned off and the manufacturer is consulted.
- DO NOT use unfiltered or re-cycled liquid N_2.

All these DO NOTs make liquid-N_2-free and minimal dead-layer SDDs rather attractive.

32.9.B Processing Variables

You need to ensure that the output counts (i.e., the spectrum) reflect the input X-ray counts. There are three things you can check to make sure the pulse-processing electronics are working properly

- First, check the calibration of the energy range of the spectrum.
- Second, check the dead-time correction circuitry.
- Third, check the maximum output count rate.

The energy resolution should not change significantly from day to day, unless you change the (analog) time constant. Electronic-circuit stability has improved to a level where such checks need only be done a couple of times a year. Will you do the check or rely on someone else?

Calibration of the energy-display range: this process is quite simple; collect a spectrum from a specimen which generates a pair of X-ray lines separated by about the width of the display range (e.g., Cu for 0–10 keV, Mo for 0–20 keV). Some systems use an internal electronic strobe to define zero, and in this case you only need a specimen with a dominant line at the high end of the energy range. Having gathered a spectrum, see if the computer markers are correctly positioned at the peak centroid (e.g., Cu L_α at 0.932 keV and Cu K_α at 8.04 keV). (You'll learn more about the specific energies in Chapter 34 and you can also go back to Chapter 4 to remind yourself of the relationship between E and Z.)

RECALIBRATE
If the peak and the marker are >1 channel (10 eV) apart, then you should recalibrate your display using the commercial software.

Checking the dead-time correction circuit: if the dead-time correction electronics are working properly, the electronics will give an increase in output counts directly proportional to the increase in input counts, for a fixed live time. This behavior is absolutely essential for valid quantification.

- Choose a pure element, say our favorite NiO foil which we know will give a strong K_α peak.
- Choose a live time, say 50s, and a beam current to give a dead-time readout of about 10%.
- Measure the total Ni K_α counts that accumulate in about 30–60s (longer is better).

Then repeat the experiment with higher input count rates (e.g., dead times of 30, 50, 70%).

MUST BE LINEAR
The processing electronics must show linear behavior for valid quantification.

To increase the count rate, increase the beam current by choosing a larger diameter beam or larger C2 aperture. The dead time should increase as the input count rate goes up, but the live time remains fixed (by your choice). If you plot the number of output counts against the beam current, measured with a Faraday cup, or a calibrated exposure-meter reading, then it should be linear, as shown in Figure 32.11. But you will see when you do the experiment that it takes an increasingly longer (clock) time to attain the preset live time as the dead time increases. If you don't have a Faraday cup, you can use the input count rate as a measure of the current; remember that the Faraday cup is useful for many other functions, such as characterizing the performance of the electron source, as we saw in Chapter 5. Remember

Determination of the maximum output count rate: again the procedure is simple

- Gather a spectrum for a fixed clock time, say 10–30s, with a given dead time, say 10%.
- Increase the dead time by increasing the beam current, C2 aperture, or specimen thickness.
- See how many counts accumulate in the Ni K_α peak in the same fixed clock time.

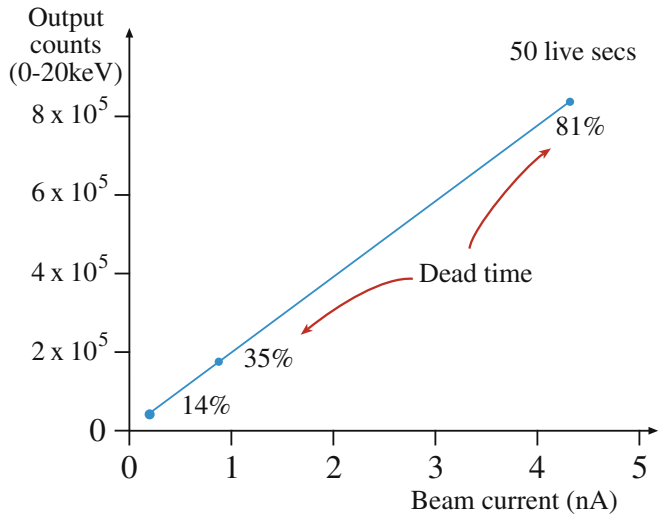

FIGURE 32.11. A plot of the output counts in a fixed live time as a function of increasing beam current showing good linear behavior over a range of dead times, demonstrating that the dead-time correction circuitry is operating correctly.

The number of counts should rise to a maximum and then drop off above a certain dead time, which depends on the system electronics. Beyond the maximum, the detector will be dead more than it is live and so the counts in a given clock time will decrease. In Figure 32.12A, this maximum is at about 60% dead time, typical of modern systems, although in older XEDS units this peak can occur at as little as 30%. If you have analog electronics, you can repeat this experiment for different time constants, τ, and the counts should increase as τ is lowered (at the expense of energy resolution), as also shown in Figure 32.12A. Clearly, if you operate at the maximum in such a curve (if you can generate enough input counts) then you will be getting the maximum possible counts in the shortest possible time. As we've already said, it is almost always better to have more counts than to have the best energy resolution, so select the shortest τ unless you have a peak overlap problem. Digital processing is easier than analog for this reason.

If your specimen is too thin it might not be possible to generate sufficient X-ray counts to reach dead times in excess of 50%, so the curve may not reach a maximum, particularly if τ is very short or you have digital processing. In this case, just use a thicker specimen.

While it is rare that a good thin foil produces enough X-rays to overload the detector electronics, there are situations (e.g., maximizing analytical sensitivity—see Chapter 36) when you need to generate as many counts as possible. However, if you use a thick specimen and high beam current, you may produce too many counts for analog processing, or even digital, systems. If high count rate is your primary mode of operation, you might want to consider an SDD. Figure 32.12B shows the prospects for high output count rates with an SDD. The problem in TEM, as we've noted, is to generate sufficient counts to make use of this extraordinary processing capability.

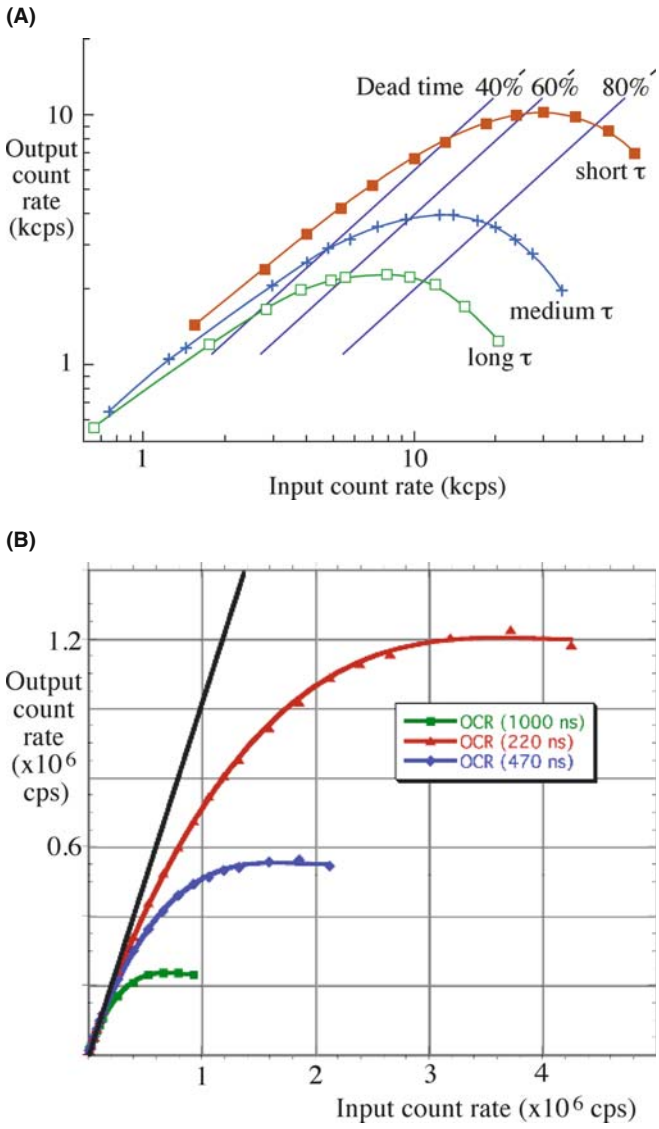

FIGURE 32.12. (A) The output count rate in a given clock time as a function of dead time. The maximum processing efficiency is reached at ~60% dead time. It is very inefficient to use the system above the maximum output rate because of the very long (clock) times needed to gather a spectrum. Increasing the (analog) time constant results in fewer counts being processed and a drop in the output count rate. (B) Data from an SDD on an SEM at three different time constants: note the enormous increase in output count rate up to 1.2 million cps.

TOO THIN

In XEDS, your specimen may be too thin: you need enough counts.

As shown in Figure 32.13, digital processing permits a higher throughput over a continuous range of energy resolution than the fixed ranges available from each specific (in this case six) τ for an analog system. We've already mentioned that C_s correction permits larger apertures to be used and therefore, significantly more current can be put into small probes, but it's unlikely that if you have a C_s-corrected AEM it will be still interfaced to an old analog XEDS system.

In summary, you should occasionally

- Check the energy calibration of the computer display.
- Check the dead-time circuitry by the linearity of the output count rate versus beam current (Figure 32.11).
- Check the counts in a fixed clock time as a function of beam current to determine the maximum output count rate (Figure 32.12).

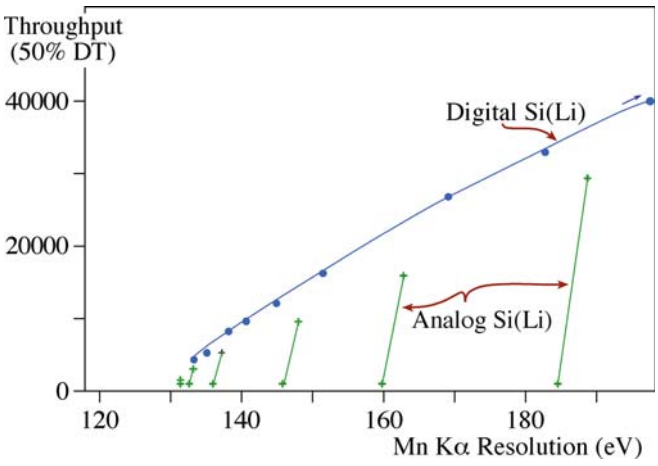

FIGURE 32.13. Digital pulse processing gives a continuous range (blue line) of X-ray throughput at 50% dead time, compared with a set of fixed throughput ranges (green lines) for specific (analog) time constants.

32.10 THE XEDS-AEM INTERFACE

In your TEM, an intense beam of high-energy electrons bombards your specimen, which scatters many electrons. The specimen *and any other part of the TEM* that is hit by these electrons emit both characteristic and bremsstrahlung X-rays (which have energies up to that of the electron beam). X-rays of several tens or hundreds of keV can penetrate long distances into the 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 32.14, it is not possible to prevent radiation from the stage and other areas of the specimen from entering the detector. As you can see from Figure 32.14, the XEDS has a collimator in front of the detector crystal. This collimator is the last line of defense against the entry of undesired radiation from the stage region of the microscope.

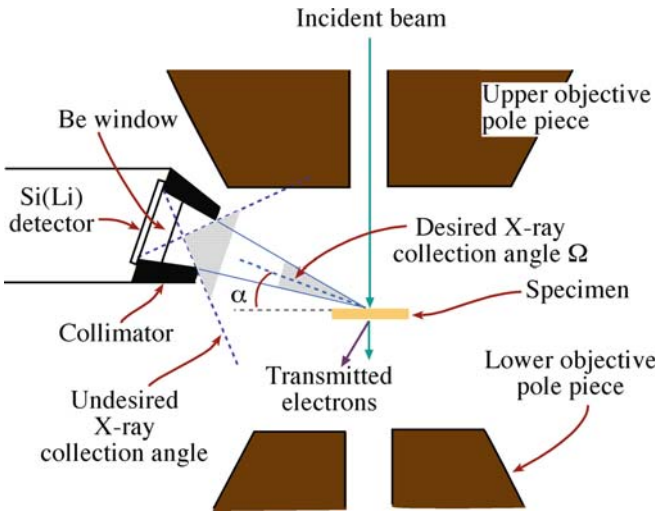

FIGURE 32.14. Schematic diagram of the interface between the XEDS and the AEM stage showing how the detector can 'see' X-rays from regions other than the beam-specimen interaction volume over the (relatively large) undesired collection angle. The (relatively small) desired collection angle Ω and take-off angle α are also shown.

It's worth checking if you have an ideal collimator, 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 minimizes the production of X-rays from backscattered electrons that happen to spiral into the collimator. The high-Z material absorbs high-energy bremsstrahlung. The inside of the collimator should be baffled to prevent any backscattered electrons from generating X-rays that then penetrate the detector. No collimator is entirely successful and we'll describe the contribution of system-produced X-rays in the next chapter.

THE COLLIMATOR
The collimator defines both the (desired) collection angle of the detector and the average take-off angle of X-rays entering the detector.

32.10.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 32.14 and is defined as

$$\Omega = \frac{A \cos \delta}{S^2} \tag{32.4}$$

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.

As we'll see, in most AEM experiments, it is the low X-ray count rate that limits the accuracy of the experiment. Commercial Si(Li) crystals have A values from 10 to 30 mm^2 and 50 mm^2 is becoming more common. As a result, values of Ω dictated by the closest distance between the specimen and detector/collimator 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 which reduces the collection angle by ~20%. IG detectors need a reflective window to prevent IR radiation from generating noise in the

detector. So, even with the largest detectors, Ω is a small fraction of the total solid angle of characteristic X-ray generation, which is, of course, 4π sr.

Ω

The value of Ω is the most important parameter in determining the quality of your X-ray analysis. You need three things for good AEM X-ray analysis: counts, counts, and more counts.

This value of Ω is calculated from the dimensions of the stage and the collimator. There is no way, however, that 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 NiO film and a known beam current. A useful figure of merit is the X-ray counts per second detected from a standard specimen, with a given beam current and 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 a beam energy of 100 keV, it is about 13,000 (Zemyan and Williams). 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. The advent of C_s-corrected AEMs has removed this limitation and will open up a new chapter in high count-rate X-ray analysis in AEMs (Watanabe and Williams). Arrays of SDDs have already been used to give solid angles >1 sr on PIXE systems (Doyle et al.), so the future of XEDS in the AEM has exciting possibilities.

32.10.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 32.14. Sometimes, it is also defined as the angle between the transmitted beam and the line to the detector, which is simply (90° + α). In the SEM/EPMA, we keep α high to minimize X-ray absorption in bulk specimens. Unfortunately, in an AEM, if we maximize α, the price we pay is lowering Ω. A high-angle detector has to be positioned above the upper objective polepiece and will be much farther 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 (counts, counts...).

In those AEMs where the detector has 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 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 EPMA is that absorption can usually be neglected. If absorption is a problem in your particular specimen, you can reduce the X-ray path length by tilting it toward the detector, thus increasing α (see Section 35.5). We don't recommend tilting because it increases spurious effects (see Chapter 33) and also lowers the *P*/*B* (peak to background) ratio in the spectrum.

TAKE-OFF ANGLE AND COUNTS

We would like to maximize the take-off angle *and* maximize the count rate, but we can't.

32.10.C Orientation of the Detector to the Specimen

There are two simple questions that you must be able to answer.

(a) *Is the detector pointing on axis?* The detector is inserted to a point 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. To find out if your system is thus aligned, take a low-magnification X-ray map from a homogeneous specimen, such as our thin NiO film. If the detector is not pointing on axis, the map will show an asymmetric intensity. Alternatively, if you can't map at a low enough magnification, simply see how the Ni K_α intensity varies from area to area on the foil with the stage 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 above or below the eucentric plane. Again, the maximum intensity should be recorded at eucentricity. If the intensity is asymmetric then the detector or the collimator is not well aligned and some of your precious X-ray counts are being shadowed from the detector, probably by the collimator. So you need to ask for technical help.

(b) *Where is the detector with respect to the image?* It is best if the detector is 'looking' toward a thin region of the specimen, rather than toward a thicker region, as shown in Figure 32.15A. This alignment minimizes the X-ray path length through your specimen. If the BF image rotates when changing magnification in your TEM then the apparent detector orientation with respect to the image (on the screen) will vary with

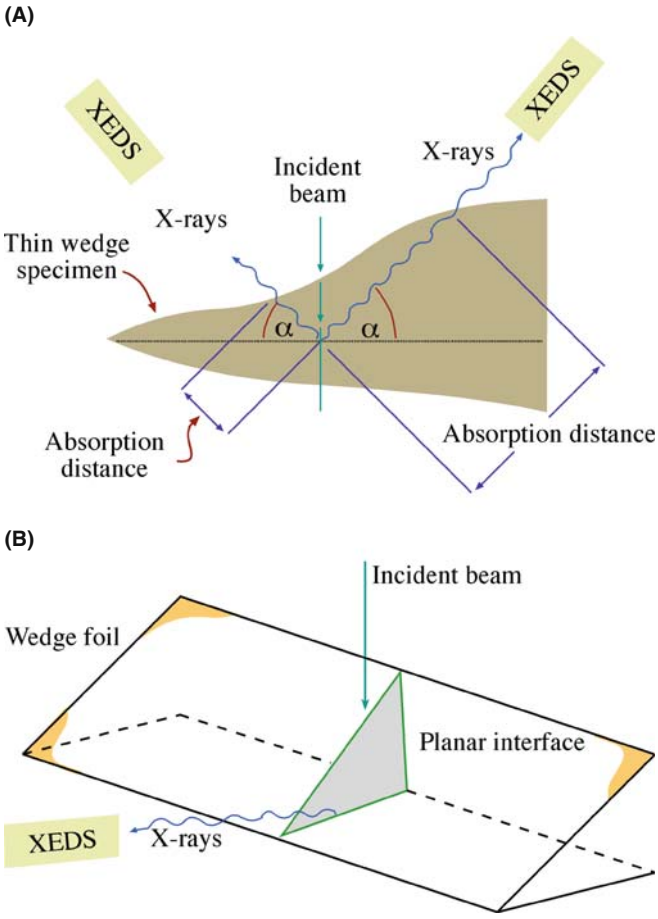

FIGURE 32.15. (A) The position of the XEDS relative to a wedge-shaped thin foil results in different X-ray path lengths. The shortest path length with the detector 'looking' at the thinnest region of the foil minimizes any X-ray absorption. (B) The preferred orientation of the XEDS when analyzing a planar defect: the interface plane is parallel to the detector axis and the incident-beam direction.

magnification. A STEM BF doesn't rotate so the relative orientation of the detector to your image is 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. If you press gently on the end of your holder, the image will move in the $+x$ direction. Then you can determine geometrically 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 might be rotated 180° with respect to the TEM image so you have to take this into account. But it's all a good exercise in 3D geometry.

If you're doing analysis or mapping across a planar interface, which is a common AEM application, then you should also orient your specimen such that the interface is parallel to the detector axis and the beam, so the detected X-rays have come through regions of similar composition and don't cross the interface. A tilt-rotation holder is ideal for this but, if a low-background version is not available, then you may need to take out the holder and re-position your foil manually a few times until the interface is in the right orientation (see Figure 32.15B).

LOOKING AT THE SPECIMEN

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

32.11 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 AEMs. As we've noted, these situations occur when you inadvertently move thick areas of your specimen under the beam, or if you are traversing around a thin specimen and the support grid hits the beam. To avoid these problems, shutter systems are built into most XEDS systems which automatically protect the Si(Li) crystal if the AEM is switched to low magnification or if the pulse processor detects too high a flux of radiation.

If you don't have a shutter then you can physically retract the detector to lower Ω (if it is retracted along a line of sight to the specimen) or remove 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. Also you may reposition your detector slightly differently each time, unless the system is designed so you can push the detector to a fixed stop, thus insuring a constant Ω and α. A shutter is highly recommended!

SHUT THE SHUTTER

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. Also, never have the objective aperture inserted.

CHAPTER SUMMARY

The XEDS (usually of the Si(Li) variety) is the only X-ray spectrometer currently used in TEMs. It is remarkably compact, efficient, and sensitive. A combination of Si(Li)/SDD and IG detectors can detect K_α lines from all the elements from Be to U. The XEDS is limited by its poor energy resolution, artifacts in the spectra, and the need for cooling, but it is simple to run and maintain. You must take care to perform certain basic procedures and refrain from certain others that can damage the detector. Sometimes, it may be too simple; beware. You need to

- Measure your detector resolution every 6 months at the Mn or Ni K_α line (at best 130–140 eV for Si(Li) or SDD and 120–130 eV for IG).
- Measure the ICC (FWTM/FWHM ratio of the Ni K_α line: ideally 1.82), every 6 months.
- Unless you have an SDD or a Peltier-cooled Si(Li), monitor ice build-up via in the Ni K_α/L_α ratio on a monthly basis.
- Check the calibration of the energy range of your computer display every 6 months especially if you have an SDD.
- Check the dead-time correction circuitry by the linearity of the output count rate versus beam current, every 6 months.
- Check the counts in a fixed clock time as a function of beam current to determine the maximum output count rate, every 6 months.
- Always operate with the shutter closed until you are ready for analysis.
- Always retract the objective diaphragm prior to analysis.
- Ensure the XEDS is pointing toward the thin edge of any wedge/disk specimen.

Interfacing your XEDS to the AEM is crucial since it determines the count rate, the need for an absorption correction, and the intrusion of spurious X-rays into your spectrum. In any decision involving XEDS in the AEM, you should always choose the option that optimizes the count rate.

For the sake of completeness, Table 32.2 shows you the relative merits of the various detectors that we have discussed in this chapter.

GENERAL TEXTS

Garratt-Reed, AJ and Bell, DC 2002 *Energy-dispersive X-ray Analysis in the Electron Microscope* Bios (Royal Microsc. Soc.) Oxford UK. Similar in scope to the XEDS chapters in this textbook.

Goldstein, JI, Newbury, DE, Echlin, P, Joy, DC, Romig, AD Jr, Lyman, C., Fiori, CE and Lifshin, E 2003 *Scanning Electron Microscopy and X-ray Microanalysis* 3rd Ed. Springer New York. In-depth treatment of all aspects of XEDS in the SEM/EPMA. Includes details of the electronics (Section 3.2.7)

Goodhew, PJ, Humphreys, FJ, and Beanland, R 2001 *Electron Microscopy and Analysis* 3rd Ed. Taylor and Francis New York. A broad introduction covering SEM, TEM, and AEM.

Jones, IP 1992 *Chemical Microanalysis Using Electron Beams* Institute of Materials London. Quantitative AEM; lots of calculations to illustrate the analytical principles; essential for the serious X-ray analyst.

Williams, DB, Goldstein, JI and Newbury, DE, Eds. 1995 *X-Ray Spectrometry in Electron Beam Instruments* Plenum Press New York. Tells all you need to know and more about X-ray detection and processing in SEM/EPMA (mainly) and TEM.

REFERENCES FOR THE CHAPTER

Doyle, BL, Walsh, DS, Kotula, PG, Rossi, P, Schülein, T and Rohde, M 2004 *An Annular Si Drift Detector μPIXE System Using AXSIA Analysis* X-Ray Spectrom. **34** 279–284. Illustrating the use of an array of SDDs.

Egerton RF and Cheng SC 1994 *The Use of NiO Test Specimens in Analytical Electron Microscopy* Ultramicrosc. **55** 43–54. As it says!.

Lund, MW 1995 *Current Trends in Si(Li) Detector Windows for Light Element Analysis* in *X-Ray Spectrometry in Electron Beam Instruments* DB Williams, JI Goldstein and DE Newbury, Eds. 21–31 Plenum Press New York. Detailed review of windows.

Lyman, CE, Newbury, DE, Goldstein, JI, Williams, DB, Romig, AD Jr, Armstrong, JT, Echlin, PE, Fiori, CE, Joy, D., Lifshin, E and Peters, KR 1990 *Scanning Electron Microscopy, X-Ray Microanalysis and*

Analytical Electron Microscopy; *A Laboratory Workbook* Plenum Press New York. Includes some standard tests for XEDS.

Michael, JR, 1995 *Energy-Dispersive X-ray Spectrometry* in *Ultra-High Vacuum Environments* in *X-Ray Spectrometry in Electron Beam Instruments* Eds. DB Williams, JI Goldstein and DE Newbury p83 Plenum Press New York. Using the Ni K_α/Ni L_α ratio.

Mott, RB and Friel, JJ, 1995 *Improving EDS Performance with Digital Pulse Processing* in *X-Ray Spectrometry in Electron Beam Instruments* Eds. DB Williams, JI Goldstein and DE Newbury 127–155 Plenum Press New York. Digital processing as we discuss in Section 32.7.

Newbury, DE 2006 *The New X-ray Mapping: X-ray Spectrum Imaging Above 100 kHz Output Count Rate with the Silicon Drift Detector* Microscopy and Microanalysis **12** 26–35. Using SDDs for mapping.

Sareen, RA, 1995 *Germanium X-ray Detectors* in *X-Ray Spectrometry in Electron Beam Instruments* Eds. DB Williams, JI Goldstein and DE Newbury 33–51 Plenum Press New York. IG detectors.

Statham, PJ 1995 *Quantifying Benefits of Resolution and Count Rate in EDX Microanalysis* in *X-Ray Spectrometry in Electron Beam Instruments* Eds. DB Williams, JI Goldstein and DE Newbury 101–126 Plenum Press New York. Balancing count rate and resolution.

Terauchi, M and Kawana, M 2006 *Soft-X-ray Emission Spectroscopy Based on TEM—Toward a Total Electronic Structure Analysis* Ultramicrosc. **106** 1069–1075. CCD-based WDS.

Terauchi, M, Yamamoto, H and Tanaka, M 2001 *X-ray Emission Spectroscopy, Transmission Electron Microscope, DOS of the Valence Band, Soft-X-ray Spectrometer, B K-emission Spectra, Hexagonal Boron-Nitride* J. Electr. Microsc. **50**(2) 101–104. Development of a sub-eV resolution soft-X-ray spectrometer for a transmission electron microscope.

Watanabe, M and Williams, DB 2006 *Frontiers of X-ray Analysis in Analytical Electron Microscopy: Toward Atomic-Scale Resolution and Single-Atom Sensitivity* Microscopy and Microanalysis **12** 515–526. C_s-corrected AEM.

Wollman, DA, Nam, SW, Hilton, GC, Irwin, KD, Bergren, NF, Rudman, DA, Martinis, JM and Newbury DE 2000 *Microcalorimeter Energy-Dispersive Spectrometry Using a Low Voltage Scanning Electron Microscopy* J. Microsc **199** 37–44. The bolometer for XEDS.

Zemyan, SM and Williams, DB 1995 *Characterizing an Energy-Dispersive Spectrometer on an Analytical Electron Microscope* in *X-Ray Spectrometry in Electron Beam Instruments* Eds. DB Williams, JI Goldstein and DE Newbury 203–219 Plenum Press New York. Summary of standard tests for XEDS.

URLs: SELECTION OF XEDS MANUFACTURERS

1) www.bruker-axs.de/
2) www.edax.com/
3) www.oxinst.com
4) www.pgt.com
5) www.thermo.com/

SELF-ASSESSMENT QUESTIONS

Q32.1 Define: XEDS, IG, SDD, AEM.
Q32.2 Explain in four steps how X-rays from the specimen are converted into a spectrum.
Q32.3 Distinguish between dead time, live time, and clock time.
Q32.4 Distinguish between dead layer(s) and active regions of detectors.
Q32.5 List four ways that you can damage your detector while you're operating the AEM.
Q32.6 What is more important during X-ray microanalysis and why: X-ray counts, X-ray energy resolution, X-ray take-off angle, or specimen tilt?
Q32.7 What is the best accelerating voltage to use for XEDS?
Q32.8 Why must Si detectors be doped with Li while IG detectors are not doped (Hint: what does the 'I' mean?)?
Q32.9 How does this Li affect the operation of the detector? Why is there no Li in a SDD?
Q32.10 What type of detector is better for detecting (a) high-Z materials, (b) lower-Z materials and why?
Q32.11 Why is pulse processing required to translate X-ray photons into a spectrum?
Q32.12 What is a reasonable dead time and how is this affected by the vintage of your detector electronics?
Q32.13 Why is digital pulse processing preferred over analog processing? Give one exception to this preference.
Q32.14 What advantage does XEDS have over WDS?
Q32.15 What are some of the disadvantages to XEDS?
Q32.16 Why is a large collection angle, Ω, useful? What limits the value of Ω in practice?
Q32.17 Why is a high take-off angle, α, useful? What limits the value of α in practice?
Q32.18 Why is a larger Ω more important than a higher α?
Q32.19 Why is the collimator so important in front of your detector?
Q32.20 What aspects of TEM design restrict the use of large arrays of detector crystals such as SDDs?
Q32.21 Why is it not a major issue that we cannot optimize the take-off angle α?

Q32.22 What materials are used in the collimator to avoid X-ray generation within the collimator and what might cause the generation of these X-rays in the first place?

Q32.23 You switch on your XEDS detector but you don't register any X-rays coming through the system. Explain what may be causing this situation.

TEXT-SPECIFIC QUESTIONS

T32.1 Explain what factors control the shape of the characteristic peaks and the background in a typical energy-dispersive spectrum such as Figure 32.2A.

T32.2 List three reasons why we cool Si(Li) or IG detectors with liquid N_2 and three undesirable consequences. Search the Web sites of the major EDS manufacturers to see if there are alternatives to liquid-N_2 cooling. Why do we not have to cool an SDD to liquid-N_2 temperatures?

T32.3 Explain why, in comparison to a Si(Li) detector, an IG detector exhibits (a) better energy resolution, (b) more resistance to high-energy electron damage, (c) less susceptibility to accidental loss of liquid N_2 and (d) better detection of high-energy X-rays. Given these advantages, why are IG detectors not more common on AEMs?

T32.4 Explain why, in comparison to a Si(Li) detector, a wavelength-dispersive (crystal) spectrometer (WDS) offers (a) better resolution, (b) more throughput of counts, (c) fewer artifacts. Given these advantages, why is the WDS not more common on AEMs?

T32.5 Why does the output X-ray count rate rise to a maximum and then fall as the input count rate continues to rise (as in Figure 32.12A)?

T32.6 So why don't we always operate the AEM at the maximum count rate (which would, inter alia, improve counting statistics, thus reducing errors), reduce the time required to acquire the spectrum (thus reducing damage to beam-sensitive specimens)?

T32.7 Consider the curves in Figure 32.12. Explain why the statements in the caption are true. (Are they?)

T32.8 Give examples of how the limitations of the curves in Figure 32.12A might be overcome?

T32.9 Explain why SDDs can operate at much higher count rates than other XEDS detectors.

T33.10 An engineer decided to remove the collimator baffles from her AEM. What does she put up with as a consequence?

T33.11 Why would it be good to have both the largest detector take-off angle and the highest detector collection angle? Why do we have to make a compromise choice in practice? Explain why correction of the spherical aberration coefficient of the objective lens would remove this compromise.

T32.12 Figure 32.9 shows a WDS system on a TEM. Why is it not commonly used now? (A careful discussion is required.)

T32.13 Look at Figure 32.9D. Why are the EDS peaks so much broader than those from the bolometer and could this possibly be improved?

T32.14 An image produced using a backscattered-electron detector shows the presence of three regions of significantly different contrast. Where should you begin to further analyze this specimen?

T32.15 A strong background appears in the 0–10 keV spectrum of a geological specimen. What is this specimen, and how can the high background be compensated for?

T32.16 Using a windowless detector it becomes apparent by comparing past and previous spectra of the same specimen that there is likely a coating of ice or hydrocarbons on the detector. Should you just thaw out the detector or not?

T32.17 After measuring XEDS spectra from a biological or polymeric specimen, you close your AEM session but find yourself physically unable to open the chamber to remove the specimen. What is likely to be the cause?

T32.18 You have decided to switch an IG detector in for the Si(Li) already in your microscope to identify X-ray lines above 20 keV. After the switch, you notice what appears to be a large increase in the number of escape peaks in your spectra. Name one reason why this might be happening.

T32.19 Barry and David are laughing about something you did in lab last week. You were attempting to optimize the energy resolution of the XEDS spectra you obtained. What is their point?

T32.20 Are there hidden peaks obscured by the low-energy edge of several of your more intense peaks and what can you do about it if there are?

T32.21 A novice at using the XEDS on the TEM decides to employ WDS instead, with the notion in mind that it wouldn't be such a bad thing to get more resolution for the spectra. Which rude awakening is this person close to discovering?

T32.22 A geological specimen is elementally analyzed using XEDS. This turns out to contain Si, Al, O, and Fe. Out of curiosity, an X-ray map in search of Cu is performed on this same region of the specimen. Multiple locations of Cu spring up in the map. Explain.