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Qualitative X-ray Analysis and Imaging

CHAPTER PREVIEW

It is a waste of time to proceed with *quantitative* analysis of your XEDS spectrum or image without first carrying out *qualitative* analysis. Qualitative analysis requires that *every* peak in the spectrum be identified unambiguously, with statistical certainty, otherwise it should be ignored for both subsequent quantitative analysis and imaging. We emphasize this point because of the many opportunities for the misidentification of small peaks in the spectrum. In this chapter, we'll deal initially with acquisition and identification of the elemental information in spectra and images. First, we will show you how to choose the best operating conditions for your particular AEM and XEDS system. Then we'll explain the best way to obtain a spectrum for qualitative analysis. You have to acquire a spectrum with sufficient X-ray counts to allow you to draw the right conclusions with a given degree of confidence. There are a few simple rules to follow which allow you to do this.

A QUALITATIVE MUST!
Although such an approach may seem time-consuming and unnecessarily tedious, the need for initial qualitative analysis of the spectrum cannot be stressed too strongly.

Two advantages are gained from rigorous qualitative analysis. First, you may be able to solve the analytical problem at hand without needing to perform full quantification. Second, when quantification is carried out (see the next chapter), you will not spend an inordinate amount of time analyzing an element that isn't there, and you can be confident that your results are valid. We'll go over the many ways to misidentify peaks in your spectra, particularly small ones, which may, in fact, arise from important trace elements but, which might be artifacts, could be peaks from another element, or are possibly statistically insignificant. Commercial peak-identification software, while improving all the time, is not error-free. We'll end with a few words about qualitative X-ray imaging.

34.1 MICROSCOPE AND SPECIMEN VARIABLES

When you first acquire a spectrum, the operating conditions should maximize the X-ray count rate to give you sufficient intensity in the characteristic peaks in your spectrum, in the shortest time, with the minimum number of artifacts. You need sufficient counts so you can detect, unambiguously, the presence of *all* the elements in your specimen (within the limitations of your XEDS detector) *with statistical certainty*. As we'll explain, the best conditions for such qualitative analyses require that you obtain the spectrum from a reasonably thick, large area of your specimen, using a large probe and a large aperture to give the most current, but in doing this you'll compromise other desirable analysis qualities, particularly high spatial resolution. So right up front you need to know two key points

- There are only three requirements for good qualitative analyses; counts, counts and more counts
- The conditions for the best qualitative (and quantitative) analysis (which are also those that give the best analytical sensitivity) are precisely the worst for obtaining the best spatial resolution.

A more complicated factor in getting the most X-ray counts in your spectrum is choosing the right operating voltage. Remember, back in Figure 33.10.C, we showed that you get a higher detection and collection efficiency if you decrease the kV because the scattering cross section (σ) increases when the kV decreases; that was a specimen effect. Now we are talking about a gun effect;

as the kV increases, the gun brightness increases (go back and check this in Chapter 5). While the two effects counter each other somewhat, the added advantage of an increased P/B ratio (which helps with detecting small peaks) with higher kV, as well as improved spatial resolution (due to less beam spreading), tips the scales in favor of using the maximum kV at all times. Only choose a lower voltage if knock-on damage is a problem, as might be the case, for example, in a 200–400 kV AEM with a beam-sensitive specimen such as a ceramic, a mineral, most semiconductors or a low-Z (<15) metal/alloy.

Pick a portion of your specimen that is single phase in the area of interest and make sure it is tilted well away from strong diffraction conditions to minimize crystallographic effects (more on this in Chapter 35) and coherent bremsstrahlung. Ideally, you will need a probe current of several tens of nanoamps. The necessary combination of probe size and final aperture depends on the type of source in your AEM. To get several tens of nanoamps from a LaB_6 source, you have to select a relatively large probe size, say, a few tens of nanometers and a large C2 aperture. An FEG source will give much less total current than a thermionic source and it won't be possible to generate more than a few nanoamps at best. So, for reasonable qualitative analysis and subsequent quantitative analysis, you'll have to accumulate your spectrum for a longer time with an FEG compared to a thermionic source. A C_s-corrector on your FEG-AEM will help tremendously, since a larger probe-forming aperture can be used without compromising the quality of the probe, and tens of nanoamps can be generated in a C_s-corrected probe of a couple of nanometers dimension. So if your institution has enough money to spend on your AEM you can minimize the otherwise necessary compromise between needing lots of counts and getting high spatial resolution

You can always gather more counts in your spectrum by choosing a thicker region of the specimen. There is nothing wrong with doing this when you are carrying out *qualitative* analysis. A thick specimen degrades your spatial resolution, but we've already agreed to compromise that aspect of the analysis during this initial qualitative procedure. The only danger is that, if you are interested in finding a few weight percent of a light element, those weak X-rays may be absorbed in your specimen and so may not be detected. However, from an experimental standpoint, having carried out qualitative analysis of a relatively large, thick region, you can always do further analyses of smaller, thinner areas, under conditions that optimize spatial resolution, which we'll discuss in Chapter 36.

Remember that we have been talking about several different 'resolutions'. Don't confuse them

- spatial resolution: distances measured in nm (see Chapter 36).
- chemical resolution: analytical sensitivity/detection limits depending on P/B (see Chapter 36).
- energy resolution: identifying elements by distinguishing their spectral peaks at different energies (see this chapter and Chapter 33).

So, just in case you haven't got the message by now, good qualitative analysis (and subsequent quantification) requires a large number of X-ray counts in the spectrum (just how many we'll tell you in a while). These counts might take a long time to generate, so you run the danger of damaging, or changing the chemistry of any beam-sensitive specimens. You may also contaminate your chosen area if your AEM is not UHV and/or your specimen is not clean. So it's always good to use a plasma cleaner before analysis, unless doing so will destroy your specimen. (Go and check Chapter 10 or the companion text where we talk about specimen preparation.) To minimize damage and contamination, you should spread the beam over as large an area as possible, either by overfocusing C2 if you're in TEM mode or by rastering the beam in STEM mode, remembering that, in doing so, your analysis will be an average over the chosen area. Use a liquid-N_2 cooled, low-background holder, especially if contamination is still a problem.

34.2 BASIC ACQUISITION REQUIREMENTS: COUNTS, COUNTS, AND MORE CAFFEINE

The first and most important step in qualitative analysis is to acquire a spectrum across the complete X-ray energy range. Analysis can often be accomplished using X-rays with energies from ~1 to 10 keV, and this is the typical range used in the SEM. However, the TEM has a much higher accelerating voltage, and the consequent increase in available overvoltage (remind yourself what this is. Hint: see Chapter 4) means that you can easily generate and detect much higher-energy X-rays. If you are using an intermediate-voltage AEM and a windowless IG detector, we noted in Chapter 32 that all the possible K_α lines from all the elements above Be in the periodic table can be detected.

ENERGY RANGE

The first thing to do is to adjust your computer display to the widest possible energy range. For a Si(Li) detector or an SDD, 0–40 keV is sufficient and for an IG detector, 0–80 keV may be more useful.

Of course, if you know the specimen you are analyzing, such a step may not seem essential, but it is still a wise initial precaution since unanticipated contaminants or trace impurities may be present. The next steps are the basics for acquiring a spectrum for qualitative analysis

- Collect a spectrum over, say, 0–40 keV for several hundred seconds (take a coffee break) and ascertain the actual energy range over which all the detectable characteristic peaks occur.
- If all the peaks that you can see are present in an energy range < 40 keV, re-gather the spectrum over that reduced range (take another coffee break), thereby improving the resolution of the computer display by lowering the number of eV per channel.
- The spectrum that you finally gather for qualitative analysis must be displayed with *no more than 10 eV per channel* resolution or better. A display range of 0–20 keV should be possible under these conditions (i.e., 2048 channels in total) in all but the most ancient of XEDS computer systems.
- If you have analog processing electronics, you can increase the counts in your spectrum by reducing the detector time constant to maximize the throughput. This step degrades the energy resolution of the XEDS but, for many qualitative analyses, this is not important. A digital system will automatically optimize the throughput of counts.
- Watch the dead-time readout while acquiring the spectrum to make sure you haven't chosen a combination of probe current and specimen thickness that overloads the detector electronics. Remember that you want to keep the dead time below about 50–60%, and an output count rate of around 10 kcps (analog) to 30 kcps (digital) is about the best that can be handled by current detector electronics under these conditions. This will rarely be a problem in thin-foil analysis!
- The total counts in this qualitative spectrum should exceed 1,000,000 *over the full energy range*. While this may seem a lot, at 3 kcps, it will take you just over 15 minutes to accumulate this number of counts (now it's probably time for a bathroom break, anyhow). So adjust the probe size/current, the size of the C2 diaphragm and (if possible) the specimen thickness until the count rate is sufficient.

When you've got a good high-count spectrum over a suitable energy range, there is a well-defined sequence of steps developed for analysis of spectra from the SEM (see Goldstein et al. as usual) that should be followed to ensure that you correctly identify each peak in the spectrum and disregard those peaks that are artifacts or are not statistically significant and we'll describe a modified form of this procedure for thin-foil specimens in the next section.

Figure 34.1 shows the effects of increasing acquisition time (i.e., increasing counts) on the visibility of small peaks. The longer the time, the better the quality of the spectrum. So coffee breaks can be very beneficial.

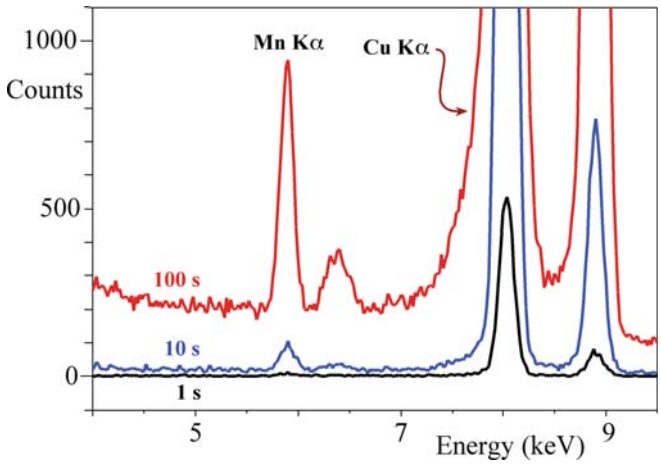

FIGURE 34.1. The improvement in the quality of a spectrum from a Cu-1% Mn thin foil with increasing acquisition time. After 1 s (black) the small Mn $K_{\alpha/\beta}$ peaks are not visible; after 10 s (blue) the MnK_{α} is detectable but the K_{β} is barely visible. After 100 s (red) all peaks are clearly visible. With increasing acquisition time it is generally much simpler to discern peaks from the background and specimen peaks from artifact peaks, so peak identification will proceed a lot more easily.

34.3 PEAK IDENTIFICATION

There are four key steps to running a successful qualitative analysis.

First: let's assume that you have read, understood, and applied the contents of Chapters 32 and 33. So you know what artifacts are likely to arise from your XEDS system and what system peaks occur in your AEM and you're aware of CB, etc. Now, ensure that the computer display is calibrated to be as accurate as the display resolution, over the energy range you've selected. If your spectrum is displayed at 10 eV per channel, the characteristic peak centroids must all be within ±10 eV of their true position on the energy scale.

Second: the computer system can be used to run an automatic identification check on the peaks in the spectrum, assuming the energy display is well calibrated. If the spectrum is simple, containing a few well-separated peaks, this automatic step may be all that is required. However, as we'll discuss in Section 34.5, misidentification occasionally occurs during such an 'auto-search' or 'peak ID' software routine. The more complex the spectrum, the more likely this is to happen, e.g., if the spectrum contains many peaks, particularly if peak overlap is occurring (e.g., Zn L_{α} confused with Na K_{α}) or if the spectrum contains complex peak families from heavier and/or rarer elements (e.g., Ta M_{α} confused with Si K_{α}). This problem is exacerbated if you don't understand the complexities of X-ray families or don't follow all the precautions that we'll go through below. In addition, even in the best software, small peaks may sometimes be missed and phenomena such as CB are often not taken into account.

THE KEY

For good qualitative analysis be suspicious. Don't just seek the peaks you expect, but be prepared to find peaks that you don't expect.

LABEL THE PEAKS

Take care to label each peak on the computer display or note it in your lab notebook when you have decided which element it comes from.

Remember, each X-ray is emitted with a very well-defined line energy (~ 1–5 eV wide) but the XEDS system degrades the line to a broad peak (FWHM ~ 80–180 eV over the energy range detected by a typical Si(Li) detector). So we'll talk about peaks in the spectrum, which correspond to X-ray lines emitted from specific elements and which are identified as belonging to families of lines that are superimposed by the computer software on the displayed spectrum.

Third: go back to Chapter 4 and remind yourself about things like critical ionization energy, X-ray line energy, K, L, M families of X-ray lines, relative weights of lines, fluorescence yield, etc., because we're assuming you know all of this backwards.

Our peak analysis will always include the following steps

- Look first at the most intense peak since this should be easiest to identify as a K, L, or M_α peak; then work on down through the associated family lines. If you can't identify the most intense peak easily then you've got a problem; e.g., the calibration is off or the electronics or software are not functioning correctly, so it's time to ask for technical help and go for yet more coffee.
- The most intense peak is also the most likely to have associated artifacts, such as an escape peak (1.74 keV below that peak energy in a Si(Li) system) and a sum peak (at twice the peak energy), so you can quickly remove such small peaks from the unknown list (most software now automatically notes the energy where these artifact peaks should appear).
- Go to the next most intense peak not included in the above step and repeat the search. Then repeat this exercise until all peaks are identified.
- Always think about pathological overlaps; look for spurious peaks, system peaks, and artifact peaks.

Fourth: the bookkeeping; in choosing the possible K, L, or M lines that could be present at a specific energy, you can either use the computer-generated X-ray line markers on the display or consult an appropriate source such as the 'slide rules' offered by most commercial manufacturers, or find them on the Web at, e.g., URLs 1 and 2. We introduced DTSA in Chapter 33 and it is great for comparing simulated spectra with acquired spectra, as well as for checking the specific energies of X-ray lines, particularly in the more complex families of lines in spectra from heavier elements. There's much more about DTSA in the companion text.

Good bookkeeping is essential during the identification sequence we will now describe, particularly if your spectrum contains many peaks.

So now we've outlined the principles, let's get down to the specifics. Follow this 8-step process

1. If a K_α line matches the peak, look for the K_β line which has about ~10% of the K_α intensity (this 10% is a line 'weight'; go back and check Table 4.1). With a modern XEDS, the K_β line *must* be present at X-ray energies above ~1.74 keV (Si K_α), so long as it is not overlapped by a more intense peak from another element. Below this energy, your detector may not be able to resolve the two lines.
2. If a K_α and K_β pair fits the peaks and the K_α energy is $>$ ~8 keV (Ni K_α), look for the L lines at ~0.9 keV if you are using a Be-window detector. For an UTW/windowless detector the L_α lines from Cl and above ($>$ ~ 0.2 keV) may be detectable but only if there's a lot of Cl, because (a) these relatively weak X-rays will be strongly absorbed and (b) their fluorescence yield is pretty abysmal. Ni L_α = 849 eV, Cl L_α = 200 eV.
3. If a K_α line does not fit, check for an L_α or M_α line fit since these are the most intense lines in the L and M families.
4. If an L_α line fits, there *must* be accompanying lines in the L family. The number of visible lines will vary depending on the intensity and energy of the L_α line, with more lines resolvable at higher line energies. The other lines in the family are all of lower intensity than the L_α line, and the following lines may be detectable (the number in parentheses is the weight relative to the L_α line); $L_{\beta 1}$ (0.7), $L_{\beta 2}$ (0.2), and $L_{\gamma 1}$ (0.08) lines at higher energies and possibly the Ll (0.04) line at lower energy. Other, even less intense, lines ($L_{\gamma 3}$ (0.03) and L_η (0.01)) may be visible if the L family is extraordinarily intense, but this is rare.
5. If the L lines fit, there *must* be a higher energy K_α/K_β pair, since the AEM beam energy is usually sufficient ($>$ 200 keV) to generate the K lines from all the elements in the periodic table. Make sure you choose a broad enough energy range to display them on your computer.
6. The M lines are usually only visible for elements above La in the periodic table if a Be-window detector is used, and above about Nb, if a UTW detector is used. Again there has to be a lot of Nb to pick up the weak M line. La M_α = 833 eV, Nb M_α = 202 eV.

7. The M_α/M_β line overlap is difficult to resolve because all the M lines are < 4 keV. If an M_α/M_β line fits, look for three very small lines M_ζ (0.06), M_γ (0.05), and $M_{II}N_{IV}$ (0.01) lines, which will be more visible if more of the element is present.
8. If the M_α line fits there *must* be a higher energy L line family and possibly the very high energy K lines may be detectable; again, this depends on the detector (IG is better for high kV lines), computer display (out to ~ 80 keV), and the accelerating voltage (higher is better).

Figure 34.2 shows the families of lines expected in the display range from 0 to 20 keV, giving you some idea of the distribution of families of elemental lines that you

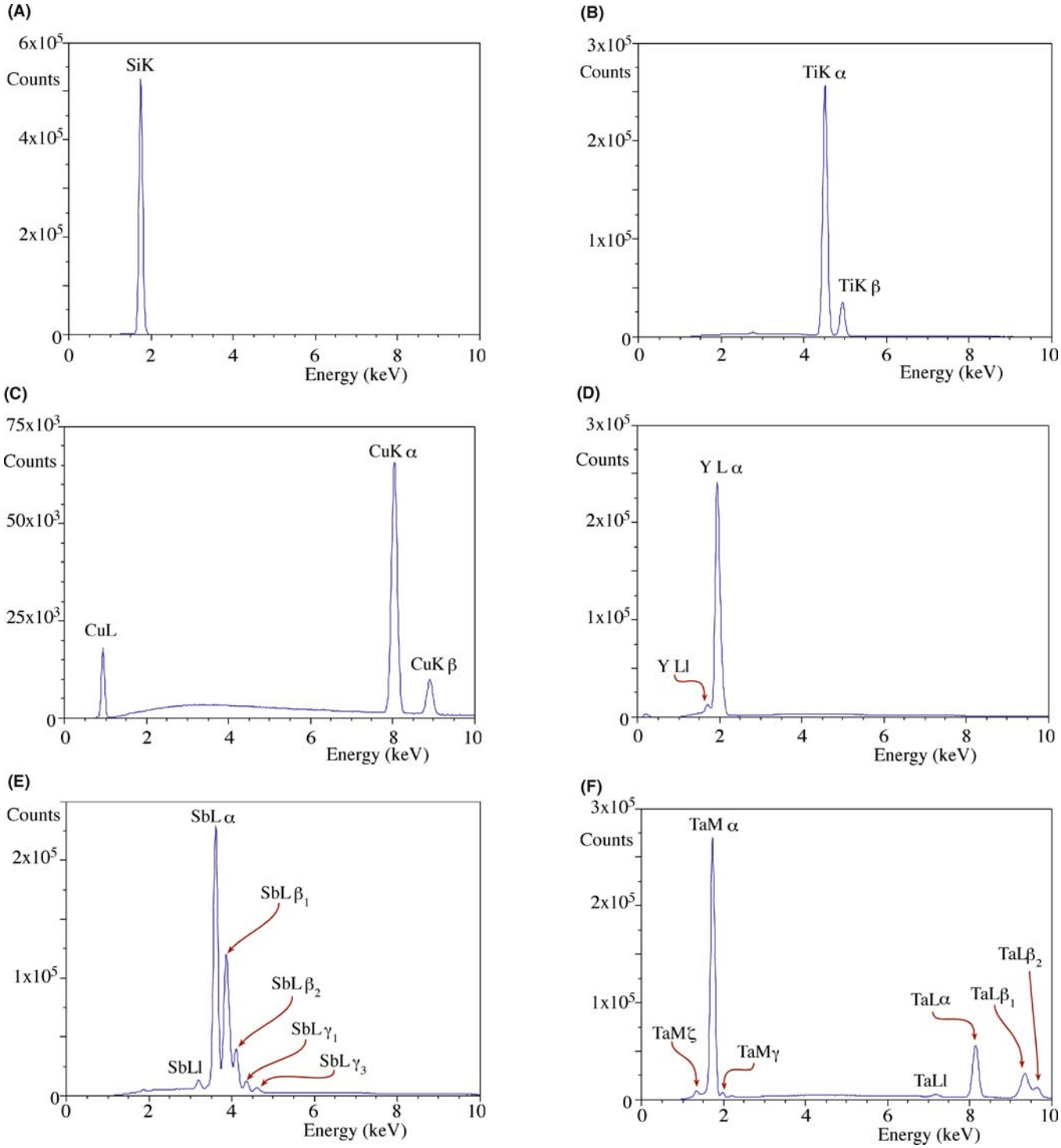

FIGURE 34.2. X-ray spectra from elements spanning much of the periodic table showing the families of characteristic lines for (A) Si, (B) Ti, (C) Cu, (D) La, (E) Sb, and (F) Ta. Starting with a single Si K_α line at low Z and low X-ray energy, the series progresses through the appearance of the families of L (Cu and La) and M (Sb and Ta) lines. Note the increasing separation of the peaks of a given family as both *Z* and keV increase.

should find when you follow the procedure outlined above. For example, you can see for which elements you should expect to see only a single K line or resolve the K_α/K_β pair, and for which elements you should expect to see both K and L families or L and M families.

FAMILIES OF PEAKS
Looking for **families** of peaks. If a family member is missing your identification may be wrong.

Reasons for a missing family member

- It may be overlapped by another peak. This is the most likely cause and you can possibly resolve it by
  (a) re-gathering the spectrum with a longer time constant (analog system only)
  (b) using peak deconvolution software (see Section 34.4)
  (c) using a higher-resolution technique, such as EELS (see Chapter 38)
- Your computer display range may be too small so the peak is cut off (easy to solve, although if you followed our instructions this should never happen)
- The keV of the beam is too low to excite the line (should never be a problem in an AEM, only in an SEM)

Repeat the exercise: Go to the next most-intense peak that has not been identified by the eight steps in the first search. Continue this process *until all the major peaks are accounted for*. As you go, remember again to look for the escape peak(s) and sum peak associated with each *major* characteristic peak that you have conclusively identified. However, these artifacts and any CB peaks will be very small and before you worry about them you should make sure that the small peaks are statistically significant and we discuss how to do this for all minor peaks in Section 34.5 below. If you have a Si(Li) detector you'll always find a small Si-K internal-fluorescence peak, the Si escape peaks will lie at 1.74 keV below major peaks in the spectrum, and will not occur for elements below phosphorus. For an IG detector there will be Ge internal-fluorescence peaks (possible K and L) and there may be both Ge K and L line escape peaks at the appropriate energy below major peaks (9.89 keV for the Ge K_α escape and 1.19 keV for the Ge L_α escape). If you suspect a sum peak at twice the energy of any major peaks then re-acquire the spectrum at a much lower dead-time ($< 20\%$) and see if the suspected sum peak disappears. If you suspect a CB peak then re-acquire the spectrum at a different accelerating voltage or specimen orientation and see if the small peak shifts.

Check for special cases: The relatively poor energy resolution of the XEDS detector means that there are several pairs of peaks that occur quite commonly in materials science specimens that cannot be resolved. These go by the delightful name of 'pathological overlaps' and include, inter alia

(a) the K_β and K_α lines of neighboring transition metals, particularly Ti/V, V/Cr, Mn/Fe, and Fe/Co
(b) the Ba L_α line (4.47 keV) and the Ti K_α line (4.51 keV)
(c) the Pb M_α (2.35 keV), Mo L_α (2.29 keV), and S K_α (2.31 keV) lines
(d) the Ti, V, and Cr L_α lines (0.45–0.57 keV) and the K lines of N (0.39 keV) and O (0.52 keV) detected in UTW/ATW or windowless XEDS systems.

PATHOLOGICAL OVERLAP
When it is impossible to separate two peaks even when you know they are both there.

These problems can often be solved by careful choice of the energy range on the computer display. For example, if you are only observing from 0 to 10 keV the S K/Mo L line overlap would be clarified by the presence or absence of the Mo K lines around 18 keV which, again, you should have seen in your first, broad energy-range, spectrum acquisition. If you suspect that any pathological peak overlaps are occurring in your spectrum, then re-gather under conditions that maximize the energy resolution of the detector system (i.e., longest (analog) time constant and low count rate (< 5 kcps)), and also maximize the display resolution to at most 5 eV per channel (you'll need more coffee).

34.4 PEAK DECONVOLUTION

If the overlap is still not resolvable, then you should run a peak deconvolution routine in your computer software (these are pretty standard and not much has changed since; see, e.g., Schamber 1981). Such routines are capable of detecting and resolving many of the classic materials science overlaps, such as the transition metal L lines and low-Z K lines and an example of such a deconvolution is shown in Figure 34.3.

In addition to deconvoluting any peak overlaps, it can be very useful to deconvolute the point-spread function of the XEDS detection system using a process called zero-peak deconvolution (which is analogous to the zero-loss peak deconvolution process used in EELS (Sections 37.5.A and 39.6)). Such a process is becoming increasingly popular in many imaging and spectroscopy techniques because of the development of various robust mathematical procedures (e.g., Janssen 1997)

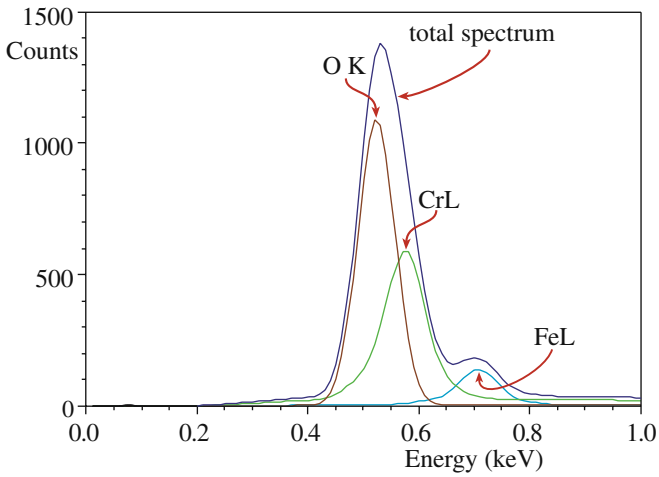

FIGURE 34.3. The total spectrum (dark blue) arises from the overlap of three Gaussian spectral peaks (the L_α lines of Fe (light blue) and Cr (green) and the O K_α line (brown)) from a mixed Fe-Cr oxide. Deconvolution of the individual contributions to the total spectrum is essential to determine the intensities in the three constituent peaks prior to any quantification attempt.

some of which are described in the companion text. In effect, this deconvolution removes the electronic-noise component of the characteristic peak width, giving a spectrum with nearer to noise-free resolution (Watanabe and Williams). This process requires that your XEDS system must display the noise peak at 0 eV in the spectrum (which not all manufacturers do) and this is called the 'strobe peak'. An iterative process can, in effect, remove the noise in your spectrum. As shown in Figure 34.4, this process obviously improves energy resolution but also improves the P/B ratio (and thus the minimum detection limit, as we'll see in Chapter 36) and can reveal peaks that would otherwise be masked by adjacent, more-intense, peaks.

Now, you always have to be careful with deconvolution, since any mathematical manipulation can introduce its own artifacts, while otherwise improving the spectrum quality. So it's best to practice deconvolution on both simple and complicated spectra that you know and understand well, until you feel confident that you understand the strengths and limitations of the procedure available in your particular software package.

Given all these steps and the multiple decisions that you have to make, it's clear that qualitative analysis can be an extraordinarily difficult procedure even for the

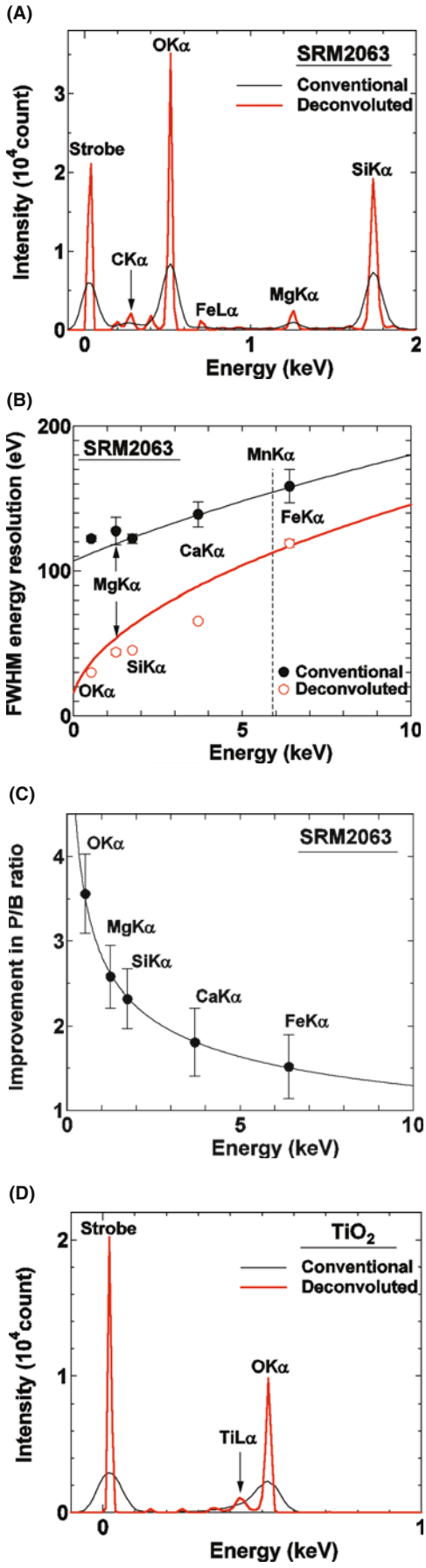

FIGURE 34.4. (A) The effects of deconvoluting the zero-energy strobe peak from an experimental XEDS spectrum of NIST SRM 2063. (B) The consequent reduction in peak FWHM (i.e., improvement in energy resolution) across the energy range 0–10 keV. (C) The improvement in P/B ratio of the major peaks in the SRM 2063 spectrum as a result of deconvolution. (D) Revealing the L_α peak from Ti in TiO_2, which is usually hidden by the O K_α.

most experienced analyst. This complexity is one reason why even the best software gets it wrong sometimes (see Section 34.6). So, as we said at the start, be suspicious!

In summary, applying the 8-step process, with appropriate deconvolution where needed, should permit you to identify all the major peaks in your spectrum. There might still be minor peaks, which may or may not be statistically significant, and you have to decide whether you are going to identify or ignore these peaks. Now we'll tell you how to make this decision.

34.5 PEAK VISIBILITY

Small intensity fluctuations are often present in your spectrum that you cannot clearly identify as peaks. In this case, there is a simple statistical criterion (Liebhafsky et al.) that you can apply to ascertain if the peak is statistically significant or if it can be dismissed as random noise. You must count for a long enough time so that the bremsstrahlung intensity is smooth and any peaks are clearly visible, as summarized in Figure 34.5.

- Increase the display gain until the average background intensity is half the total full scale of the display, so the small peaks are more easily observed.
- Get the computer to draw a line under the peak to separate the peak and background counts.
- Integrate the peak (I_A) and background ((I_A^b)) counts over the same number of channels; use FWHM if it can be discerned with any confidence; if not, then the whole peak integral will do.

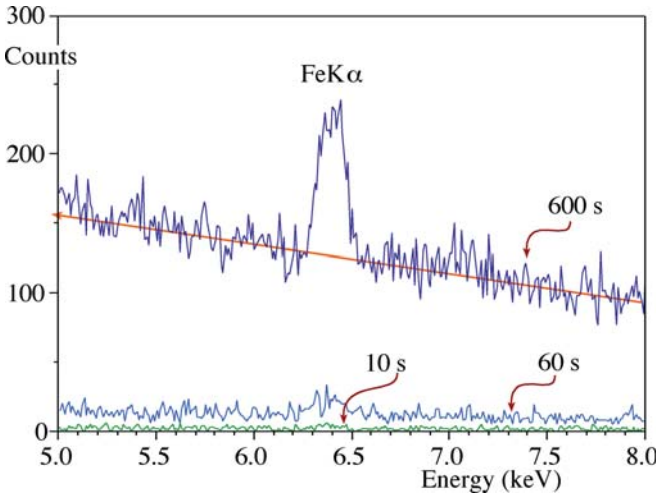

FIGURE 34.5. With increasing counting time, a clear characteristic Fe K_α peak develops above the background in these spectra from Si-0.2% Fe, thus demonstrating the need to acquire statistically significant counts before deciding if a peak is present or absent. As indicated (orange line), the background in the 600 s spectrum approximates to a straight line making the peak clearly visible. Note that Fe K_β is beginning to appear at 7.05 keV, although it is not yet statistically significant.

If $I_A > 3\sqrt{I_A^b}$ then the peak is statistically significant at the 99% confidence limit and must be identified. Remember, you'll still make an erroneous peak identification in ~ 1% of analyses using this criterion; just hope it isn't the one that derails your PhD or gets you fired!

If $I_A < 3\sqrt{I_A^b}$ then the peak is not significant and should be ignored.

If the insignificant peak is at an energy where you expect a peak to be present, but you think there is only a small amount of the suspected element in your specimen, then *count for a longer time* to see if the statistical criterion can be satisfied in a reasonable length of time. If this peak is a critical one, and it is often the minor or trace elements that are most important, then take *whatever time is necessary* to detect the peak. There is no reason not to gather the spectrum for many minutes or even an hour or more, so long as doing so does not change/damage or contaminate your specimen. Lunch breaks now become beneficial.

TIME

When you count for long times to search for characteristic peaks of low intensity, you will also begin to detect more easily the small peaks from the various spurious effects; e.g., CB peaks, Si or Ge internal-fluorescence peaks, and system peaks such as Fe and Cu. You also increase the possibility of contamination and beam damage to your specimen.

However, do *not* obtain more counts by raising the count rate above that which the processing electronics can handle, because you may introduce extra sum peaks and also degrade the energy resolution of the spectrum.

If you're worried about damaging the analysis area, as we stated at the beginning, it is best to spread the probe over as large an area as possible, either by defocusing the C2 lens in TEM mode or by using a scan raster in STEM mode.

Identifying the statistically significant peaks by the above method is one thing. Quantifying the amount of the element responsible for the peak is another matter and usually many more counts are required, as we'll see when we talk about detection limits in Chapter 36. However, once you're happy with the peak ID, you may be able to identify the phase/nanoparticle/precipitate that is being analyzed without any further work. For example, in the material that you are investigating, thermodynamics may tell you that there are only a few possible phases that can exist after the processing/thermal treatment given to it, and these phases may have very different chemistries. A glance at the relative peak intensities may be sufficient to conclude which phase you have just analyzed because, as we'll see below and in

more detail in the next chapter, one of the marvelous advantages of thin-foil analysis in the AEM is that the peak intensities are often directly proportional to the elemental concentrations. As a result, quantification can be extremely simple.

To conclude this section, we'll look at two examples before going into the details of quantification in the next chapter.

The oxide-glass example: let's run a qualitative analysis on the spectrum in Figure 34.6. The spectrum is from a thin NIST oxide-glass film on a carbon support film on a Cu grid. X-rays were accumulated for 1000 s with a Be-window, IG detector at an accelerating voltage of 300 kV. Because of the Be window, we do not expect to see lines below ~0.8 keV and so the O K_α (0.52 keV) will not be detectable. The spectrum only contained peaks in the range from 0 to 10 keV and the first peak to be examined was the most intense high-energy peak, line #1, which was consistent with the Si K_α line at 1.74 keV. (The K_α/K_β pair cannot be resolved by the detector at this energy.) A similar treatment of the next most intense high-energy line (#2) at 3.69 keV produced a match with the Ca K_α and it is also possible to identify the associated K_β at 4.01 keV (the Ca L line is not detectable). The third most intense line #3 is at an energy of 6.4 keV. The K-line markers identified it, along with the smaller one to its right, as being the Fe K_α and K_β pair. No L line fit was reasonable (Dy L_α at 6.5 keV being the only alternative) and there are no M lines above about 4 keV. The Fe L line at 716 eV will not be detectable because of the Be window.

Next, the smaller peaks were tackled and the Cu K_α (and K_β) was identified at 8.04 keV, the Ar K_α at 2.96 keV (the K_β was too small to be visible), and the Mg K_α was the last to be identified at 1.25 keV.

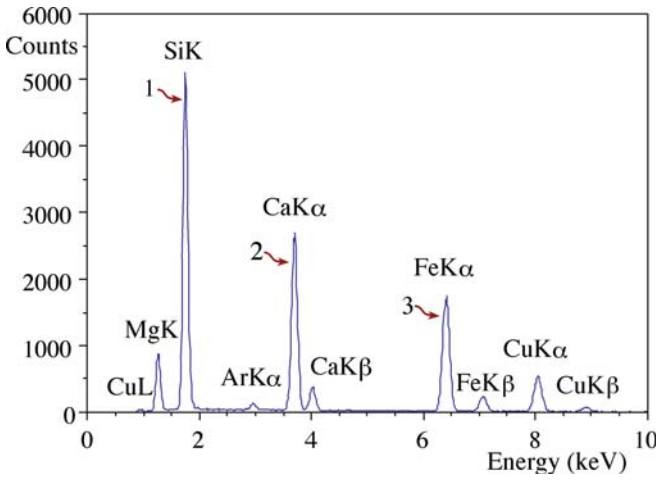

FIGURE 34.6. Energy-dispersive spectrum obtained at 300 kV from a thin oxide-glass film. The characteristic peaks were identified through the procedure outlined in the text.

Mg (as its oxide) is a common element in glasses, so this peak is expected. But Ar isn't such a common element in glasses. It probably arises from Ar implanted during ion-beam thinning and, as we discussed earlier and in detail back in Chapter 10, many specimen preparation processes can affect the chemistry of the specimen surface. You should also be aware that Ar K at 2.96 keV is often confused with the Al K sum peak (2×1.49 keV). But since there is no Al in the glass, and no major peak at half the Ar K energy, then Ar is the best answer.

SPECIMEN PREPARATION

Now you see why it is very useful to have some knowledge about your specimen and how it was prepared.

Likewise, Cu is not a common glass-forming element, but, since the specimen was on a Cu support grid, the Cu peaks are most probably due to post-specimen scatter of electrons or X-rays and so we cannot conclude that there is any Cu within the specimen. No escape or sum peaks were detectable.

ABSENCE OF THE Cu L_α Line

The absence of the line at 0.93 keV in Figure 34.6 is evidence that the thick Cu grid is responsible for a Cu line; the low-energy L X-rays will be absorbed in the grid itself before they can be detected.

The Fe-Cr-Ni example is shown in Figure 34.7 and this spectrum contains six Gaussian peaks, which can easily be identified following the procedure outlined above as the K_α and K_β pairs from Fe, Cr, and Ni. Even the average metallurgist will know that this specimen can only be some kind of stainless steel and this may be all the information that is required, making subsequent quantitative analysis redundant. But if you need more information, e.g., the specific grade of stainless steel, then you have to make measurements of the relative peak intensities, and this is the first step in the quantification procedure. In fact, we will see in Chapter 36 that the thin-foil quantification equation, to a first approximation, predicts that the amount of each element is directly proportional to the peak height. If you measure the relative heights of the K_α peaks in Figure 34.7 with a ruler, you can estimate the composition as ~ Fe-20% Cr-10% Ni which is within 10% of the classic 316 stainless composition of Fe-18% Cr-8 % Ni.

One real advantage of thin foil X-ray analysis is that you can get a good estimation of the composition of the analysis volume just by measuring the relative peak heights with a ruler.

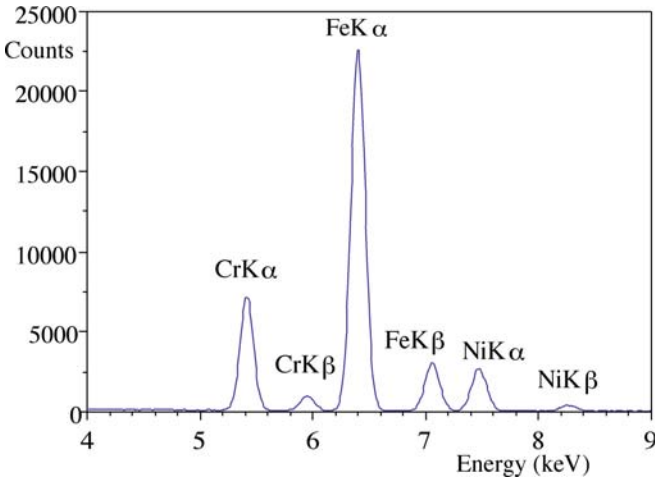

FIGURE 34.7. Spectrum from a stainless-steel foil in which the peaks are resolved and quite close in energy. To a first approximation, quantification is possible simply by measuring the relative heights of the K_α peaks.

Now there must be a good reason why, despite the fact that a 50-cent plastic ruler can give you a reasonable quantitative analysis of your spectrum in a few seconds, all AEMs have tens of thousands of dollars of computer hardware and software attached to the XEDS detector. This is because the stainless-steel spectrum is not really a challenge since all the peaks are close in energy, the peaks have lots of counts in them and there are no small peaks from trace elements. If the peaks were far apart in energy then relative X-ray absorption might occur, which can change the simple relationship between peak height and composition. Also if we really wanted to be sure that we had 304 rather than 316-stainless steel, then we would need a full quantification using the procedures described in the next chapter. If you were to do this, then you'd find that a full quantification would give a very similar result, but you could have much greater confidence in the true composition.

34.6 COMMON ERRORS

As we've seen, there's lots of room to misidentify peaks, particularly small ones that may be one of the many artifacts from the detector, the processing electronics, or the AEM-XEDS system. The first thing to realize is that if you (or even your advisor) can make mistakes, then the software can also do so. Remember, the software is only as good as the programmer. So while commercial automated peak-ID software is generally outstanding and getting better with every iteration, don't automatically believe it is always correct. By all means, as we said right at the start of Section 34.3, push the peak-ID button and get a quick analysis of your spectrum, but after you've done that, you might want to read the paper by Newbury which indicates some errors produced by a range of software systems. (See also the subsequent discussion noted in that reference.) The specimens used by Newbury to show the errors were often quite complex, with multiple peaks from rare, high-Z elements, but the article is instructive and illustrates the point that simply believing the software output is not always wise and suspicion is healthy.

As we've mentioned, it can be really useful to know something about your specimen chemistry *before* you put it into the AEM (and of course the TEM should be just about the last technique you use to study a completely unknown foil). It can also be very useful to remember how your specimen was thinned, since most thinning methods can change the surface chemistry of the foil. For example, electro-thinning methods can preferentially remove, or re-deposit one element from the foil or leave surface residue from the polishing medium. The thinner the foil is the more such changes in surface chemistry are exacerbated. Likewise, ion-beam thinning can result in the implantation of Ar, and FIB thinning can do likewise for Ga. So your foil may oxidize preferentially during thinning or pick up Cl from the perchloric-acid polishing solution, and so on. Ultramicrotomy is about the only method of thin-foil preparation that doesn't change the surface chemistry (although the freshly cut surface may be prone to rapid corrosion in the atmosphere and the defect structure is seriously changed from the bulk sample). So always be suspicious.

34.7 QUALITATIVE X-RAY IMAGING: PRINCIPLES AND PRACTICE

Individual-point analyses or multiple-point profiles across an interface are not the only ways to display X-ray data. As we saw in the previous chapter, we can produce X-ray images by a variety of methods and, if you are careful, such images can be used as compositional maps in which the intensity of the signal in the map is directly proportional to the generated X-ray intensity I_A. Under most circumstances, as we just described, we can take the next step and assume that, to some reasonable degree of accuracy, the X-ray intensity from element A in a thin foil is proportional to the concentration C_A. But there are some limitations to drawing a direct correlation, which we'll deal with in the next chapter on quantitative analysis. While there are obvious advantages to comparing maps of elemental distributions with other TEM images, this process is limited by the relatively poor statistics of X-ray acquisition, as should be eminently obvious to you by now. As you'll see in the next chapter, good quantification requires ~10,000 counts in the characteristic peak from element A, I_A. In early AEMs, such intensity

would easily take you a minute or so to acquire, even if there was a large amount of A present in your specimen. At this acquisition rate, even a 56×56 pixel image would take 50 hours to gather, so imaging didn't see a lot of practitioners and we just had to make do with qualitative, noisy maps, as shown back in Figure 33.13. However, as we've told you already, a lot has changed in recent years to improve the X-ray acquisition rate. First, to generate more X-rays, we have intermediate-voltage FEGs and spherical-aberration correctors to permit larger final apertures while maintaining small probes sizes. Second, to permit greater throughput of X-rays, we have developed digital pulse-processing, larger X-ray collection angles, and SDD arrays. Consequently, particularly if you can get away with using a reasonably thick specimen, X-ray mapping is a viable option on most modern AEMs where digital-display technologies and new image-processing software also makes life much easier.

The older X-ray dot maps, such as in Figure 33.13, simply register a dot when an X-ray is registered in a particular energy window in the XEDS spectrum. It doesn't matter whether the X-ray is a characteristic X-ray, a bremsstrahlung X-ray, a spurious X-ray, or a system X-ray, it is still registered, so problems like thickness or atomic number effects can occur since thicker/higher-Z specimens will generate more bremsstrahlung (as well as more characteristic) X-rays. These problems are a lot greater in bulk-specimen, SEM X-ray imaging, which has grappled with these issues for many decades (summarized in 1990 by Newbury et al.). To account for all these effects, a full quantitative procedure has to be applied to the intensity in each pixel and we'll cover this in detail in the next chapter.

For qualitative mapping, gray-scale images are still acceptable, but for full quantification, there is no way around the use of full-color images because of the many more color signal levels that your eye can discern and the advantages of color overlays to compare maps of different elements, and an example is shown in Figure 34.8, where the final RGB color image shows the chemical inhomogeneity of the Au-Pd nanoparticles, thus giving insight into why they work as catalysts for the peroxide-synthesis process. (Similar qualitative maps were shown in Figures 33.14 and 33.15.)

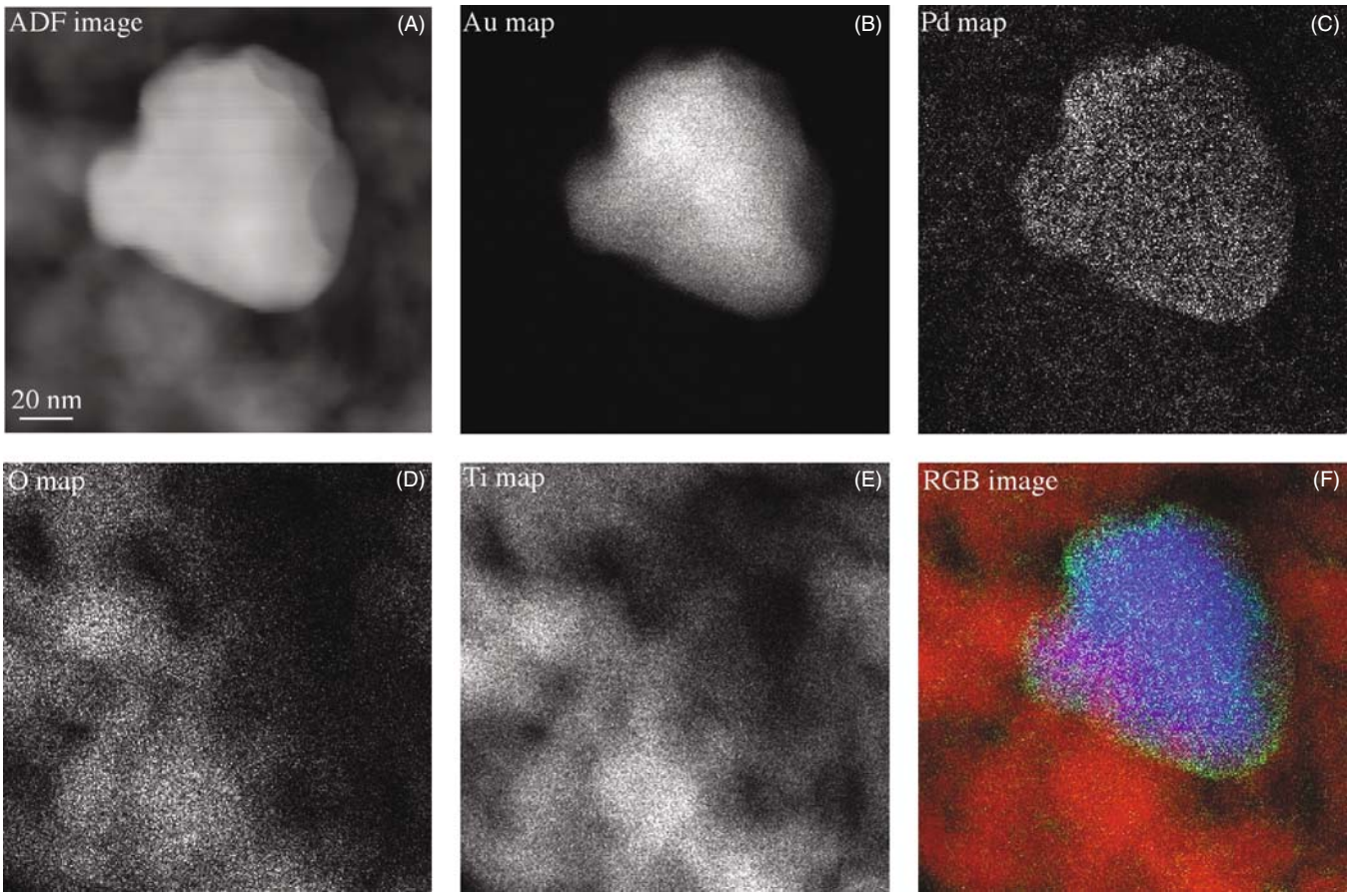

FIGURE 34.8. (A) STEM ADF image and qualitative X-ray maps showing the distribution of the (B) Au, (C) Pd, (D) O, and (E) Ti in a Au-Pd/TiO_2 catalyst nanoparticle. Such particles are used for peroxide synthesis. (F) The overlay of the color images from Ti (red), Pd (green), and Au (blue) reveals the core-shell nature of the particles with Pd on the outside and Au on the inside.

So how do you acquire a qualitative map like Figure 34.8?

- First you have to be in STEM mode, so your beam is scanning the specimen under digital control. Then select the largest probe size that will be still compatible with the desired X-ray image resolution. (Mapping with < 5 nm spatial resolution as in Figure 34.8 is challenging (see Chapter 36 on the factors controlling spatial resolution)). Only the best intermediate-voltage FEG instruments approach 1–2 nm, so a 5 nm probe would be a good start.
- Second, select a region of the X-ray spectrum that you want to map (e.g., set a window around a principal characteristic peak).
- Third, set a dwell time for the probe at each pixel that will permit sufficient X-ray counts to be acquired. Much more than a few seconds/pixel will make the acquisition time rather long, and < 0.1 s is only worthwhile if you have an intermediate-voltage FEG. (The best aberration-corrected FEG-AEMs can gather acceptable maps with dwell times of < 10 ms/pixel.) But, unless you have access to one of these instruments, start at about 1 s/pixel and gather a 64×64 pixel map and this will take you just over an hour. Do all the things we've told you to maximize the count rate: large beam diameter, large C2 aperture, and shortest (analog) pulse-processing time (this will minimize the chances of the processing electronics rejecting any of the few counts that are generated in such short dwell time).
- Last, start the scan and allow the map to commence building up on the computer display. If the intensity is acceptable and useful gray-scale information is obtained, it might be worthwhile to stop and regather the map for a longer period of time, e.g., for several hours, or even overnight, if it is a crucial map, However, for such long mapping times, you'll need to apply drift-correction software so that the map comes from the intended region of your specimen. Also it is obviously paramount that your specimen and AEM are clean, otherwise carbon contamination will build up to the point where the X-ray detection can be compromised, Also, as we've now told you innumerable times, specimen damage/contamination becomes an issue with longer scan times.

There are many other things you can do with the quantitative-analysis software and, given the time involved for even a simple qualitative map as just described, it's probably only worth doing fully quantitative maps. So we'll return to this technique in a lot more detail after you've learned all the steps necessary to translate the X-ray intensity into the elemental composition.

CHAPTER SUMMARY

One last time; doing the qualitative analysis first is not an option. The following steps are essential

- *Always be suspicious of any small peaks.*
- Get an intense spectrum across the energy range that contains all the characteristic peaks.
- Starting at the high-energy end of the spectrum, identify all the major peaks and any associated family lines and artifacts.
- If in doubt, collect for a longer time to decide if the intensity fluctuations are in fact peaks.
- Beware of pathological overlaps and be prepared to deconvolute any that occur.
- If you have the time, take a qualitative image using any crucial X-ray peaks.

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URLs

1) http://microanalyst.mikroanalytik.de/index_e.phtml
2) http://www.cstl.nist.gov/div837/Division/outputs/DTSA/DTSA.htm

SELF-ASSESSMENT QUESTIONS

Q34.1 Why is it important to know the relative weights of characteristic X-ray family lines?
Q34.2 Why can't we predict the relative weights of the lines in different X-ray families (e.g., the K_α/L_α ratio) while we can predict the ratios within a family (e.g., K_α/K_β?)
Q34.3 Why should you identify the largest, high-energy X-ray peak first?
Q34.4 What factors determine whether or not an X-ray peak is visible?
Q34.5 What units give a good measure of the total efficiency of X-ray generation and detection?
Q34.6 Why should you do qualitative analysis anyhow?
Q34.7 What are the three kinds of resolution we worry about in XEDS analysis and how do they rank in importance?
Q34.8 Why is careful bookkeeping so important when doing qualitative analysis?
Q34.9 Why is it essential to calibrate your XEDS display and how often should you do it?
Q34.10 Why is Ray Dolby equally applauded by TEM and audio enthusiasts?
Q34.11 Why is it necessary to define a minimum criterion for peak visibility?
Q34.12 State the minimum visibility criterion.
Q34.13 Why would you choose a 99% confidence limit for peak visibility rather than a lesser value and what does this 99% confidence limit mean?
Q34.14 Why are you wasting your time if you gather spectra for very long times (such as overnight) in order to maximize the counts in the spectrum?
Q34.15 Why are characteristic-peak overlaps described as 'pathological'?
Q34.16 List a few key pathological overlaps that might affect you if you are a metallurgist.
Q34.17 Why do X-ray spectra get more complex as your specimens get higher in atomic number?
Q34.18 If you can't conclusively identify a small peak in the spectrum, what should you do?
Q34.19 If you can't conclusively identify a large peak in your spectrum, what should you do?
Q34.20 Can you think of an occasion when qualitative analysis might preclude the necessity for future quantitative analysis?

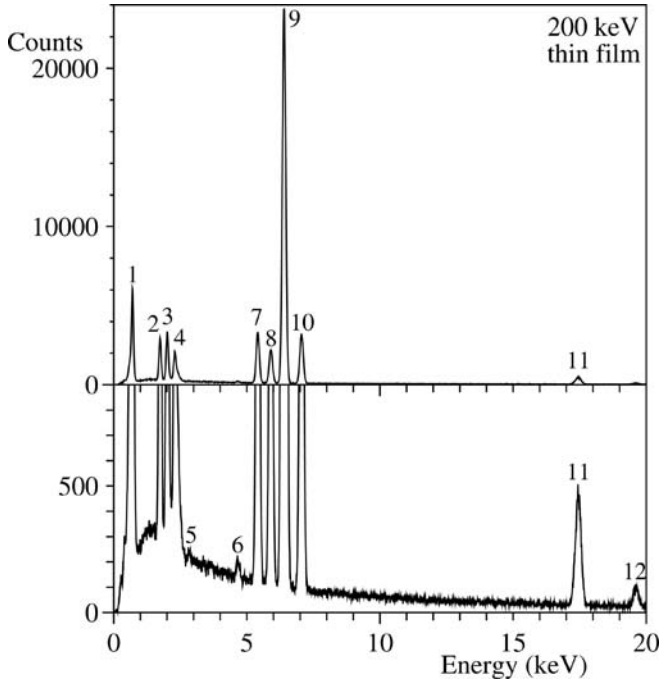
TEXT-SPECIFIC QUESTIONS

T34.1 Using Figure 34.2 as a basis, list the key characteristics of each of the principal families of lines that we see in XEDS spectra between 0 and 10 keV.
T34.2 Why don't we see N X-ray lines?
T34.3 There isn't an Fe K_β peak in Figure 34.5. Should you be concerned? If you are concerned, what should you do to lower your blood pressure?
T34.4 If you acquire spectra from a Ni jet-polished disc, why does the NiK_α/NiL_α ratio vary as you move the probe away from the thin edge surrounding the hole in the specimen?
T34.5 If you are analyzing an electropolished Al-Cu thin foil, why might the Cu signal increase substantially at the thinnest edges of the foil? (Hint: go back and look at Chapter 10.)
T34.6 Why is it difficult to analyze spectra from transition elements adjacent to one another in the periodic table, especially if the lower-Z transition metal is present in significantly greater amounts?
T34.7 When acquiring a qualitative spectrum from an unknown specimen, explain why you use as large a probe size as possible.
T34.8 When acquiring a qualitative spectrum from an unknown specimen, explain why you use as short a time constant as possible.
T34.9 When acquiring a qualitative spectrum from an unknown specimen, explain why you count for as long as possible.
T34.10 No. 13 of Murphy's Law of Microanalysis* states that 'The probability of detecting argon in aluminum decreases with time'. Justify the validity of this law. (*Copyright Kevex Inc.; reproduced with permission.)

T34.11 Look at the spectrum in Figure 34.6 and explain why

- you cannot confuse the Si K_α peak with the Si internal fluorescence artifact peak?
- the Cu K and L lines are from the Cu support grid and not from Cu in the specimen?
- the Cu L_α peak is present but not the Fe L_α peak?
- the Ar peak is not an artifact? Explain from whence it came.
- the Ca K_α and K_β peaks (at 3.69 and 4.01 keV, respectively) are not, in fact, the Sn L_a and L_β peaks (at 3.66 and 4.13 keV)?
- the Ca K_α and K_β peaks are not in fact the Te L_α and L_β peaks (at 3.77 and 4.03 keV)?
- there are no detectable escape and sum peaks?

T34.12 Look at the following spectra (which are really two different 'magnifications' of the vertical (counts) scale of the same spectrum to reveal both the small peaks and more intense peaks). This was taken from a thin-foil specimen in a 200-keV AEM with an ATW-XEDS Si(Li) detector. Carry out a qualitative analysis and identify unambiguously all the peaks labeled as #1–#12. When you have successfully finished the qualitative analysis of the above spectrum, use DTSA and try to reproduce this same spectrum.



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