Qualitative X-ray Analysis

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CHAPTER PREVIEW

It is a waste of time to proceed with *quantitative* microanalysis from your XEDS spectrum without first carrying out *qualitative* analysis. First we will show you how to choose the best operating conditions, for both the microscope and the XEDS system. Then we will explain the best way to obtain a spectrum for qualitative analysis. Qualitative analysis requires that every peak in your spectrum be identified unambiguously, and with statistical certainty, otherwise it should be ignored. So you have to acquire a spectrum with sufficient X-ray counts to allow you to draw the right conclusions with confidence. There are a couple of simple rules to follow which allow you to do this.

> 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 this approach. First, you may be able to solve the problem at hand without the necessity of a full quantification routine. Second, when quantification is carried out, you will not spend an inordinate amount of time analyzing an artifact or a statistically insignificant peak, and you can be confident that your results are valid.

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34.1. MICROSCOPE VARIABLES

When you first acquire a spectrum, the operating conditions should maximize the X-ray count rate to give you the most intensity in the spectrum, in the shortest time, with the minimum of artifacts. In addition, you want to get a good idea of which elements in your specimen are detectable. The best conditions for qualitative analysis require that you obtain the spectrum from a large area of the specimen, using a large probe, and so spatial resolution will be poor. Having carried out qualitative analysis of a relatively large region, you may then wish to do further analysis of smaller areas, under conditions that optimize spatial resolution, which we discuss in Chapter 36.

To get the most X-ray counts in your spectrum, use the highest operating voltage, since this gives the highest brightness. Notice that in Chapter 33 we said that you get a higher count rate 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. While the two effects counter each other, the added advantage of increased peak-to-background ratio with increased kV tips the scales in favor of using the maximum kV. Only choose a lower voltage if knock-on damage is a problem, as might be the case, for example, in a 200-kV to 400-kV instrument. Pick a portion of your specimen that is single phase in the area of interest and is well away from strong diffraction conditions, so as to minimize crystallographic effects and coherent bremsstrahlung. You will need a probe current of several tens of nanoamps. The necessary combination of probe size and final aperture obviously depends on the type of source in your microscope. To get several tens of nanoamps, from a thermionic source, you will have to select a relatively large probe size, say several tens of nanometers, and a large C2 aperture. As we shall see later, these are just the opposite of the requirements for microanalysis at high spatial resolution. In contrast to the limitations of a thermionic source, under most operating conditions an FEG source will give sufficient current for both initial qualitative analysis and subsequent quantitative analysis for high spatial resolution. However, the lower current from an FEG may mean that you have to count X-rays for a longer time compared to a thermionic source.

You can always gather a more intense spectrum by choosing a thicker region of the specimen. There is nothing wrong with doing this when you are carrying out *qualitative* microanalysis. The only danger is that, if you have a few weight percent of a light element present in the sample, the X-rays may be absorbed within the specimen and so may not be detected. Also, a thick specimen degrades the spatial resolution, but we've already agreed to compromise that aspect of the microanalysis during the initial qualitative analysis.

So, good qualitative analysis requires a large number of X-ray counts in the spectrum. These counts take a long time to generate, so you run the danger of damaging or changing the chemistry of beam-sensitive specimens. You may also contaminate the chosen area. To minimize these effects 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. Use a liquid-N_2-cooled low-background holder if contamination is still a problem.

34.2. ACQUIRING A SPECTRUM

The first and most important step in qualitative analysis is to acquire a spectrum across the complete X-ray energy range. Microanalysis can often be accomplished using X-rays with energies from ~1–10 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 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.

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

Of course, if you know the specimen you are analyzing, such a step may not seem essential, but it is still a wise precaution since unanticipated contaminants or trace impurities may be present. Collect a spectrum for several hundred seconds and ascertain the actual energy range over which all the characteristic peaks occur. Then, if all the peaks are present in an energy range <40 keV, regather the spectrum over that reduced range, thereby improving the resolution of your MCA display by lowering the number of eV per channel. The spectrum that you finally gather for qualitative analysis should be displayed with no more than 10 eV per channel resolution on the MCA, and a display range of 0–20 keV should be possible under these conditions (i.e., 2048 channels in total).

You can also increase the intensity of the spectrum by lowering the detector time constant to maximize the throughput of counts. This step also degrades the energy resolution of the XEDS but, for many qualitative analyses, this is not important.

> You should use the shortest time constant while maintaining adequate resolution to discriminate the characteristic peaks in the spectrum.

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 5000–10,000 cps is about the best that can be handled by most analog detector electronics under these conditions.

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	detectability depending on P/B (see Chapter 36).
■ Energy resolution	identifying elements by distinguishing peaks; different eV (this chapter).

When you've got a good intense spectrum over a suitable energy range, there is a well-defined sequence of steps that should be followed to ensure that you correctly identify each peak in the spectrum and disregard those peaks that are not statistically significant. 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, if your spectrum contains many peaks, and particularly if peak overlap is occurring, then misidentification may occur during such an "autosearch" routine, especially if there is no operator intervention. In addition, small peaks may sometimes be missed and phenomena such as coherent bremsstrahlung may not be taken into account. Under these circumstances there is a well-established manual sequence, developed for analysis of spectra from the SEM by Goldstein *et al.* (1992), and we will describe a modified form of this procedure in the next section.

34.3. PEAK IDENTIFICATION

First of all, we assume that you know what system peaks, if any, occur in your AEM, and what artifacts are likely to occur in your XEDS system. Now, ensure that the MCA display is calibrated to be accurate at the display resolution over the energy range you selected. So if your spectrum is displayed at 10 eV per channel, the peak centroids must be within 10 eV of their true position on the energy scale.

> The key to good qualitative analysis is to be suspicious and to not just seek the peaks you expect, but to be prepared also to find peaks that you don't expect.

Our peak analysis will always include three steps:

- Look at the most intense peak and work on down through its family; this is just bookkeeping.
- Go to the next most intense peak not included in the previous step and repeat the search. Then repeat this exercise until all peaks are identified.
- Think about pathological overlaps; look for spurious peaks, system peaks, and artifact peaks.

The bookkeeping. Starting from the high-energy end of the spectrum, select the most intense peak and determine the possible K, L, or M lines that could be present at that energy, either by using the computer-generated X-ray line markers on the MCA screen or by consulting an appropriate source, such as the "slide rules" offered by most commercial manufacturers. Good "bookkeeping" is essential during the sequence we will now describe, particularly if the spectrum contains many peaks. You must take care to label each peak when you have decided on its source. Proceed as follows:

- If a K_α line matches the peak, look for the K_β line which has ~10–15% of the K_α intensity. The K_β line *must* be present at X-ray energies above ~2.3 keV (S K_α), but below this energy the detector may not be able to resolve the two lines.
- If a K_α and K_β pair fit 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 a UTW detector, the L_α lines from Cl and above (>0.2 keV) may be detectable. Ni L_α = 849 eV, Cl L_α = 200 eV.
- If a K_α line does not fit, check for an L_α or M_α line fit.
- 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. 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 intensity 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 L_ℓ (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-line family is extraordinarily intense, but this is rare.
- If the L lines fit, there *must* be a higher-energy K_α/K_β pair, assuming the beam energy is sufficient to generate the K lines and the MCA energy range is wide enough to display them.
- The M lines are only usually 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. La M_α = 833 eV, Nb M_α = 200 eV.
- The M_α/M_β line overlap is difficult to resolve because all the M lines are below 4 keV. If an M_α/M_β line fits, look for three very small M_ζ (0.06), M_γ (0.05), and $M_{II}N_{IV}$ (0.01) lines .
- If the M_α line fits, there *must* be a higher-energy L-line family and possibly the very high energy K lines may exist; again, this depends on the detector, MCA display, and the accelerating voltage.

Figure 34.1 shows the families of lines expected in the display range from 0 to 10 keV, giving you some idea of the distribution of families of elemental lines that you should expect when you follow the procedure outlined above. For example, you can see for which elements you should expect to see 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.

> The idea is that you are looking for families of peaks. If a family member is missing your identification may be wrong.

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.* Finally, look for the escape peak(s) and sum peak associated with all *major* characteristic peaks that you have conclusively identified. Remember that these artifacts and any CB peaks will be very small, and before you worry about them you should make sure that the peaks are statistically significant; we discuss how to do this for all minor peaks in Section 34.4 below. If you have a Si(Li) detector, 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 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 (much less intense) 1.19 keV for the Ge L_α escape). If you suspect a sum peak at twice the energy of any major peaks, then reacquire the spectrum at a much lower dead time (<20%) and see if the suspected sum peak disappears. If you suspect a CB peak, then reacquire 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 samples that cannot be resolved. These are called "pathological overlaps" and include (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; and finally (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 systems.

> *Pathological overlap:* When it is impossible to separate two peaks even when you know they are both there.

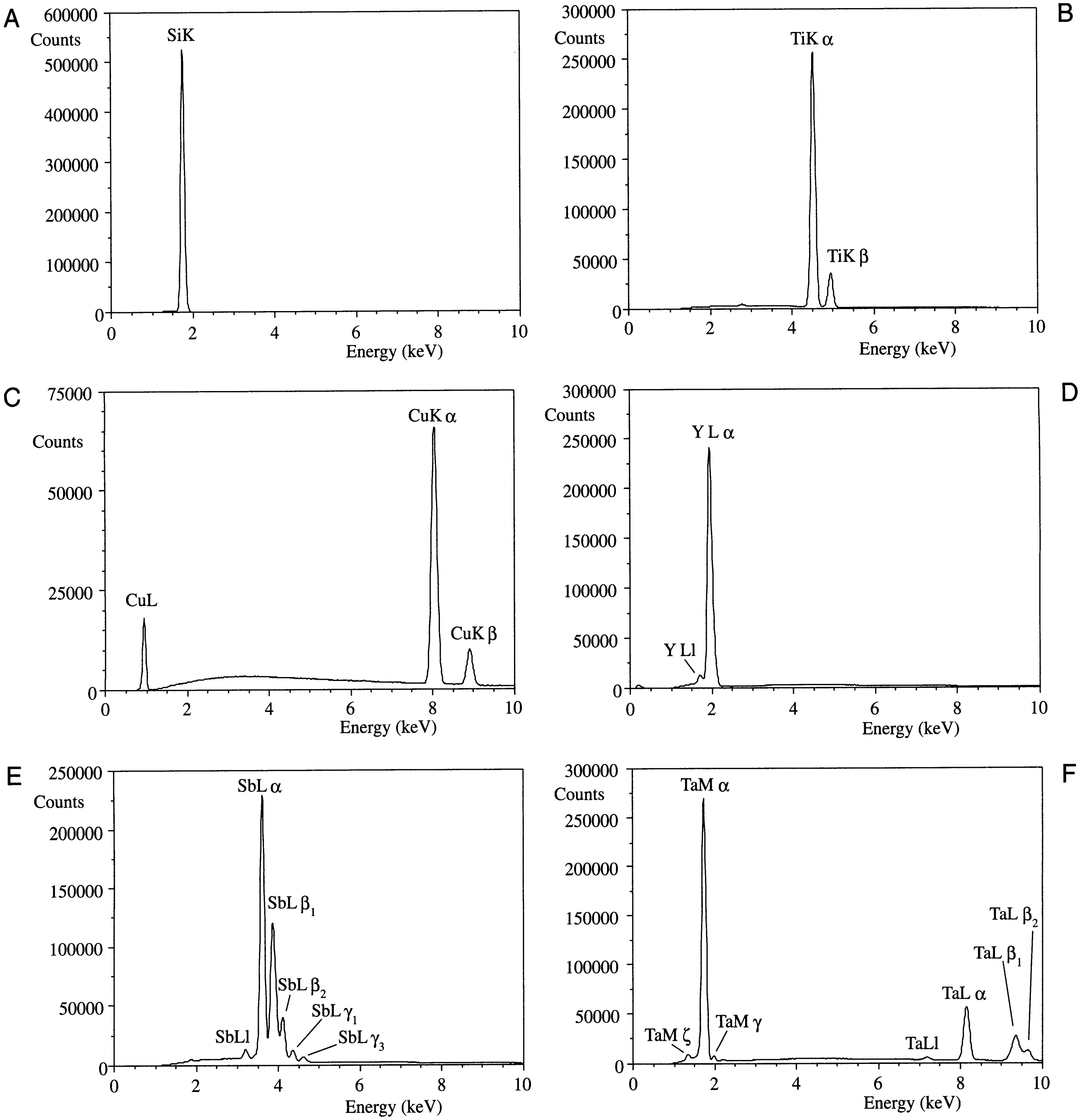

Figure 34.1. X-ray spectra from six elements spanning much of the periodic table, showing the families of characteristic lines. Starting with a single K_α line at low Z and low X-ray energy, the series progresses through the appearance of the L- and M-line families. Note the increasing separation of the lines in a given family as Z and keV increase.

These problems can sometimes be approached by careful choice of the MCA display range. For example, if you are only observing from 0–10 keV, the S K/Mo L line overlap would be clarified by the presence or absence of the Mo K lines around 18 keV. If you suspect that these or any other pathological peak overlap is occurring in your spectrum, then the first thing to do is to regather the spectrum under conditions that maximize the energy resolution of the detector system (i.e., longest time constant and count rate below 5000 cps), and also maximize the display resolution to at least 5 eV per channel. If the overlap is still not resolvable, then you should run a peak deconvolution routine that should be present in the available computer programs (e.g., Schamber 1981). Such routines are capable of detecting and resolving many of the classical materials science overlaps such as Mo L_α and S K_α, and a schematic deconvolution is shown in Figure 34.2.

A historical aside: peak deconvolution has been of great concern to microanalysts since the earliest days of EPMA, using pulse-height analyzers, and the first primitive attempt to deconvolute overlapping peaks was developed by Dolby (1959). With hindsight, it is not difficult to make the connection between the problems of extracting peak information from a low-resolution spectrum and the problem of extracting clear sound signals from noisy recording tape. Dolby, however, saw the potential before anyone else and went on to commercialize his ideas with resounding success, prompting his Ph.D. supervisor Ellis Cosslett to remark that Dolby was the only graduate student he had known to become a millionaire from his Ph.D. research!

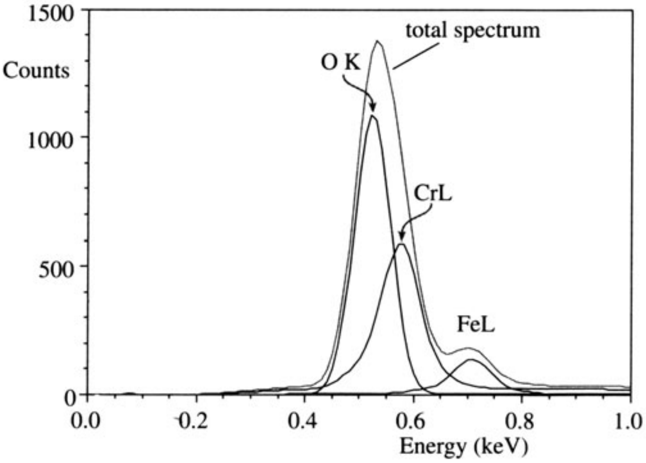

Figure 34.2. The total spectrum arises from the overlap of three Gaussian spectral peaks (the L_α lines of Fe and Cr and the O K_α line) from a mixed Fe-Cr oxide. Deconvolution is essential to determine the intensities in the three constituent peaks, prior to any attempt at quantification.

This procedure should permit you to identify all the major peaks in the spectrum, but there may still be minor peaks which may or may not be significant and you have to decide whether you are going to identify or ignore these peaks. We'll tell you how to make this decision in the next section.

34.4. PEAK VISIBILITY

Small-intensity fluctuations that you cannot clearly identify as peaks are often present in your spectrum. In this case, there is a simple statistical criterion (Liebhafsky *et al.* 1972) 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 relatively smooth and any peaks are clearly visible, as summarized in Figure 34.3.

- 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.

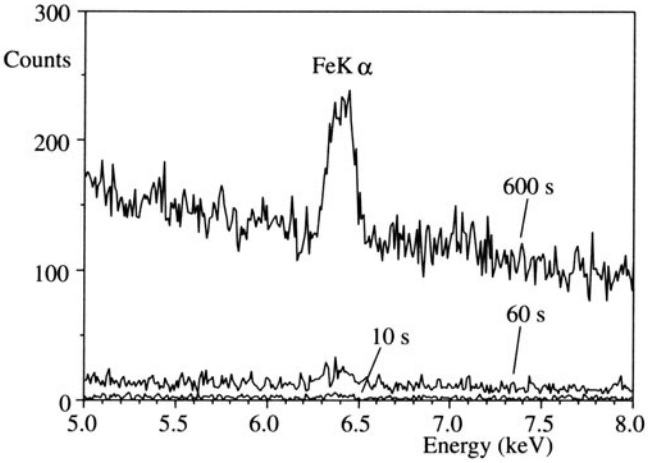

Figure 34.3. With increasing counting time a clear characteristic Fe K_α peak develops above background in a spectrum from Si-0.2% Fe. This demonstrates the need to acquire statistically significant counts before deciding if a small peak is present or absent.

If $I_A > 3\sqrt{I_A^b}$, then the peak is statistically significant at the 99% confidence limit and must be identified. You will make an erroneous peak identification in less than 1% of analyses using this criterion.
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 sample, 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, as long as doing so does not change or contaminate 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. Be aware that when you count for long periods of time to search for characteristic peaks of low intensity, you will also begin to detect the small peaks that arise from the various spurious effects that were discussed in detail above, e.g., CB peaks, Si or Ge internal-fluorescence peaks, and system peaks such as Fe and Cu. Also, you increase the possibility of contamination and beam damage to your specimen. So, 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 detectability limits in Chapter 36. However, you may be able to identify the phase that is being analyzed without any further work. For example, in the material that you are investigating, there may be 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 shall see in the next chapter, one of the marvelous advantages of thin-foil microanalysis 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:

> *An example* of qualitative microanalysis is shown in the spectrum in Figure 34.4. 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 0–10 keV and the first peak to be examined was the most intense high-energy peak, labeled #1 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). 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 K_β) and line #3 was consistent with the Si K_α line at 1.74 keV (the K_α/K_β pair cannot be resolved at this energy). 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. No escape or sum peaks were detectable, 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 we cannot conclude that there is any Cu within the specimen.

The absence of the Cu L_α line at 0.93 keV is evidence that the thick Cu grid is responsible, since the low-energy L X-rays will be absorbed in the grid itself before they can be detected.

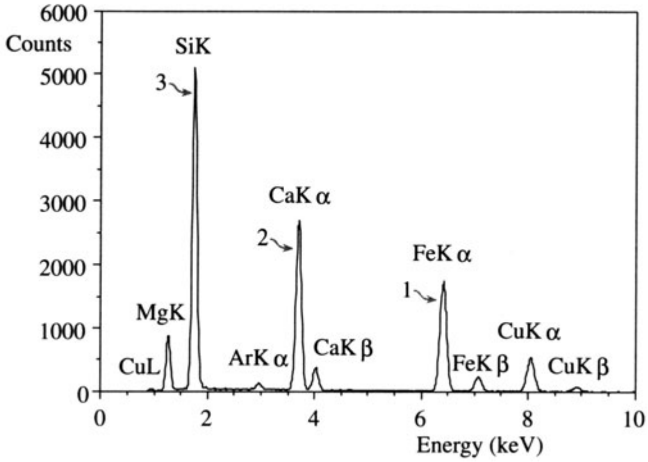

Figure 34.4. Energy-dispersive spectrum obtained at 300 kV from a thin oxide glass film on a Cu grid, with the characteristic peaks identified through the procedure outlined in the text.

Another example is shown in Figure 34.5 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. To the average metallurgist, this sample 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 more information is required, such as the specific grade of stainless steel, then it is necessary to make some measurements of the relative peak intensities, and this is the first step in the quantification procedure. In fact, we will see that the quantification equation, to a first approximation, predicts that the amount of each element is directly proportional to the peak height, and so measuring the relative heights of the K_α peaks in Figure 34.5 with a ruler will give an estimate of the composition as ~Fe-20% Cr-10% Ni. A full quantification using the procedures described in the next chapter gives a very similar result, but with much greater confidence in the true composition.

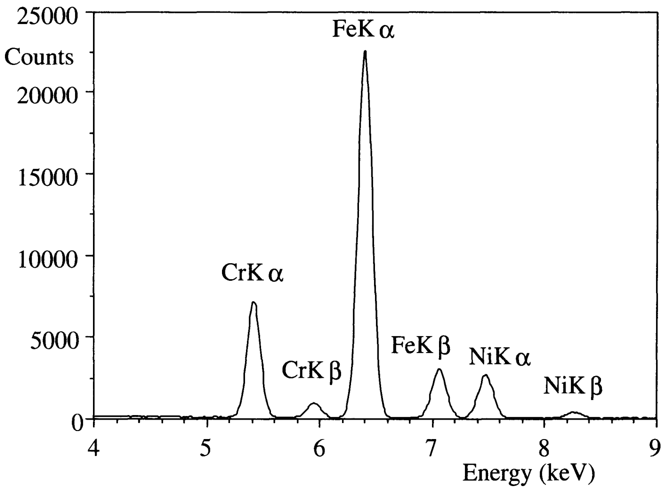

Figure 34.5. Spectrum from a stainless-steel foil. From such a spectrum, in which the peaks are resolved and close together in energy, a first-approximation quantification is possible simply by measuring the relative heights of the K_α peaks.

CHAPTER SUMMARY

One last time: doing the qualitative analysis first is not an option. It is essential.

- 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.

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