

# CHAPTER FOUR

## ENERGY DISPERSIVE SPECTROSCOPY



When the atoms in a material are ionized by a high-energy radiation they emit characteristic X rays. EDS is an acronym describing a technique of X-ray spectroscopy that is based on the collection and energy dispersion of characteristic X rays. An EDS system consists of a source of high-energy radiation, usually electrons; a sample; a solid state detector, usually made from lithium-drifted silicon, Si (Li); and signal processing electronics. EDS spectrometers are most frequently attached to electron column instruments. X rays that enter the Si (Li) detector are converted into signals which can be processed by the electronics into an X-ray energy histogram. This X-ray spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak may be further converted into elemental weight concentration either by comparison with standards or by standardless calculations.

Range of elements	Boron to uranium
Destructive	No
Chemical bonding information	Not readily available
Quantification	Best with standards, although standardless methods are widely used
Accuracy	Nominally 4–5%, relative, for concentrations > 5% wt.
Detection limits	100–200 ppm for isolated peaks in elements with $Z > 11$ , 1–2% wt. for low- $Z$ and overlapped peaks
Lateral resolution	.5–1 $\mu\text{m}$ for bulk samples; as small as 1 nm for thin samples in STEM
Depth sampled	0.02 to $\mu\text{m}$ , depending on $Z$ and keV
Imaging/mapping	In SEM, EPMA, and STEM
Sample requirements	Solids, powders, and composites; size limited only by the stage in SEM, EPMA and XRF; liquids in XRF; 3 mm diameter thin foils in TEM
Main use	To add analytical capability to SEM, EPMA and TEM

Cost \$25,000–\$100,000, depending on accessories (not including the electron microscope)

entire spectrum of X-rays emitted from the surface. However, as we have by now learnt to expect, the 'ideal' is rarely attainable in practice. In the present case we generally have to choose between two very different methods of obtaining the data. Parts of the spectra obtained using these techniques, from the silver solder joint whose microstructure is shown in Figure 5.21, are shown in Figure 6.3. The *wavelength dispersive* spectrometer or WDS is the basis of the purpose-built electron probe microanalyser. The spectrum obtained with a wavelength dispersive spectrometer is shown in Figure 6.3(a). These devices can determine extremely accurately the position of a single X-ray line (i.e. its wavelength or energy), can resolve closely spaced lines and are particularly suited to measuring the height (intensity) of a peak above the background level. Alternatively, many SEMs and TEMs are equipped with an *energy dispersive spectrometer* or EDS detection system which is able to detect and display most of the X-ray spectrum, but with some loss of precision and resolution as indicated in Figure 6.3(b). Nowadays, the distinction between analytical scanning microscopes and electron probe microanalysers is not clear, as some SEMs are fitted with WDS systems and some microanalysers use EDS as well as WDS. We shall now consider the two types of analysis system in more detail, to see why there is still a need for both.

### 6.2.1 Energy-dispersive analysis

We shall deal with the energy-dispersive detection system first, since, although it is historically the more recent, it is now the more generally applicable and certainly the more versatile system. The development of EDS analysis has been responsible for a major revolution over the past twenty five years in the use of electron beam instruments for the microcharacterization of materials.

In outline, the detector normally consists of a small piece of semiconducting silicon or germanium which is held in such a position that as many as possible of the X-rays emitted from the specimen fall upon it. Since X-rays cannot be deflected, the detector must be in the line of sight of the specimen. This means that in a scanning electron microscope it normally occupies a similar position to the secondary electron detector (see Figure 5.9). In order to collect as many X-rays as possible the silicon should be as near to the specimen as is practicable. In a SEM it may be possible to place the detector 20 mm or less from the specimen, but the problems are greater with a TEM because the specimen is within the objective lens.

The detector works in the following way. Each incoming X-ray excites a number of electrons into the conduction band of the silicon leaving an identical number of positively charged holes in the outer electron shells. The energy required for each of these excitations is only 3.8 eV; consequently the number of electron-hole pairs generated is proportional to the energy of the X-ray photon being detected. For example, an Al K<sub>α</sub> X-ray, with an energy of

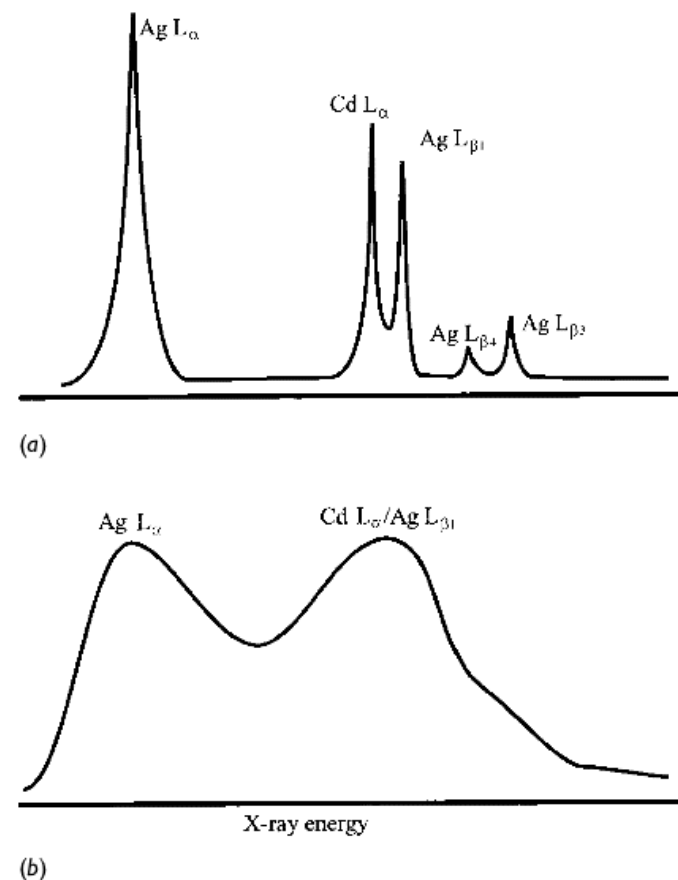


Figure 6.3 Part of the spectra obtained from a specimen of silver solder, a copper–silver–cadmium alloy. (a) Spectrum obtained using wavelength dispersive analysis. (b) The same region of the spectrum, obtained using energy dispersive X-ray analysis. Using this technique, the  $\text{Ag } L_{\beta}$  and  $\text{Cd } L_{\alpha}$  peaks are not resolved and the  $\text{Ag } L_{\alpha}$  and  $\text{Cd } L_{\alpha}$  are barely resolvable.

1.49 keV, will give rise to approximately 390 electron-hole pairs. If a voltage is applied across the semiconductor a current will flow as each X-ray is absorbed in the detector and the magnitude of the current will be exactly proportional to the energy of the X-ray. In practice, if pure silicon is used the current generated is minute compared with the current which flows normally when a voltage is applied; in other words the resistivity is too low. This is overcome by three stratagems which combine to make the final detector seem rather more complicated than it really is. Figure 6.4 shows the result, and contains the features which are common to virtually all energy-dispersive detectors.

The resistivity of the silicon is increased by (a) making the whole detector a semiconductor p–i–n junction which is reverse biased, (b) doping the silicon with a small concentration of lithium, and (c) cooling the whole detector to liquid nitrogen temperature (77 K). The current which normally passes between the gold electrodes is now very small indeed until an X-ray enters the detector, then the resultant current can be amplified and measured fairly easily. The

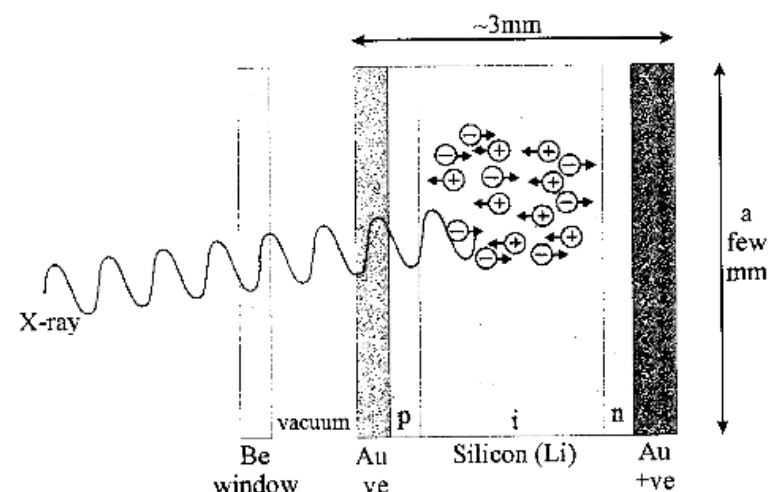


Figure 6.4 A silicon energy-dispersive X-ray detector. The beryllium window and gold contact layers are grossly exaggerated in thickness; typical thicknesses would be 7–8  $\mu\text{m}$  for the Be, and 10–20 nm for the Au.

detector shown schematically in Figure 6.4 consists of a Si(Li) semiconductor junction in which the i region occupies most of the 3 mm thickness. Thin layers of gold are necessary on both surfaces of the detector so that the bias potential can be applied. The film of gold on the outer face of the detector must be as thin as possible so that very few X-rays are absorbed in it; a layer only 20 nm thick provides adequate conductivity. The gold-coated outer surface is usually further protected by a thin window of beryllium or a polymer. This window is necessary to prevent contaminants from the specimen chamber of the microscope from condensing on the very cold surface of the detector and forming a further barrier to the entry of X-rays. Unfortunately the window itself, despite being made of beryllium ( $Z = 4$ ) or carbon ( $Z = 6$ ) and only being a few micrometres thick, absorbs a significant proportion of the low energy X-rays falling on the detector and therefore makes light elements particularly difficult to detect. It is impracticable to detect X-rays of energy less than 1 keV with this type of detector, and this therefore eliminates all elements lighter than sodium. Windowless detectors, or detectors with ultra-thin windows of formvar or some other polymer film are now available, and these extend the analytical range down to boron. However, such detectors need to be used in microscopes which have extremely good vacuum systems, and need very careful protection from accidental air leaks such as those that occur during specimen changes.

The current which flows between the electrodes when an X-ray enters the detector lasts for an extremely short time (less than  $1 \mu\text{s}$ ) and is normally referred to as a *pulse*. Each pulse is amplified and then passed to a computer acting as a multichannel analyser (MCA), which decides which of perhaps 1000 channels, each representing a different X-ray energy, the pulse should be registered in. The MCA thus effectively collects a histogram of the energies of all the



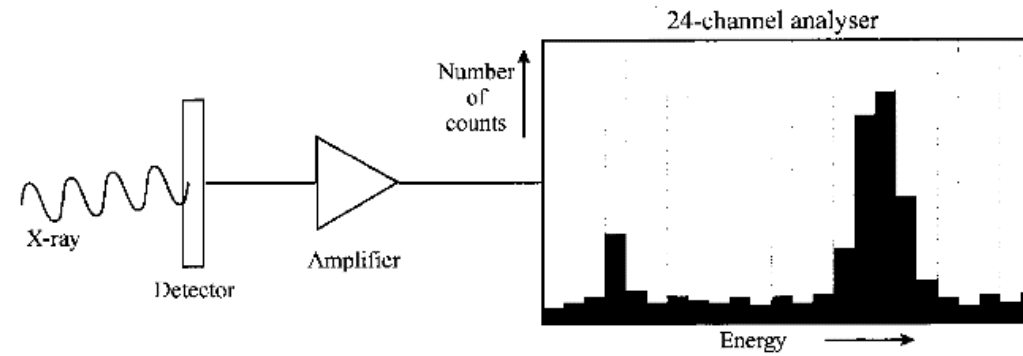


Figure 6.5 A simplified energy-dispersive analysis system. Pulses from the detector are amplified and then stored in the appropriate channel of multi-channel analyser. In reality, the MCA would contain perhaps 1000 channels instead of the 24 shown here.

X-rays arriving at the detector, as indicated in Figure 6.5. This histogram is then displayed on a screen, and usually appears as a smooth curve such as is shown in Figure 6.3(b).

The solid state detector is very efficient, and almost 100% of the X-rays entering the detector crystal will produce a pulse. However, the pulse processing time, during which an X-ray photon is detected and the resulting pulse amplified and sorted by the MCA, is short but finite, and this process must be completed before the next pulse can be dealt with. The pulse pile-up rejection circuit manages this operation, which is a very critical aspect of the EDS system. Pulse processing speed limits the rate at which X-rays can be counted, and at the time of writing this is typically about ten thousand counts per second (cps). If the count rate is less than a few thousand cps, then most of the incoming pulses are processed, but as the count rate rises, an increasing fraction of the pulses are rejected. The total time elapsed during an analysis consists of the time for which the detector was counting (*live time*), plus the time for which the detector was ignoring incoming X-rays (*dead time*). In determining the X-ray count rate from a specimen, it is therefore the number of counts collected for a given *live time*, not *elapsed time*, which is required. Fortunately, modern EDS systems will record both times, and this should cause the analyst no problems.

The high efficiency of the EDS detector, coupled with the relatively large collection angle (typically greater than 0.5 steradians in an SEM) means that data may be collected rapidly at quite low beam currents. From a typical sample, a reasonable spectrum can usually be obtained within a minute or two.

The EDS system is controlled by a computer which also stores the energies of the X-rays from all the elements; consequently it is a simple matter for the computer to identify the element giving rise to a line in the spectrum, or alternatively to indicate on the screen the positions on the spectrum at which lines for any chosen element would appear. Thus qualitative analysis is extremely rapid with such a system. Figure 6.6 shows typical spectra