Chapter 6

Chemical analysis in the electron microscope

It has been stressed in Chapter 2 that whenever electrons with several kilo electron volts of energy strike a solid specimen, X-rays characteristic of the atoms present in the specimen are produced. In discussing the formation of images in the TEM and SEM we have largely ignored these X-rays. However, to do so is to discard a great deal of information about the composition of the specimen. This was realized in the 1950s and since then increasing use has been made of all types of electron microscopes for *microanalysis*. This term implies that an analysis can be performed on a very small amount of material, or, more usually, a very small part of a larger specimen. As conventional chemical or spectrographic methods of analysis cannot do this, microanalysis in the electron microscope has become an important tool for characterizing all types of solid material.

In principle we can determine two things from the X-ray spectrum emitted by any specimen. Measurement of the wavelength (or energy) of each characteristic X-ray that is emitted enables us to find out which elements are present in the specimen, i.e. to carry out a *qualitative analysis*. Measurement of how many X-rays of any type are emitted per second should also tell us how much of the element is present, i.e. enable a *quantitative analysis* to be carried out. However, as this chapter will show, the instrumental and specimen requirements for quantitative analysis are such that the step from qualitative to quantitative analysis is not easily made.

We should note there are three types of electron microscopes commonly used for microanalysis. These are the SEM with X-ray detectors, the electron probe microanalyser, which is essentially a purpose-built analytical microscope of the SEM type, and transmission electron microscopes (TEM and STEM) fitted with X-ray detectors. The role of these different instruments will be discussed later in this chapter.

In a transmission electron microscope we can also obtain compositional information by measuring the energy loss of the transmitted electrons, and this technique will also be discussed.

6.1 The generation of X-rays within a specimen

We have seen in section 2.8 that bombardment of a material with high energy electrons will result in the emission of 'characteristic' X-rays, whose wavelengths depend on the nature of the atoms in the specimen, together with white radiation (or Bremsstrahlung) of all wavelengths down to a minimum corresponding to the incident electron energy (Figure 2.8). (The reader to whom these concepts are unfamiliar might find it helpful to re-read section 2.8 before continuing.) Before we can use the X-rays for analytical purposes we need to know which of the many characteristic X-ray lines for each element is the most intense; this enables us to choose the best line to use as an index of how much of each element is present in the sample. The situation at first appears to be very complex since, as Figure 6.1 shows, there is a large number of electron transitions possible in a large atom, each of which should lead to an X-ray of a unique wavelength.

It transpires, fortunately for the microanalyst, that in the K series the lines $K_{\alpha 1}$ and $K_{\alpha 2}$ (which may be so close together that they cannot be distinguished) are seven to eight times more intense than $K_{\beta 1}$ and $K_{\beta 2}$ (another close pair). Consequently the K 'doublet', as it is called, is most frequently used for analysis. However, it is not always possible to excite the K series of lines in an electron beam instrument since, as the atomic number of the emitting element increases, the energy required to knock out a K-shell electron also increases. For example, elements heavier than tin ($Z = 50$) need electrons of more than 25 keV to excite any K lines at all, and are not efficient producers of
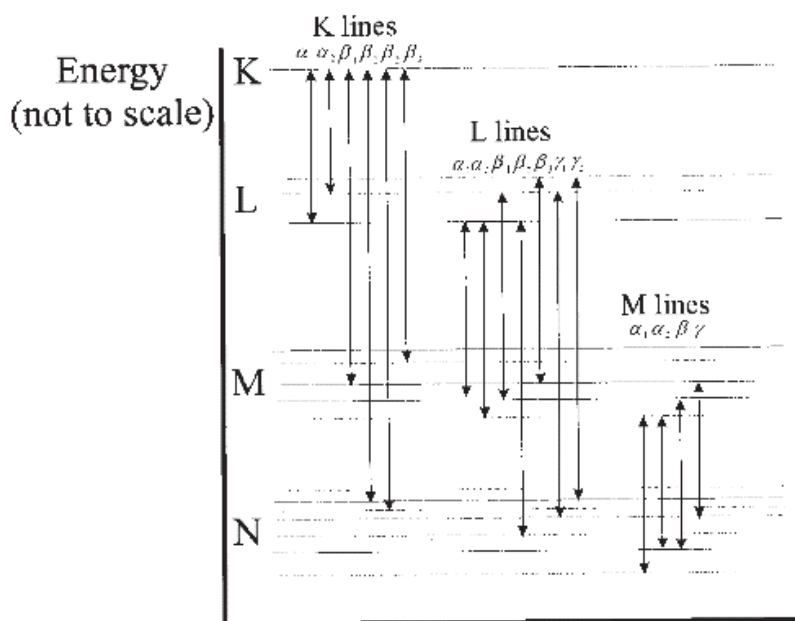

Figure 6.1 Some of the more common transitions between the K, L, M and N shells of an atom which lead to the X-ray lines indicated. The nomenclature is that of Figure 2.1.

K X-rays until the incident electron energy is about 75 keV. Since we would like to be able to analyse a specimen in an SEM, where electron energies of perhaps only 30 keV are available, we must look for other characteristic X-rays which are more easily excited in order to detect heavy elements. Fortunately the L series of lines shown in Figure 6.1, or even the M series for very heavy elements, has very suitable properties. Again it turns out that of the vast number of possible lines, $L_{\alpha 1}$ and $L_{\alpha 2}$ are far stronger than the remainder, which can normally be ignored. A similar effect narrows the M series down to a few useful lines. Table 6.1 shows the energy and associated wavelength of the strongest K, L and M lines of the elements. The most efficient production of X-rays generally occurs when the bombarding electrons have about three times the X-ray energy. A study of Table 6.1 will show that all elements have at least one strong X-ray line with energy less than 10 keV and therefore there should be no difficulty in analysing for all the elements, using a scanning electron microscope operating at 25–30 keV.

In addition to direct excitation by electrons there is a further mechanism of X-ray production which must be considered in microanalysis. X-rays which are passing through a specimen (perhaps having been generated previously by electron excitation) can themselves excite atoms which then emit characteristic X-rays of a slightly lower energy. Thus, for example, in a brass specimen the zinc K_{α} X-rays (energy 8·64 keV) can excite extra copper K_{α} X-rays whose energy is less (8·05 keV, see Table 6.1). This effect is known as *fluorescence*. It is not a very efficient process, since only a few per cent of the higher energy rays will successfully excite the lower energy radiation. However, it may significantly alter the relative amounts of characteristic radiation coming from alloys or compounds, particularly when elements with quite similar atomic numbers are present. In the example quoted we would expect that if the composition of the brass were 70% Cu/30% Zn we would find that rather more than the expected proportion of X-rays emitted were Cu K_{α} and rather fewer than expected were Zn K_{α}, because of the fluorescence effect. We shall see later that fluorescence is one of the effects which make accurate quantitative analysis difficult.

One of the key factors which determines the scale on which microanalysis can be carried out is the volume of the specimen which is penetrated by electrons (the interaction volume), and the volume of the specimen from which the detected X-rays originate (the sampling volume). As discussed in Chapter 5, and shown in Figure 5.6, because X-rays generated deep in the specimen can escape from the specimen and be detected, the sampling volume for X-rays is almost as large as the interaction volume. The interaction volume is smallest for low energy electrons and heavy elements, and it is difficult to make it much smaller than $1\,\mu m \times 1\,\mu m \times 1\,\mu m$ without reducing the energy of the electron beam (E_0) so much that no useful X-rays are emitted. As a consequence the smallest volume which it is practicable to analyse in a scanning microscope is $\sim 1\,(\mu m)^3$. This sounds like a small volume but it

Table 6.1 The energy and associated wavelength of the strongest K, L and M lines of the elements.

Element	Atomic Number Z	Relative Atomic Mass A_r	$K_{\alpha 1}$ E (keV)	λ (nm)	$L_{\alpha 1}$ E (keV)	λ (nm)	$M_{\alpha 1}$ E (keV)	λ (nm)
			(a)	(b)	(a)	(b)	(a)	(b)
Hydrogen	1	1·0						
Helium	2	4·0						
Lithium	3	6·9	0·05					
Beryllium	4	9·0	0·11	11·40				
Boron	5	10·8	0·18	6·76				
Carbon	6	12·0	0·28	4·47				
Nitrogen	7	14·0	0·39	3·16				
Oxygen	8	16·0	0·52	2·36				
Fluorine	9	19·0	0·68	1·83				
Neon	10	20·2	0·85	1·46				
Sodium	11	23·0	1·04	1·19				
Magnesium	12	24.3	1·25	0·99				
Aluminium	13	27.0	1·49	0·83				
Silicon	14	28·1	1·74	0·71				
Phosphorus	15	31·0	2·01	0·61				
Sulphur	16	32·1	2·31	0·54				
Chlorine	17	35·5	2·62	0·47				
Argon	18	39·9	2·96	0·42				
Potassium	19	39·1	3·31	0·37				
Calcium	20	40·1	3·69	0·34	0·34	3·63		
Scandium	21	45·0	4·09	0·30	0·39	3·13		
Titanium	22	47·9	4·51	0·27	0·45	2·74		
Vanadium	23	50·9	4·95	0·25	0·51	2·42		
Chromium	24	52·0	5·41	0·23	0·57	2·16		
Manganese	25	54·9	5·90	0·21	0·64	1·94		
Iron	26	55·8	6·40	0·19	0·70	1·76		
Cobalt	27	58·9	6·93	0·18	0·77	1·60		
Nickel	28	58·7	7·48	0·17	0·85	1·46		
Copper	29	63·5	8·05	0·15	0·93	1·33		
Zinc	30	65·4	8·64	0·14	1·01	1·23		
Gallium	31	69·7	9·25	0·13	1·10	1·13		
Germanium	32	72·6	9·88	0·12	1·19	1·04		
Arsenic	33	74·9	10·54	0·12	1·28	0·97		
Selenium	34	79·0	11·22	0·11	1·38	0·90		
Bromine	35	79·9	11·92	0·10	1·48	0·84		
Krypton	36	83·8	12·65	0·10	1·59	0·78		
Rubidium	37	85·5	13·39	0·09	1·69	0·73		
Strontium	38	87·6	14·16	0·09	1·81	0·69		
Yttrium	39	88·9	14·96	0·08	1·92	0·64		
Zirconium	40	91·2	15·77	0·08	2·04	0·61		
Niobium	41	92·9	16·61	0·07	2·17	0·57		
Molybdenum	42	95·9	17·48	0·07	2·29	0·54		
Technetium	43	98·0	18·36	0·07	2·42	0·51		
Ruthenium	44	101·1	19·28	0·06	2·55	0·48		
Rhodium	45	102·9	20·21	0·06	2·70	0·46		

Table 6.1 (continued)

Element	Atomic Number Z	Relative Atomic Mass A_r	$K_{\alpha 1}$ E (keV) (a)	λ (nm) (b)	$L_{\alpha 1}$ E (keV) (a)	λ (nm) (b)	$M_{\alpha 1}$ E (keV) (a)	λ (nm) (b)
Palladium	46	106·4	21·17	0·06	2·70	0·44		
Silver	47	107·9	22·16	0·06	2·98	0·41		
Cadmium	48	112·4	23·17	0·05	3·13	0·39		
Indium	49	114·8	24·21	0·05	3·29	0·38		
Tin	50	118·7	25·27	0·05	3·44	0·36		
Antimony	51	121·7	26·36	0·05	3·60	0·34		
Tellurium	52	127·6	27·47	0·04	3·77	0·33		
Iodine	53	126·9	28·61	0·04	3·94	0·31		
Xenon	54	131·3	29·77	0·04	4·11	0·30		
Caesium	55	132·9	30·97	0·04	4·29	0·29		
Barium	56	137·3	32·19	0·04	4·46	0·28		
Lanthanum	57	138·9	33·44	0·04	4·65	0·27	0·83	1·49
Hafnium	72	178·5	55·78	0·02	7·90	0·16	1·64	0·75
Tantalum	73	181·0	57·52	0·02	8·14	0·15	1·71	0·73
Tungsten	74	183·8	59·31	0·02	8·40	0·15	1·77	0·70
Rhenium	75	186·2	61·13	0·02	8·65	0·14	1·84	0·67
Osmium	76	190·2	62·99	0·02	8·91	0·14	1·91	0·65
Iridium	77	192·2	64·88	0·02	9·17	0·14	1·98	0·63
Platinum	78	195·1	66·82	0·02	9·44	0·13	2·05	0·60
Gold	79	197·0	68·79	0·02	9·71	0·13	2·12	0·58
Mercury	80	200·6	70·81	0·02	9·99	0·12	2·19	0·56
Thallium	81	204·4	72·86	0·02	10·27	0·12	2·27	0·55
Lead	82	207·2	74·96	0·02	10·55	0·12	2·34	0·53
Bismuth	83	209·0	77·10	0·02	10·84	0·11	2·42	0·51
Polonium	84	210·0	79·28	0·02	11·13	0·11	?	?
Astatine	85	210·0	81·50	0·02	11·43	0·11		
Radon	86	222·0	83·77	0·01	11·73	0·11		
Francium	87	223·0	86·09	0·01	12·03	0·10		
Radium	88	226·0	88·45	0·01	12·34	0·10		
Actinium	89	227·0	90·87	0·01	12·65	0·10		
Thorium	90	232·0	93·33	0·01	12·97	0·10	3·00	0·41
Proactinium	91	231·0	95·85	0·01	13·29	0·09	3·08	0·40
Uranium	92	238·0	98·42	0·01	13·61	0·09	3·17	0·30

contains about 10^{11} atoms! The sampling volume will also depend on the energy of the X-ray being emitted, because an X-ray of energy E_c will only be emitted if the electron energy E is greater than E_c. Thus, the maximum depth from which X-rays originate is effectively the depth at which the electron energy falls below E_c. Several attempts have been made to calculate the depth of X-ray production (R), and one commonly used approximation is that R is given (in micrometres, when E_o and E_c are in keV) by

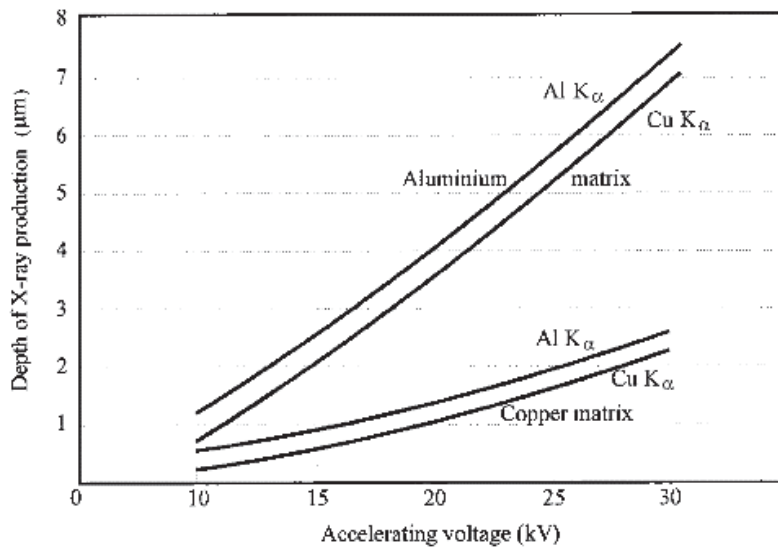$$R = P(E_o^{1.68} - E_c^{1.68}) \tag{6.1}$$

Figure 6.2 The depth from which X-rays are produced in a specimen as a function of the electron energy, the nature of the X-rays being detected, and the composition of the matrix.

where P is about 10^{-2} for materials with medium average atomic mass. To illustrate this point, Figure 6.2 shows the depth from which $Cu\,K_\alpha$ and $Al\,K_\alpha$ X-rays may be produced by electrons in an Al–Cu alloy in which the major element is either aluminium or copper.

If X-ray fluorescence occurs, then the sampling volume may actually be larger than the interaction volume.

The fraction of the generated X-rays which reach the specimen surface and are emitted will depend both on the energy of the X-rays and the average atomic weight of the specimen. For example, soft (low energy, long wavelength) X-rays such as carbon K_α are readily absorbed by solids and therefore relatively few escape from the surface. On the other hand, hard (high energy, short wavelength) X-rays such as molybdenum K_α can penetrate many micrometres of most solids, and are depleted only a little by absorption in the specimen. Clearly therefore both the volume which is being analysed, and the fraction of the X-rays which are emitted from the specimen depend very critically on (*a*) the energy of the electron beam, (*b*) the energy (wavelength) of the X-ray being studied and (*c*) the local atomic weight of the specimen.

As was stressed earlier, this complexity makes accurate analysis extremely difficult.

6.2 Detection and counting of X-rays

Ideally a system which is to be used for the analysis of a specimen in a scanning or transmission electron microscope should be able to reproduce for us the

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_α X-ray, with an energy of
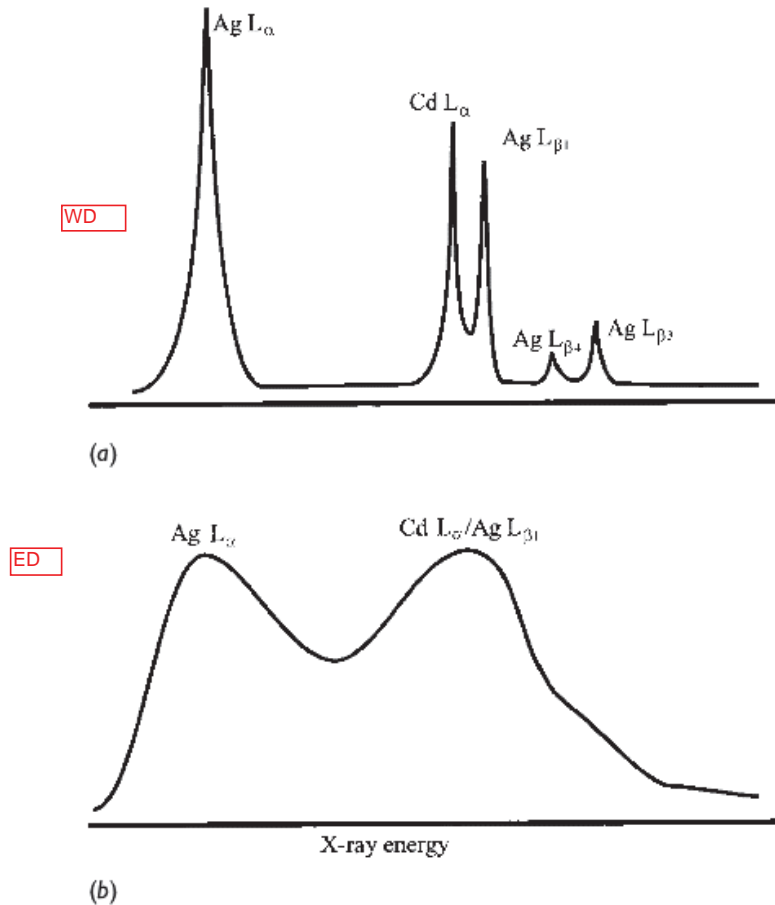
(a)

(b)

X-ray energy

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 Ag L$_\beta$ and Cd L$_\alpha$ peaks are not resolved and the Ag L$_\alpha$ and 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
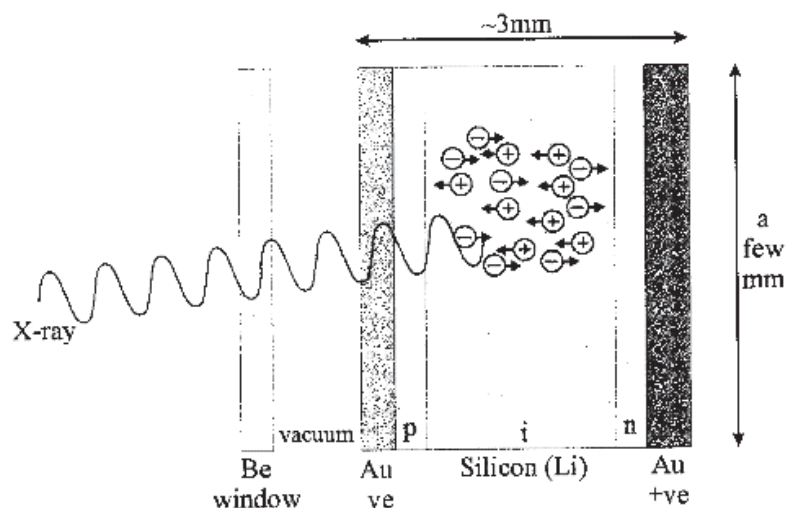
Figure 6.4 A silicon energy-dispersive X-ray detector. The beryllium window and gold contact layers are grossly exaggerated in thickness; typical thicknesses would be 7–8 µm for the Be, and 10–20 nm for the Au.

برای اعمال اختلاف پتانسیل از لایه نازک رسانای طلا و پوششی از بریلیوم یا پلیمر استفاده می شود.

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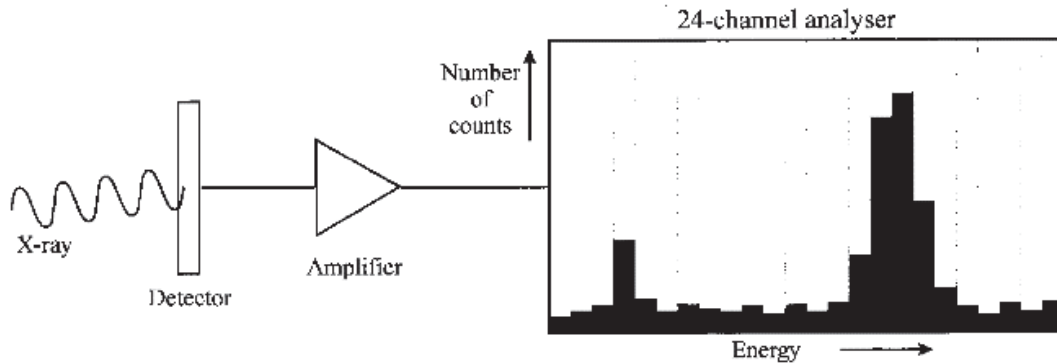
Figure 6.5 A simplified energy-dispersive analysis system. Pulses from the detector are amplified and then stored in the appropriate channel of multi-channel analyser. In reality, the MCA would contain perhaps 1000 channels instead of the 24 shown here.

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
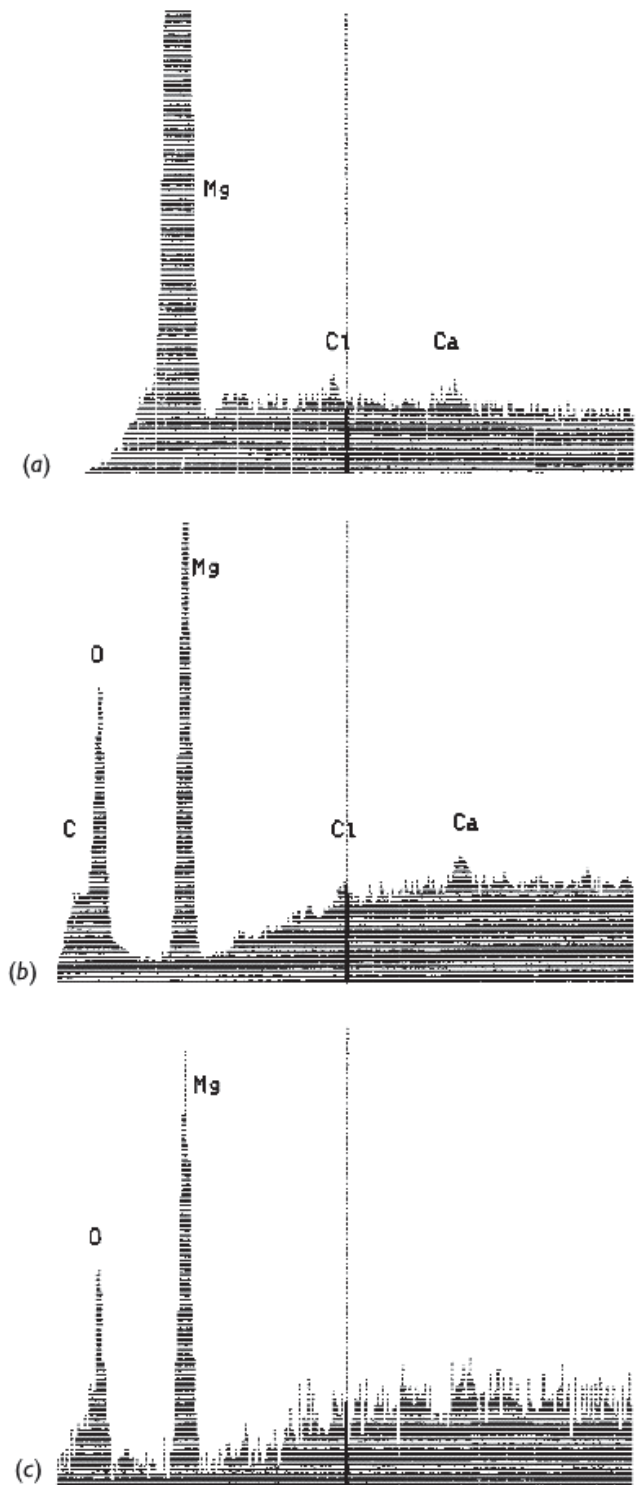
Figure 6.6 EDS spectra obtained from a particle of impure MgO on a carbon support film. The vertical line in the centre of the spectrum is the computer cursor from which the operator can read off the energy of any channel of the spectrum. (*a*) Spectrum from a standard detector with a beryllium window. (*b*) Spectrum obtained in 300 s using an ultra-thin window, light element detector, (*c*) as (*b*) but with a 50 s count time.

obtained from impure MgO particles on a carbon substrate. The microscope was equipped with a normal Be window detector as well as a thin-window detector for light element analysis, and the difference in performance of the detectors at the light element end of the spectrum can be clearly seen.

From the foregoing description it would seem that the EDS is an ideal system for presenting all the available X-ray data from a specimen in a convenient form from which both qualitative and quantitative analyses could be deduced. However there are some serious limitations to be considered.

First as discussed above, detection of elements lighter than sodium is impossible with a standard detector.

Secondly, in order to both preserve the detector crystal and to reduce noise in the system, the detector must be kept at 77 K at all times, which is clearly an experimental difficulty.

Thirdly, the energy resolution of the detector is poor; in other words, each X-ray line is not detected as a sharp line, but, as seen in Figure 6.6, as a broad peak, typically 100–200 eV wide. Not only does this make it impossible to resolve closely spaced lines, as may be seen by comparing the Ag_L and Cd_L lines in Figures 6.3(a) and 6.3(b), but, as any X-ray line now occupies several channels of the MCA, the peak height is reduced. This factor, together with the relatively large amount of electronic noise in the system results in rather low peak to background ratios compared to WDS. As we shall see later, a low peak to background ratio will affect not only the limit of detectability of the analyser, but also its use for quantitative analysis.

A further problem with an energy dispersive system is that under certain circumstances spurious peaks in the spectrum may be produced. The most important of these effects are the *sum peak* and the *silicon escape peak*. As discussed above, the energy of an X-ray photon entering the detector is determined from the number of electron-hole pairs created. If two identical photons enter the detector simultaneously, then twice as many hole pairs are created, the detector system will interpret this as being due to a single photon of twice the energy, and this pulse will be sorted accordingly to produce a sum peak at an energy of twice that of the X-rays being detected. The escape peak is due to an X-ray entering the detector and ionizing a silicon atom in the detector crystal by knocking out a K-shell electron. The original X-ray photon loses 1·74 keV in energy (i.e. the energy of SiK_α X-rays), and unless the resulting SiK_α X-ray photon is absorbed by the detector, thus releasing its energy to the detector, then a peak 1·74 keV below the main peak is produced.

Both escape peaks and sum peaks are only significant under conditions where there is a very strong main peak and a high count rate. As they occur in predictable positions in the spectrum, they are easily recognized by an experienced microscopist, and by the computer.

Having painted such a gloomy picture of the energy-dispersive analysis system we should emphasize the advantages. With an energy-dispersive system we can place a detector very close to the specimen in a TEM or SEM

and therefore collect the X-rays very efficiently, and as X-rays of all energies are collected at the same time we can acquire a complete spectrum, and therefore a qualitative analysis, in a few minutes.

6.2.2 Wavelength-dispersive analysis

مزایا ی WD نسبت به ED

The three areas in which the EDS system performs badly – light element detection, peak separation, and peak to background ratio – are the strong points of the other major X-ray detection system for electron microscopes, the wavelength-dispersive spectrometer (WDS).

The principle of the WDS is that the X-radiation coming from the specimen is filtered so that only X-rays of a chosen wavelength (usually the characteristic wavelength of the element of interest) are allowed to fall on a detector. The 'filtering' is achieved by a crystal spectrometer which employs diffraction to separate the X-rays according to their wavelength. A common arrangement for the spectrometer is illustrated in Figure 6.7. The X-rays leaving the specimen at a certain angle, the *take-off angle* (ϕ), are allowed to fall onto a crystal of lattice spacing d. If the angle between the incident X-rays and the crystal lattice planes is θ, then the only X-rays which will be diffracted by the crystal and thus reach the detector will be those obeying Bragg's Law (section 3.1). The wavelength of the transmitted X-rays is therefore given by

$$\lambda = \frac{2d \sin \theta}{n}$$

زاویه با توجه به طول موج آنالیت محاسبه و اسپکترومتر در آن زاویه تنظیم می شود.

(6.2)

If the spectrometer is to be used to detect, say Fe K_α, then the characteristic wavelength (0·19 nm from Table 6.1) is substituted into equation 6.2, and the appropriate value of θ can be calculated for the particular crystal in use. If the spectrometer is set to this angle then only the Fe K_α characteristic X-rays will reach the detector and be counted. The detector no longer has to discriminate between X-rays of different energies – it is sufficient for it to count the X-ray photons arriving. A much simpler detector than is found for EDS is used. This is the gas proportional counter, in which much faster count rates can be tolerated. One of the disadvantages is that because the X-rays must be reasonably well collimated before reaching the crystal, two sets of slits (S_1 and S_2) are generally used. In order that as many as possible of the X-rays leaving the crystal arrive at the detector the geometry of the spectrometer is chosen so that, as shown in Figure 6.7, all possible X-ray paths are focused onto the detector.

In order to achieve this focusing effect the specimen, crystal and detector must all lie on a circle of radius R known as the Rowland circle and shown dotted in Figure 6.7. Also the crystal must be curved – in the Johan type of spectrometer shown in the figure it is bent to a radius $2R$. These requirements place several restrictions on the analysis system: the spectrometer is necessarily quite large; its mechanism is complicated, since it has to be able to alter θ while keeping both the crystal and the detector on the Rowland circle; precision
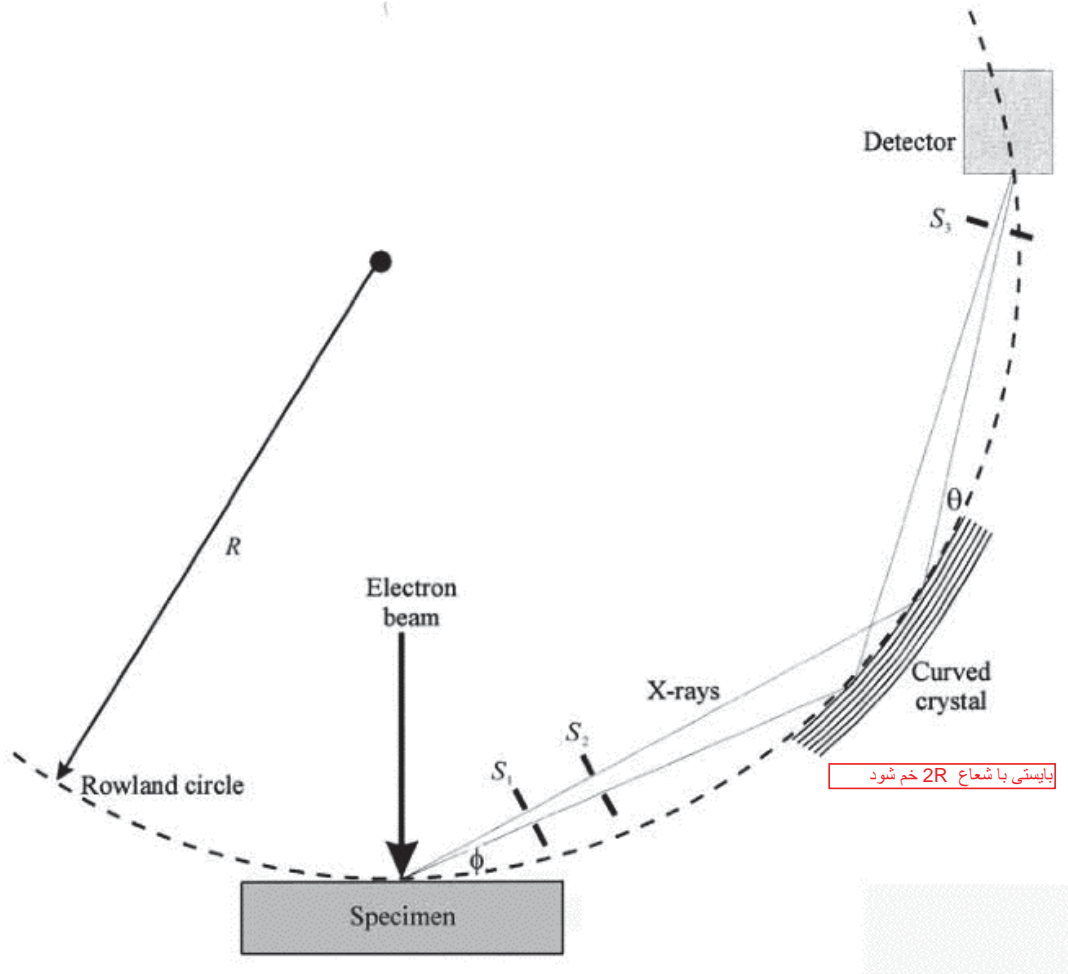
Figure 6.7 A crystal X-ray spectrometer. X-rays emitted from the specimen are collimated by two slits S_1 and S_2, diffracted by the curved crystal, and then focused on to the detector. For the maximum efficiency the specimen, crystal and detector must all lie on the Rowland circle of radius R.

engineering is required, since, in order to discriminate between very close lines, the angle θ must be set to an accuracy of better than one minute of arc; finally the position of the specimen is absolutely critical, since if it lies off the Rowland circle by as little as a few micrometres the number of X-rays reaching the spectrometer will be severely reduced. These restrictions make the design of a crystal spectrometer difficult and expensive. The mechanics of a crystal spectrometer allow the angle θ to be altered only over a limited range, and therefore to cover the whole X-ray spectrum a range of crystals, normally four, with different lattice spacings, are required. Although some spectrometers are designed to hold only one crystal, requiring the instrument to be equipped with four spectrometers, many spectrometers now have two or four crystals which may be interchanged automatically.

Because of the design of a crystal spectrometer, the geometric efficiency is low, and a solid collection angle of 0·01 steradians is typical. The detector

efficiency is also quite low, typically less than 30%, because of losses both in the diffracting crystal and at the counter. Despite the difficulty and expense of a crystal spectrometer, it remains an essential tool for analysis in the electron microscope because of four major advantages:

(a) The resolving power of a crystal spectrometer is excellent. As may be seen in Figure 6.3(a), the lines are sharp and there is rarely a problem of adjacent lines overlapping.

(b) The peak-to-background ratio of each line is much higher (often by a factor of ten) than can be achieved with a solid detector.

(c) Since the X-ray detector normally used in a crystal spectrometer is capable of counting at very high rates (perhaps 50 000 cps) it may be possible to collect data from a single element in a very short counting time.

(d) One of the main reasons for using a crystal spectrometer is its ability to detect X-rays from light elements. With suitable crystals of large lattice spacing it is possible to detect and count X-rays as soft as boron Kα or even beryllium Kα.

Although, as mentioned above, a windowless EDS detector can be used down to the limit of boron, the greater sensitivity and better resolving power of the crystal spectrometer give this technique a distinct advantage at the present time.

On the other hand, the disadvantages of an X-ray spectrometer make its use very time-consuming and hence restrict its major applications to the things it does well – detection of low concentrations, detection of light elements, and quantitative measurement of peak heights. There are some obvious disadvantages in using a crystal spectrometer for qualitative analysis. These are that as only one wavelength of X-ray is detected at any time, a scan of all the required wavelengths can take a considerable time. Also, since the spectrometer employs diffraction there will be not one angle of the crystal (θ) at which a certain line is detected but several, one corresponding to each value of n in equation 6.1. Thus there may be as many as seven or eight *orders of reflection* detectable from a major X-ray line and therefore the spectrum contains far more lines than that collected by the energy-dispersive detector.

In summary, the two main X-ray detection and measurement systems, EDS and WDS, each have their strong points. The EDS is clearly better suited to rapid qualitative analysis, while the WDS may give more accurate quantitative results. As we shall see in the next section, both have wide application in electron microscopy.

6.3 X-ray analysis of bulk specimens

6.3.1 Instrumentation

The earliest electron probe microanalysers pre-dated the SEM and were simply instruments which generated a beam of electrons, directed it at a specimen and used one or more crystal spectrometers to analyse the X-radiation emitted. This represented a great advance in analytical technique, since the electron beam could be directed at a relatively small area of a solid specimen and an analysis obtained without destroying the specimen. The region of the specimen to be analysed was selected using a light microscope, and the accuracy with which the beam could be positioned was rather limited. It was soon realized that by scanning the electron beam and installing an electron detector, an imaging system could be incorporated. Since the size of the sampling volume discussed in section 5.1 implies that no useful analysis can be made of a region smaller than $1\,\mu m \times 1\,\mu m \times 1\,\mu m$ there seemed to be no point in making the electron beam smaller than this. Indeed, as the low geometric efficiency of a crystal spectrometer means that a probe current of the order of $1\,\mu A$ is required, the arguments of section 5.5, and equation 5.13, show that a probe of diameter $\sim 1\,\mu m$ is needed to obtain this level of beam current.

However, electron probe microanalysers have progressed considerably, and an example is shown in Figure 6.8. A typical instrument is equipped with four computer controlled crystal spectrometers, containing a range of crystals such that the whole spectrum can be covered. An EDS system for preliminary qualitative analysis is fitted. Secondary and backscattered imaging can be carried out, and the spatial resolution in secondary electron mode is better than $10\,nm$. A fixed focus light microscope is retained, not only for examination of the specimen, but more importantly for ensuring that the specimen height may be adjusted until it is on the Rowland circle. In the design of such an instrument, particular attention is paid to the electron gun which must be capable of providing the large beam currents necessary coupled with the extreme stability which is required if an analysis is to be carried out over a period of several hours.

As well as automation of the spectrometers, the specimen stage will be motorized and be capable of computer control. Thus, areas of interest may be selected by the operator, and the instrument may then be left to carry out the analysis, perhaps running for several hours under automation. Such an instrument is ideally suited to an environment where accurate quantitative analysis is required from a large number of specimens on a routine basis.

An alternative approach is to mount an energy dispersive detector on to an existing scanning microscope. This is ideal for qualitative analysis, and the majority of scanning electron microscopes are now equipped with an EDS system, an example being seen in Figure 5.3. For reasons which are discussed in section 6.5, this may not be an ideal combination for the purposes of quantitative analysis; nevertheless, some scanning microscopes
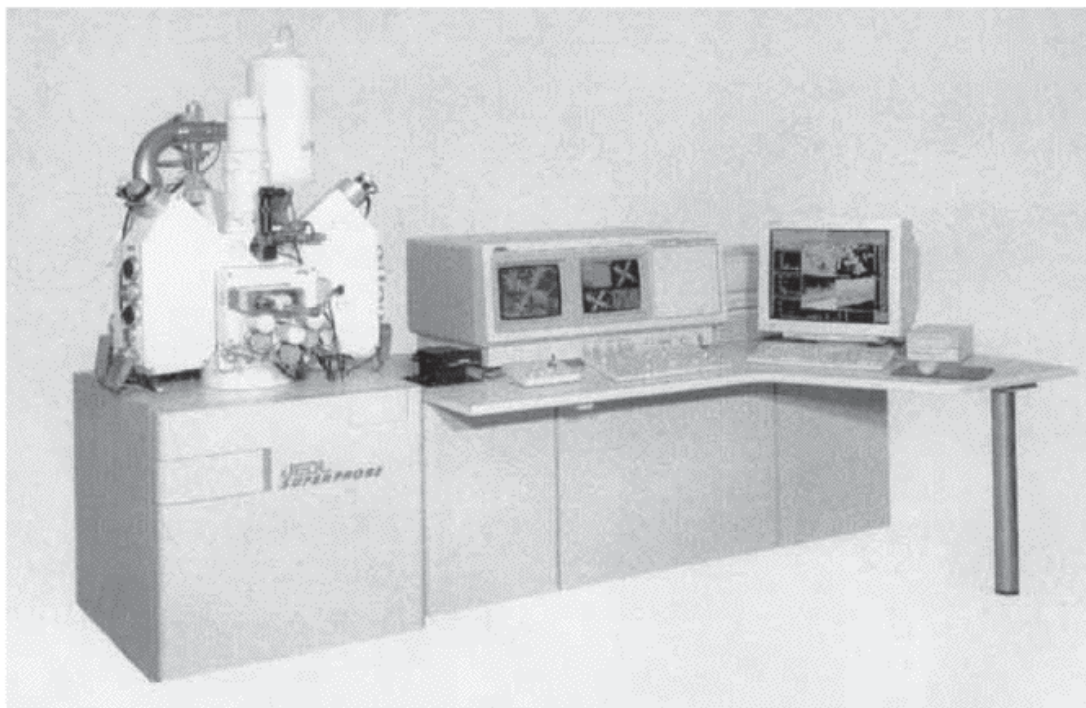
Figure 6.8 An electron probe microanalyser. (JEOL Ltd.)

are capable of quantitative analysis, and some may also be fitted with crystal spectrometers. For a laboratory which does not have the requirement for a dedicated electron probe microanalyser, a good analytical SEM provides an acceptable and cheaper alternative.

6.3.2 The presentation of analytical information

For all the instruments discussed in this section, which are based on a scanning electron beam, there are various ways in which qualitative analytical information obtained from a suitable (ideally, flat) specimen can be presented, and the method selected will depend upon which of three types of information is required. This will be either (*a*) an analysis of a selected region of chemically homogeneous composition such as a phase, (*b*) an overall analysis of the whole or part of a sample, or (*c*) an analysis to determine the variation of composition within a region of the sample.

The first type of analysis is usually accomplished simply by a 'spot analysis', in which the electron beam is stopped and positioned carefully on the point to be analysed, which has been selected on the SEM screen while the image was still being displayed. The X-ray data, either a single peak or series of peaks being detected by a crystal spectrometer, or the whole spectrum being accumulated by an EDS system, can be collected for as long as is necessary and the composition at the selected point (or more correctly in the sampling volume of

about $1\,\mu m^3$) can be determined. As an alternative, instead of using a stationary beam, we might, while analysing, scan a small raster on the specimen, making sure that the raster was contained within a chemically homogeneous region.

The second type of analysis entails obtaining data from a larger area of the specimen, the actual area being, of course, dependent on the scale of the chemical heterogeneity in the specimen. For an EDS system this only requires scanning the beam over a suitable area which might be $100\,\mu m \times 100\,\mu m$, as the X-rays are detected. The analysis is then an average of the area of the image on the screen. However, for a WDS system this is not possible, because, as may be seen from Figure 6.7, only one point P (strictly, one line) of the specimen lies on the Rowland circle. Therefore as the beam scans a raster, X-rays from regions other than those within a few micrometres of P will not be focused on the detector, will not be collected effectively, and a misleading result may be obtained. If an analysis of an area greater than about $5\,\mu m \times 5\,\mu m$ is required by WDS, then this must be done by scanning the specimen and not the beam.

In order to examine the variation of chemical composition within a sample, many analyses must be carried out over the area of interest. There are three approaches to this problem; the simplest, and probably the best, is to use backscattered electron compositional imaging (section 5.7) to identify regions of chemical homogeneity, and then to carry out spot analyses of these areas.

An alternative is to select the X-ray signal from an element of interest, and to display its intensity as the beam (or for a WDS system, the specimen) is scanned. For a crystal spectrometer, this simply requires the use of a *ratemeter* which will measure the instantaneous count rate, rather than the total number of counts from the selected peak. For an EDS system, it is necessary to make the ratemeter sensitive only to the counts going to a selected number of channels. If the X-ray count rate measured by the ratemeter is used to deflect a spot on the display screen then a trace of composition versus distance as illustrated in Figure 6.9 can be obtained. Notice that although for ease of recognition the 'line' of the analysis is shown superimposed on a micrograph of the specimen, these were taken separately. First an electron image of the specimen was recorded, then the spot was scanned along the chosen line and recorded on the same photographic exposure. Then the spot was scanned very slowly, taking 100–500 s, while the trace shown in Figure 6.9 was displayed and photographed.

As can be seen from the example illustrated, this technique makes it quite simple to find the regions where there is a significant change in the concentration of an element. An accurate analysis is difficult, as the electron beam spends only a short time on each spot, and the counting statistics are poor.

Another way of displaying information about the distribution of a single element is by what is often termed X-ray mapping. Using this technique, the X-ray counter is used in a similar way to any of the other detectors in the SEM to
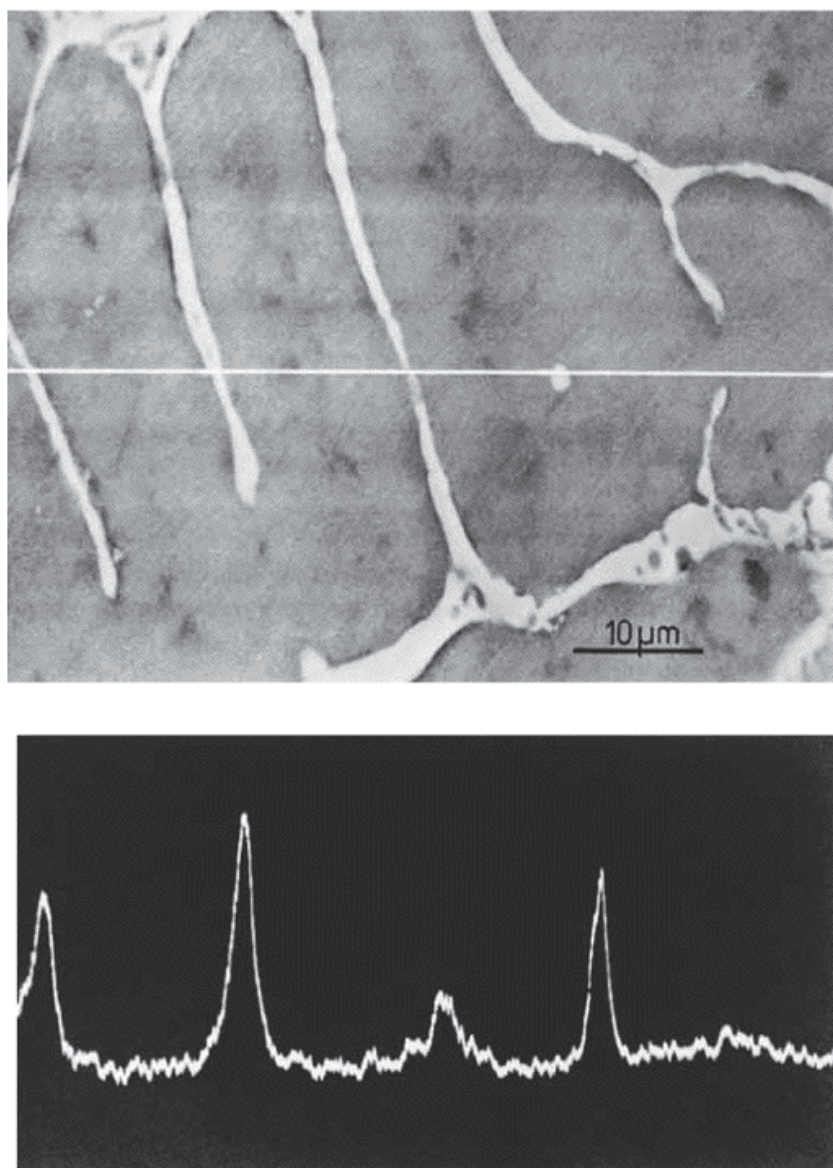
Figure 6.9 The variation of copper concentration across a section of an aluminium–copper alloy. The trace in the lower part of the figure is the copper count rate (i.e. the output of the ratemeter) as the electron beam was scanned along the line indicated in the micrograph.

form an image. This is essentially an extension of the linescan method discussed above, to two-dimensional scanning. In its simplest form, the display is made bright every time an X-ray photon is counted. The image then consists of bright dots, the dot density being a qualitative measure of the concentration of the element of interest. As may be seen in Figure 6.10, the quality of such dot maps is not very good, primarily because the counting statistics are very poor even for exposures of more than 1000 s.
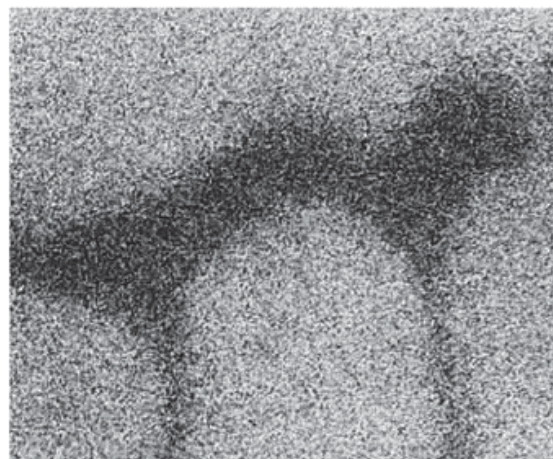
A great improvement is obtained by using *digital X-ray mapping* to obtain this type of information. The concept of digital scanning electron microscopy
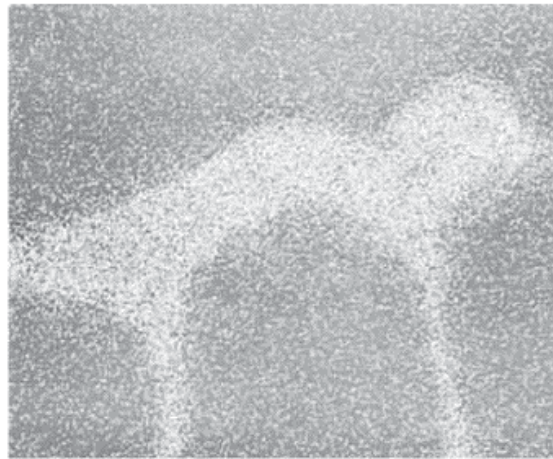
Figure 6.10 X-ray 'dot' distribution maps from the aluminium–copper alloy of Figure 6.9. (*a*) Secondary electron image. (*b*) Copper K_α map. (*c*) Aluminium K_α map. Despite the obvious presence of fine details within the copper-rich phase, the dot maps do not show it because of poor spatial resolution and poor counting statistics.