Introduction to Energy Dispersive X-ray Spectrometry (EDS)

1. Introduction

1.1 Principles of the technique

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, but can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. There is thus a considerable overlap in the functions of these instruments.

1.2 Accuracy and sensitivity

X-ray intensities are measured by counting photons and the precision obtainable is limited by statistical error. For major elements it is usually not difficult to obtain a precision (defined as 2σ) of better than ± 1% (relative), but the overall analytical accuracy is commonly nearer ± 2%, owing to other factors such as uncertainties in the compositions of the standards and errors in the various corrections which need to be applied to the raw data.

As well as producing characteristic X-ray lines, the bombarding electrons also give rise to a continuous X-ray spectrum (section 2.4), which limits the detachability of small peaks, owing to the presence of 'background'.

Using routine procedures, detection limits are typically about 1000 ppm (by weight) but can be reduced by using long counting times

1.3 Spatial resolution

Spatial resolution is governed by the penetration and spreading of the electron beam in the specimen (Figure 1). Since the electrons penetrate an approximately constant mass, spatial resolution is a function of density. In the case of silicates (density about 3 g cm^{-3}), the nominal resolution is about 2 μm under typical conditions, but for quantitative analysis a minimum grain size of several micrometers is desirable.

Better spatial resolution is obtainable with ultra-thin (~100 nm) specimens, in which the beam does not have the opportunity to spread out so much. Such specimens can be analyzed in a transmission electron microscope (TEM) with an X-ray spectrometer attached, also known as an analytical electron microscope, or AEM.

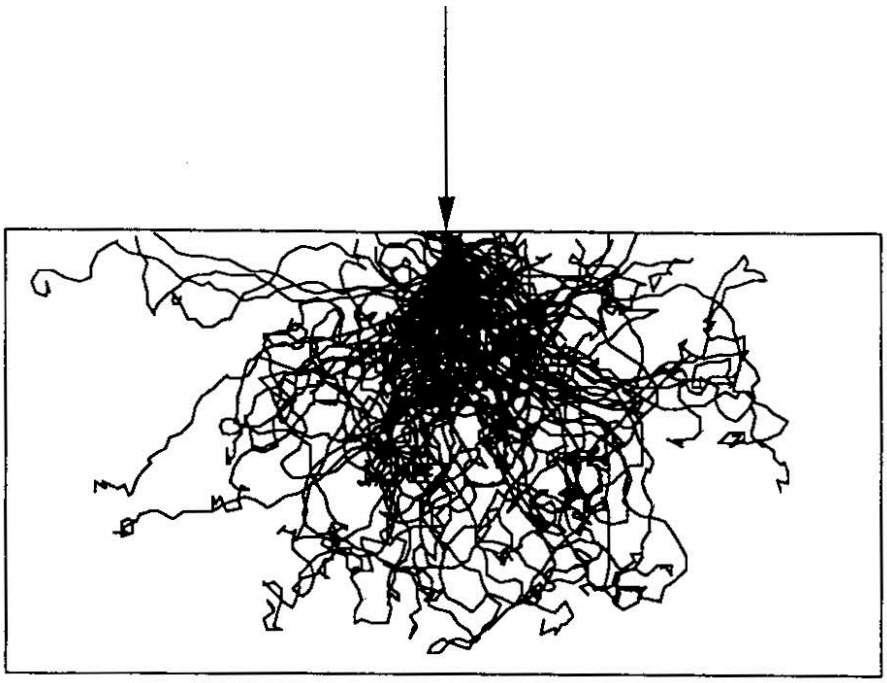

Figure 1 Simulated trajectories of electrons (energy 20 keV) in Si (rectangle = 1x2μm.

1.4 Sample preparation

Since the electron probe analyses only to a shallow depth, specimens should be well polished so that surface roughness does not affect the results. Sample preparation is essentially as for reflected light microscopy, with the provision that only vacuum compatible materials must be used. Opaque samples may be embedded in epoxy resin blocks. For transmitted light viewing, polished thin sections on glass slides are prepared.

In principle, specimens of any size and shape (within reasonable limits) can be analyzed. Holders are commonly provided for 25mm (1") diameter round specimens and for rectangular glass slides. Standards are either mounted individually in small mounts or in batches in normal-sized mounts.

Many samples are electrically non-conducting and a conducting surface coat must be applied to provide a path for the incident electrons to flow to ground. The usual coating material is vacuum-evaporated carbon (~10nm thick), which has a minimal influence on X-ray intensities on account of its low atomic number, and (unlike gold, which is commonly used for SEM specimens) does not add unwanted peaks to the X-ray spectrum. However, steps should be taken to maintain as constant a thickness as possible.

2. X-ray spectroscopy

2.1 *Atomic structure*

According to the Rutherford-Bohr model of the atom. Electrons orbit around the positive nucleus. In the normal state the number of orbital electrons equals the number of protons in the nucleus (given by the atomic number, Z). Only certain orbital states with specific energies exist and these are defined by quantum numbers (see standard texts). With increasing Z, orbits are occupied on the basis of minimum energy, those nearest the nucleus, and therefore the most tightly bound, being filled first. Orbital energy is determined mainly by the principal quantum number (n). The shell closest to the nucleus (n = 1) is known as the K shell; the next is the L

shell (n = 2), then the M shell (n = 3), etc. The L shell is split into three subshells designated L1, L2 and L3, which have different quantum configurations and slightly different energies (whereas the K shell is unitary). Similarly, the M shell has five subshells. This model of the inner structure of the atom is illustrated in Figure 2.

The populations of the inner shells are governed by the Pauli exclusion principle, which states that only one electron may possess a given set of quantum numbers. The maximum population of a shell is thus equal to the number of possible states possessing the relevant principal quantum number. In the case of the K shell this is 2, for the L shell 8, and for the M shell 18. Thus for $Z \geq 2$ the K shell is full, and for $Z \geq 10$ the L shell is full.

Electrons occupying outer orbits are usually not directly involved in the production of X-ray spectra, which are therefore largely unaffected by chemical bonding etc.

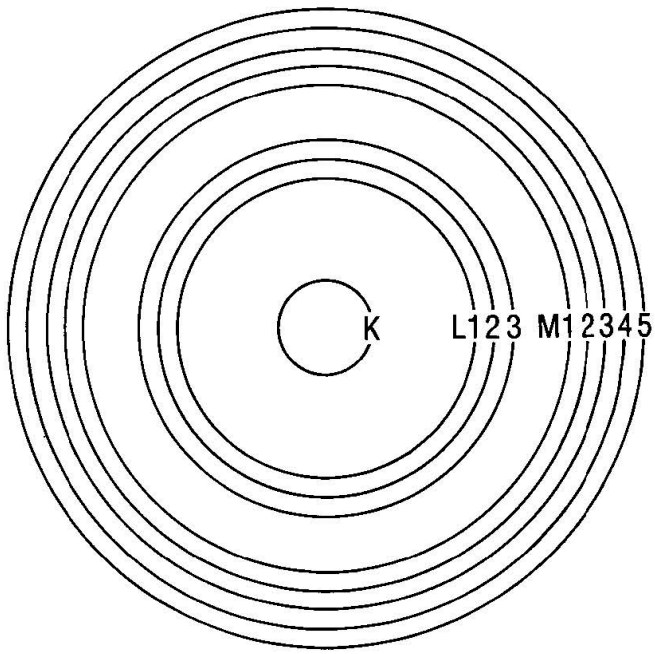

Figure 2. Schematic diagram of inner atomic electron shells.

2.2 *Origin of Characteristic X-rays*

'Characteristic' X-rays result from electron transitions between inner orbits, which are normally full. An electron must first be removed in order to create a vacancy into which another can 'fall' from an orbit further out. In electron probe analysis vacancies are produced by electron bombardment, which also applies to X-ray analysis in the TEM.

X-ray lines are identified by a capital Roman letter indicating the shell containing the inner vacancy (K, L or M), a Greek letter specifying the group to which the line belongs in order of decreasing importance α, β, etc.), and a number denoting the intensity of the line within the group in descending order (1, 2, etc.). Thus the most intense K line is $K\alpha_1$ (The less intense $K\alpha_2$ line is usually not resolved, and the combined line is designated $K\alpha_{1,2}$ or just $K\alpha$). The most intense L line is $L\alpha_1$. Because of the splitting of the L shell into three subshells, the L spectrum is more complicated than the K spectrum and contains at least 12 lines, though many of these are weak.

Characteristic spectra may be understood by reference to the energy level diagram

(Figure 3), in which horizontal lines represent the energy of the atom with an electron removed from the shell (or subshell) concerned. An electron transition associated with X-ray emission can be considered as the transfer of a vacancy from one shell to another, the energy of the X-ray photon being equal to the energy difference between the levels concerned. For example, the Kα line results from a K-L3 transition (Figure 3).

Energies are measured in electron volts (eV), 1 eV being the energy corresponding to a change of 1 V in the potential of an electron (= 1.602 x10^{-19} J). This unit is applicable to both X-rays and electrons. X-ray energies of interest in electron probe analysis are mostly in the range 1-10 keV.

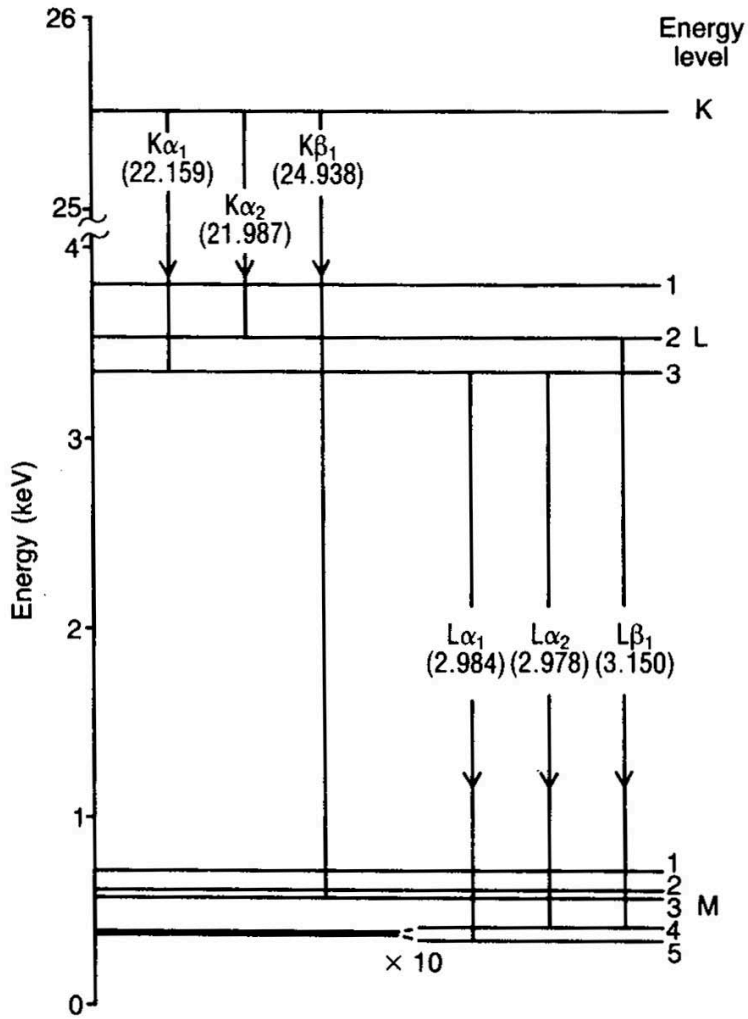

Figure 3. Energy level diagram for Ag showing transitions responsible for main K and L emission lines (arrows show direction of vacancy movement), energy of emission line indicated in brackets.

The 'critical excitation energy' (E_c) is the minimum energy which bombarding electrons (or other particles) must possess in order to create an initial vacancy. Figure 4 shows the dependence of E_c on Z for the principal shells. In electron probe analysis the incident electron energy (E_0) must exceed E_c and should preferably be at least twice E_c to give reasonably high excitation efficiency. For atomic numbers above about 35 it is usual to change from K to L lines to avoid the need for an excessively high electron beam energy (which has undesirable implications with respect to the penetration of the electrons in the sample, and in any case may exceed the maximum available accelerating voltage).

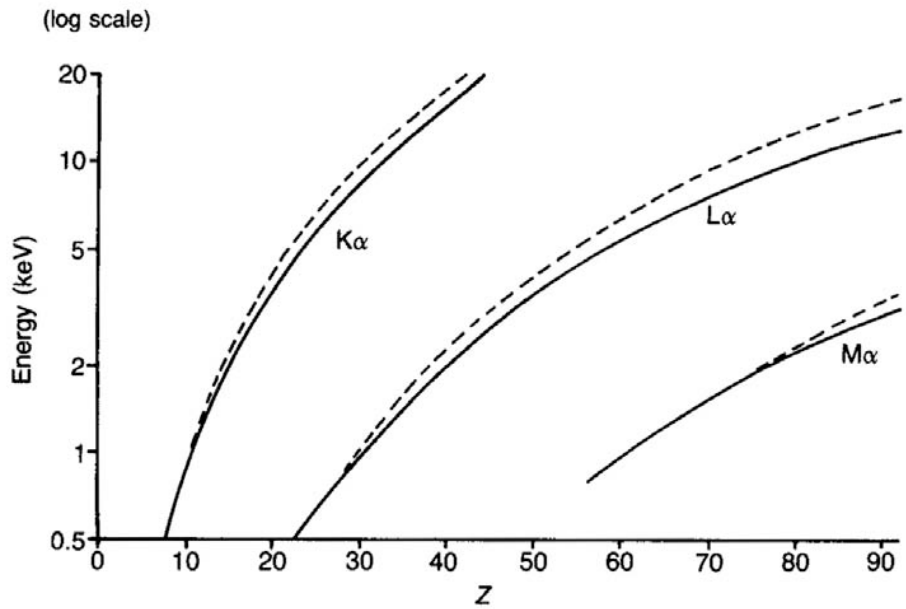

Figure 4. Energies of principal characteristic lines (_) and their excitation energies (----).

2.3 *Wavelengths, energies and intensities of X-ray lines*

The preceding discussion treated X-rays as photons possessing a specific energy (E). Sometimes it is more appropriate to describe X-rays by their wavelength (λ), which is related to energy by the expression:

$$E\lambda = 12396$$

where E is in electron volts and λ is in **Å**, where 1**Å** = 10^{-10}m.

Since X-ray lines originate in transitions between inner shells, the energy of a particular line shows a smooth dependence on atomic number, varying approximately as Z^2 (Moseley's law). The energies of the $K\alpha_1$, $L\alpha_1$ and $M\alpha_1$ lines are plotted against Z in Figure 4.

The total X-ray intensity for a particular shell is divided between several lines. In the case of the K shell, more than 80% of the total intensity is contained in the combined $K\alpha_{1,2}$ line (Figure 5). The relative intensity of the Kβ line decreases with decreasing atomic number, in accordance with the electron occupancies of the relevant energy levels.

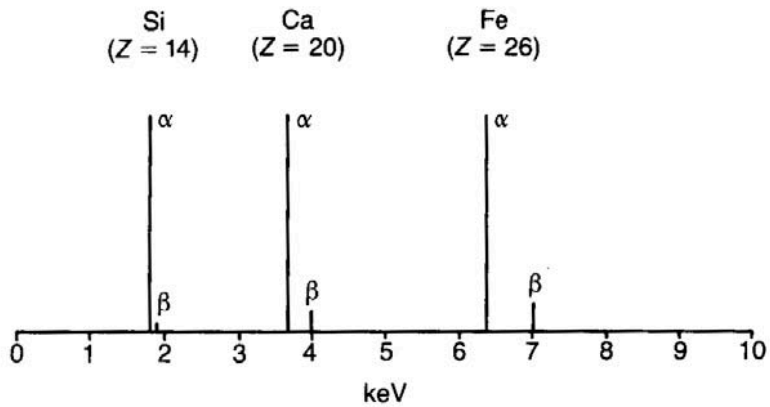

Figure 5 Typical K spectra.

2.4 *The continuous spectrum*

Electron bombardment not only produces characteristic X-ray lines resulting from electron transitions between inner atomic shells but also a continuous X-ray spectrum or (continuum', covering all energies from zero to E_0 (the incident electron energy). This continuum arises from interactions between incident electrons and atomic nuclei. The intensity of the continuum decreases monotonically with increasing X-ray energy, and is approximately proportional to Z. The main significance of the continuum in the present context is that it contributes the 'backgrounds' upon which characteristic elemental lines are superimposed.

3. **Energy-dispersive spectrometers**

Energy-dispersive spectrometers (EDSs) employ pulse height analysis: a detector giving output pulses proportional in height to the X-ray photon energy is used in conjunction with a pulse height analyzer (in this case a multichannel type). A solid state detector is used because of its better energy resolution. Incident X-ray photons cause ionization in the detector, producing an electrical charge, which is amplified by a sensitive preamplifier located close to the detector. Both detector and preamplifier are cooled with liquid nitrogen to minimize electronic noise. Si(Li) or Si drift detectors (SDD) are commonly in use.

3.1 *Energy resolution*

The ED spectrum is displayed in digitized form with the x-axis representing X-ray energy (usually in channels 10 or 20 eV wide) and the y-axis representing the number of counts per channel (Figure 6). An X-ray line (consisting of effectively mono-energetic photons) is broadened by the response of the system, producing a Gaussian profile. Energy resolution is defined as the full width of the peak at half maximum height (FWHM). Conventionally, this is specified for the Mn Kα peak at 5.89 keV. For Si(Li) and SDD detectors, values of 130-150 eV are typical (Ge detectors can achieve 115eV). The resolution of an EDS is about an order of magnitude worse than that of a WDS, but is good enough to separate the K lines of neighboring elements (Figure 6).

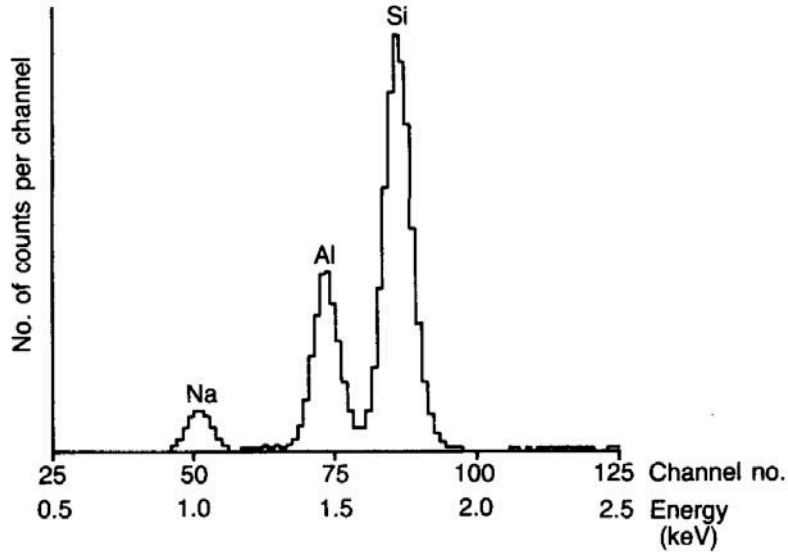

Figure 6 ED spectrum of jadeite (part), showing K peaks of Na, A1 and Si.

3.2 *Dead time and throughput*

In processing the pulses from a solid state detector prior to pulse-height analysis, it is necessary to use certain integrating time to minimize noise. The system consequently has a specific 'dead time', or period after the arrival of an X-ray photon during which the system is unresponsive to further photons. This limits the rate at which pulses can be processed and added to the recorded spectrum. ‘Throughput' passes through a maximum above which it decreases with further increases in input count rate. The maximum throughput rate is a function of the integration time and the design of the system.

Energy resolution is determined partly by the statistics of the detection process and partly by noise fluctuations in the baseline upon which the pulses are superimposed. The longer the integration time, the more the noise is smoothed out, and the better the energy resolution. There is thus a 'tradeoff' between resolution and throughput. Hitherto, maximum throughput rates have been typically in the region of 20 000 counts s^{-1} for Si(Li) and 100 000 counts s^{-1} and above for SDD.

4 Qualitative analysis

4.1 *Line identification*

The object of qualitative analysis is to find what elements are present in an 'unknown' specimen by identifying the lines in the X-ray spectrum using tables of energies or wavelengths. Ambiguities are rare and can invariably be resolved by taking into account additional lines as well as the main one.

4.2 *Qualitative ED analysis*

The ED spectrometer is especially useful for qualitative analysis because a complete spectrum can be obtained very quickly. Aids to identification are provided, such as facilities for superimposing the positions of the lines of a given element for comparison with the recorded spectrum (Figure 7).

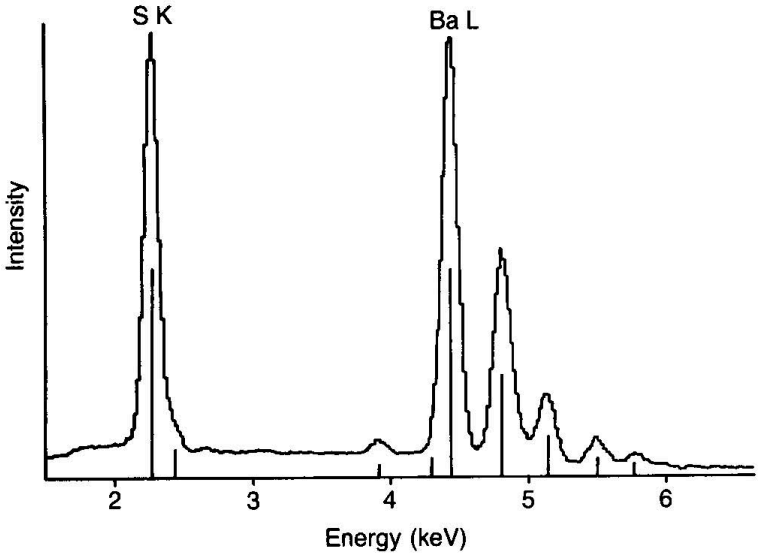

Figure 7 Line markers for S K and Ba L lines in the ED spectrum of barite.

Owing to the relatively poor resolution, there are cases where identification may not be immediately obvious. An example showing unresolved S K and Pb M lines is given in Figure 8.

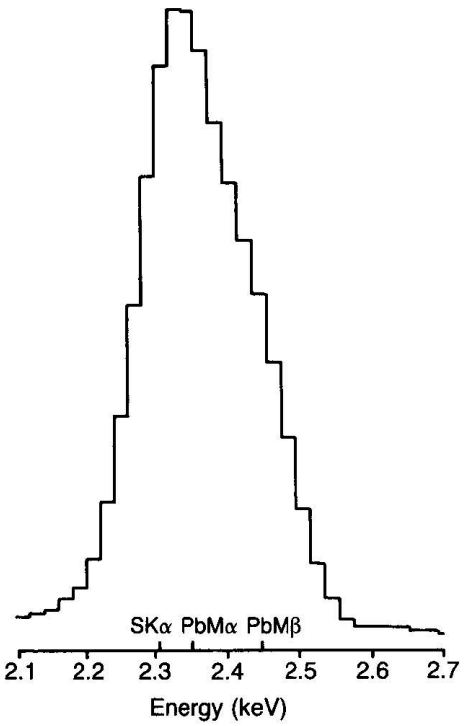

Figure 8 Unresolved peaks in an ED spectrum (PbS sample).

In performing qualitative x-ray analysis, we have to identify the specific energy of the characteristic x-ray peaks for each element. This information is available in the form of tabulations, graphs or as computer database. The energy-dispersive x-ray spectrometer is an attractive tool for qualitative x-ray microanalysis. The fact that the total spectrum of interest, from 0.1 keV to the beam energy (e.g., 20 keV) can be acquired in a short time (10 - 100 s) allows for a rapid evaluation of the specimen. Since the EDS detector has virtually constant efficiency (near 100%) in the range 3 to 10 keV, the relative peak heights observed for the families of x-ray lines are close to the values expected for the signal as it is emitted from the sample. On the negative side, the relatively poor energy resolution of the EDS compared to the WDS leads to frequent spectral interference problems as well as the inability to separate the members of the x-ray families, which occur at low energy (< 3 keV). Also, the existence of spectral artifacts such as escape peaks or sum peaks increases the complexity of the spectra.
The approximate weights of lines in a family provide important information in identifying elements. The K family consists of two recognizable lines $K\alpha$ and $K\beta$ for energies above 3 keV. The ratio of intensities of the $K\alpha$ and $K\beta$ peaks is approximately 10:1, when the peaks are resolved this ratio should be apparent in the identification of an element. Any substantial deviation from this ratio should be viewed with suspicion as originating from a misidentification or the presence of a second element. The L series as observed by EDS consists of $L\alpha$ (1), $L\beta_1$(0.7), $L\beta_2$(0.2), $L\beta_3$(0.08), $L\beta_4$(0.05), $L\gamma_1$(0.08), $L\gamma_3$(0.03), $L\lambda$(0.04), and $L\eta$(0.01). The observable M series consists of $M\alpha$ (1), $M\beta$ (0.6), $M\gamma$(0.05), $M\zeta$(0.06), and $M_{II}N_{IV}$(0.01). The values in parentheses give approximate relative intensities, since these intensities vary with the element in question and with the over-voltage.
Below 3 keV, the separation of the members of the K, L, or M families becomes so small that the peaks are not resolved with an EDS system. Note that the unresolved low-energy $K\alpha$ and $K\beta$ peaks appear to be nearly Gaussian (because of the decrease in the relative height of the $K\beta$ peak to about 0.01 of the height of the $K\alpha$), while the L and M lines are asymmetric because of the presence of several unresolved peaks of significant weight near the main peak.

All x-ray lines for which the critical excitation energy is exceeded will be observed. Therefore in a qualitative analysis, all lines for each element should be located. In carrying out accurate qualitative analysis, a conscientious "bookkeeping" method must be followed. When an element is identified, all x-ray lines in the possible families excited must be marked off, particularly low-relative-intensity members. Artifacts such as escape peaks and sum peaks, mainly associated with the high-intensity peaks, should be marked off as each element is identified. As a final step, the analyst should consider what peaks may be hidden by interference. If it is important to know of the presence of those elements, if impossible to resolve interference problems it will be necessary to resort to WDS analysis.

5 Quantitative analysis – experimental

5.1 Counting statistics

X-ray intensities are measured by counting pulses generated in the detector by X-ray photons, which are emitted randomly from the sample. If the mean number of counts recorded in a given time is n, then the numbers recorded in a series of discrete measurements form a Gaussian distribution with a standard deviation (σ) of $n^{1/2}/n$. A suitable measure of the statistical error in a single measurement is $\pm 2\sigma$. It follows that 40 000 counts must be collected to obtain a 2σ precision of ± 1% (relative). Such statistical considerations thus dictate the time required to measure intensities for quantitative analysis.

5.2 *Choice of conditions*

The optimum choice of accelerating voltage is determined by the elements present in the specimen. The accelerating voltage (in kV) should be not less than twice the highest excitation energy Ec (in keV) of any element present, in order to obtain adequate intensity. For instance, in silicates, the element with the highest atomic number is commonly Fe, which also has the highest excitation energy (7.11 keV), hence the accelerating voltage should be at least 15 kV. Line intensities increase with accelerating voltage, but so does electron penetration, making spatial resolution worse and increasing the absorption suffered by the emerging X-rays.

The other important variable selected by the user is beam current. The higher the current the higher the X-ray intensity, but there are practical limitations. Some samples are prone to beam damage, which necessitates the use of a low current. In the case of ED analysis, the limited throughput capability of the system has to be considered and a current as low as a few nA may be appropriate.

6 Quantitative analysis - data reduction

6.1 *Castaing's approximation*

As shown by Castaing (1951), the relative intensity of an X-ray line is approximately proportional to the mass concentration of the element concerned. This relationship is due to the fact that the mass of the sample penetrated by the incident electrons is approximately constant regardless of composition. (The electrons are decelerated by interactions with bound electrons and the number of these per atom is equal to the atomic number, which, in turn, is approximately proportional to the atomic weight). Given this approximation, an 'apparent concentration' (C') can be derived using the following relationship:

$$C' = \left(\frac{I_{sp}}{I_{st}}\right) C_{st}$$

where I_{sp} and I_{st} are the intensities measured for specimen and standard respectively, and C_{st} is the concentration of the element concerned in the standard. To obtain the true concentration, certain corrections are required.

6.2 Background Correction for EDS

As a starting point to perform an accurate background correction, we need to view the characteristic peak and the adjacent background. Because the EDS peaks are so broad, the tails of the Gaussian peak extend over a substantial energy range, interfering with our view of the adjacent background. Background measurements with the EDS are therefore made difficult because of the problem of finding suitable background areas adjacent to the peak being measured. For a mixture of elements, the spectrum becomes more complex, and interpolation is consequently less accurate.

Compensation for the background, by subtraction or other means, is critical to all EDS analysis. Basically there are two approaches to this problem. In the first approach, a continuum energy-distribution function is either calculated or measured and combined with a mathematical description of the detector response function. The resulting function is then used to calculate a background spectrum, which can be subtracted from the observed spectral distribution. This method can be called background modeling.

In the second approach, the physics of x-ray production and emission is generally ignored and the background is viewed as an undesirable signal, the effect of which can be removed by

mathematical filtering or modification of the frequency distribution of the spectrum. Examples of the latter technique include digital filtering and Fourier analysis. This method can be called background filtering. It must be remembered here that a real x-ray spectrum consists of characteristic and continuum intensities both modulated by the effects of counting statistics. When background is removed from a spectrum, by any means, the remaining characteristic intensities are still modulated by both uncertainties. We can subtract away the average effect of the background, but the effects of counting statistics cannot be subtracted away. In practice, both background filtering and background modeling have proved successful.

6.3 *Matrix corrections*

'Apparent concentrations' require various corrections which are dependent on the composition of the matrix within which the element concerned exists. The first of these corrections arises because the mass penetrated is not strictly constant, but is affected by differences in the stopping power' of different elements. This is the 'stopping power correction'. The second allows for the loss of incident electrons, which escape from the surface of the sample after being defected by target nuclei and thus can make no further contribution to X-ray production: this is the 'backscattering correction'. The third takes account of attenuation of the X-rays as they emerge from a finite depth in the sample ('absorption corrections'), and the fourth allows for enhancement in X-ray intensity, arising from fluorescence by other X-rays generated in the sample ('fluorescence corrections').

The absorption correction is generally the most important. It is dependent on the angle between the surface of the specimen and the X-ray path to the spectrometer, or 'X-ray take-off angle' (Figure 9), which is about 40° for current models of electron probes, although earlier instruments used different angles. The angle of incidence of the beam is also relevant: standard correction methods assume normal incidence and modifications are required for non-normal incidence (as sometimes applies in SEMs).

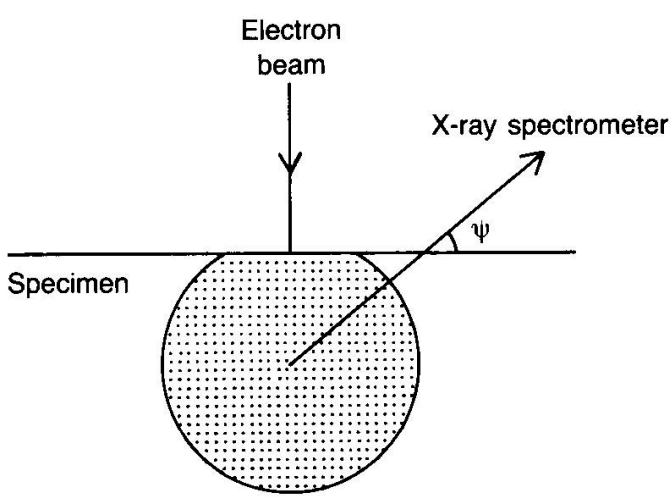

Figure 9 X-ray source region, with path of X-rays to the spectrometer ψ= take-off angle).

6.4 *ZAF corrections*

The acronym 'ZAF' describes a procedure in which corrections for atomic number effects (Z), absorption (A) and fluorescence (F) are calculated separately from suitable physical models.

(The atomic number correction encompasses both the stopping power and backscattering factors). Certain specific methods of calculating these corrections, developed in the 1960s, constitute the standard form of the ZAF correction, which is still used quite successfully. Its main drawback is that the absorption correction is inadequate when the correction is large; alternative absorption correction procedures are therefore preferable.

6.5 *Accuracy*

For major elements, it is usually possible to obtain a statistical precision of ±1% relative (2σ). However, various factors apply which limit the accuracy obtainable in the final result. Instrumental instabilities should be less than 1%, and uncertainty in standard compositions may be similarly small (though not always). The largest uncertainties are generally in the matrix corrections, especially the absorption correction when absorption is severe. Generalization is difficult, but ±1% is attainable in favorable cases.

6.6 *Detections limits*

With decreasing concentration, statistical errors and uncertainties in background corrections become dominant. For a concentration in the region of 100 ppm the intensity measured on the peak consists mainly of background. The smallest detectable peak may be defined as three times the standard deviation of the background count.

An order-of-magnitude detection limit estimate can be obtained as follows. If the count rate for a pure element is 1000 counts s^{-1} and the peak-to-background ratio is 500:1, the background count rate is 2 counts s^{-1}. In 100 s a total of 200 background counts will be accumulated, giving a relative standard deviation of ($200^{½}$ /200) or 0.07. Since the background intensity in this case is equivalent to the peak count rate for a concentration of 1000 ppm, three standard deviations is thus equivalent to a concentration of 0.07 x 3 x 1000 = 212 ppm.

Reducing the detection limit requires more counts, which can be obtained by increasing the counting time and /or the beam current. In ED analysis, detection limits are typically about 0.1%, although reduction can be achieved by using long counting times or better count rate using SDD detectors.

Values given here for detection limits refer to samples such as silicates, for which the mean atomic number (which determines continuum intensity) is quite low. Phases containing heavy elements give higher detection limits due to the higher background. Further, detection limits for heavy elements (using L or M lines) tend to be somewhat higher because the peak-to-background ratio is lower than for K lines.

Further reading

Agarwal B.K. (1991) X-ray Spectroscopy, 2nd edn, Springer-verlag, Berlin.
Goldstein, J. I., *et al*. (2003) Scanning Electron Microscopy and X-ray Micronalysis, 3rd ed, Plenum Press, New York.
Reed, S.J.B. (1993) Electron Microprobe Analysis, 2nd ed. Cambridge University Press, Cambridge.
Reimer, L. (1985) Scanning Electron Microscopy, Springer-Verlag, Berlin .
Russ, J. C. (1984) Fundamentals of Energy Dispersive X-ray Analysis, Butterworths. London.
Scott, V. D. and Love, G. (1994) Quantitative Electron Probe Microanalysis, 2nd edn. Ellis Horwood, Chichester.