ENERGY DISPERSIVE X-RAY (EDS) MICROANALYSIS
OF THIN SPECIMENS
IN THE ANALYTICAL ELECTRON MICROSCOPE

The advent of x-ray analysis in the analytical TEM has revolutionized the study of fine-scale microstructures of materials. In general it is used to obtain qualitative and quantitative chemical analyses from materials with a spatial resolution down to nanometer scale.

Principles of the technique

In the TEM one of the interactions of the beam electrons with the specimen is inelastic scattering of beam electrons, this leads to production of x-rays by two distinctly different processes. First is bremsstrahlung or continuous x-ray radiation and the second is inner-shell ionization, which can lead to the emission of characteristic x-rays. When beam electrons strike the specimen they can undergo deceleration in the Coulombic field of the atoms, which is formed by the positive field of the nucleus and the negative field of the bound electrons. The loss of energy from the electron that occurs in such a deceleration event is emitted as a photon of electromagnetic energy (Fig. 1). This radiation is referred to as x-ray bremsstrahlung or braking radiation. Because of the random nature of the interaction, the electron may lose any amount of energy in a single deceleration event. The bremsstrahlung can therefore take on any value from 0 up to the incident electron energy, thus forming continuous electromagnetic spectrum.

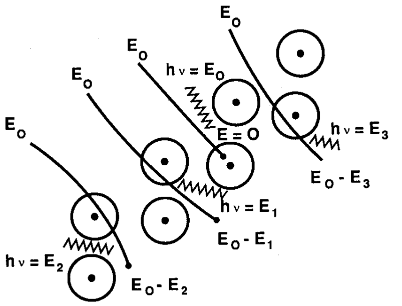


Figure 1

(after Goldstein, 1992)

The intensity of the x-ray continuum I_c at any energy has been quantified according to Kramers as

$$I_c \approx \frac{iZ(E_0 - E_v)}{E_v},$$

where Z is the average atomic number of the specimen, E_0 is the incident beam energy, I is the beam current, and E_v is the continuum photon energy. It can be seen that the x-ray continuum intensity decreases as the photon energy increases, reaching zero at the beam energy. At low photon energies the intensity increases rapidly because of the greater probability for slight deviations in trajectory caused by the Coulombic field of the atom.

Inner-shell ionization takes place when sufficiently energetic electron causes ejection of a tightly bound inner-shell atomic electron, leaving the atom in an excited state. Subsequent decay of this excited state results in the emission of characteristic x-ray or Auger electron (Fig. 2).

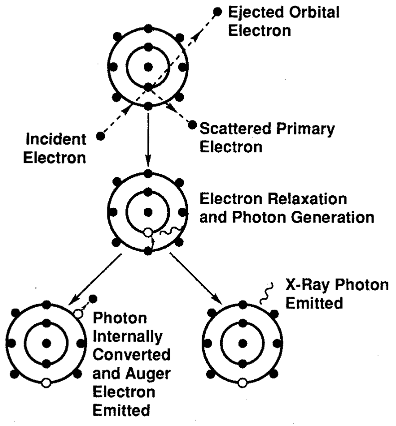


Figure 2

The main advantage of using a thin specimen for x-ray microanalysis is the improved spatial resolution over that obtainable in a bulk sample. In the bulk samples normally analyzed in SEM, the electron beam diffuses in the sample to a depth of 1-5 μm. X-rays are produced from a bell shape region (Figure 3a). Thus, the spatial resolution is limited to the micrometer scale. In a thin foil, on the other hand, the electron beam passes through the sample and X-rays are generated in a volume dictated by the size of the focused probe (Figure 3b) and the extent of the electron scattering, which is a function of both the thickness (t) of the sample and the accelerating voltage.

A further advantage of using a thin foil for x-ray microanalysis is that x-ray absorption and secondary fluorescence are minimal and the measured intensity is, to a first approximation, the same as the generated intensity. This fact leads to a much simpler quantification procedure than the ZAF corrections that must be employed for bulk samples.

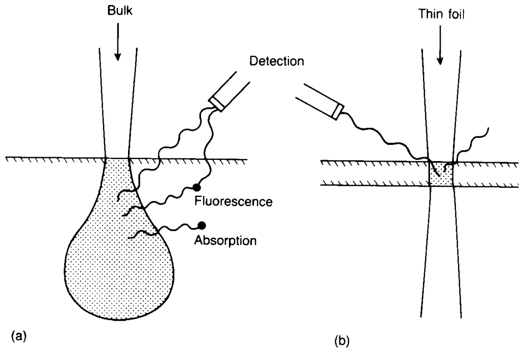


Figure 3

Probe size and spatial resolution

Typically the electron density (number of electrons per unit area) in the electron probe can be represented as a function of radius by a Gaussian function. In this case, 50% of the total current is contained within a disc of diameter equal to the full width at half maximum (FWHM) of the Gaussian and 90% of the total current is contained within the full width at tenth maximum (FWTM). Both of these widths are widely used as definitions of the probe size and spatial resolution for analysis, the former being the normal one quoted by manufacturers. However, spherical aberration can produce large 'tails' in the intensity distribution of the highly convergent probes used in AEM. Quoting the FWHM of such a probe gives a highly misleading picture of the spatial resolution for analysis. If the spatial resolution is defined as the diameter that contains 90% of the current, the spatial resolution for a TEM probe can be more than 40x the FWHM. It is possible to reduce the convergence of the beam and hence the tail produced by spherical aberration, by reducing the size of the C2 aperture, but this is at the expense of the total probe current.

When the analysis probe is a few nanometers in diameter, beam broadening within the specimen plays a critical role in determining the spatial resolution for analysis. Ignoring the effects of diffraction and fast secondary electrons, the average size of the interaction diameter, R, midway through the foil for a Gaussian probe, is given by

$$R = \frac{\left(d + \sqrt{d^2 + b^2}\right)}{2\sqrt{2}}$$

where d is the incident beam diameter and b is the beam broadening. Using a single-scattering approximation:

$$b = 7.21 \times 10^5 \left(\sqrt{\frac{\rho}{A}}\right)\left(\frac{Z}{E_0}\right) . t^{3/2}$$

where ρ is the density, A is the average atomic weight, Z is the average atomic number, E_o is the accelerating voltage and t is the thickness of the specimen. To minimize R, one should use as thin a specimen, as small a probe diameter and as high an accelerating voltage as possible. Unfortunately, the thinner the specimen the lower is the intensity of the x-ray signal! Nevertheless, a spatial resolution (R) of about 2 nm is attainable for quantitative analysis with current instrumentation using an FEG. With a LaB_6 gun, the equivalent value is about l0 nm.

Operational conditions for x-ray analysis of thin specimens

If the x-ray spectrum from a specimen is to be quantified, it must be assumed that (i) none of the x-rays produced in the specimen are absorbed on their way to the detector and (ii) all the x-rays collected come from the region of interest in the sample and not from other areas of the specimen, the holder, etc. In general, this assumption may not be justified, although modern instruments have modifications that seek to minimize the effects of spurious x-rays contributing to the spectrum. The main reason for these problems is that the AEM uses high-energy electrons and these electrons and the x-rays that are generated are scattered by the specimen in the very constricted region of the microscope stage (Fig. 4). As is apparent from figure 9, the specimen holder must be in such a position during analysis that no part of it intercepts the cone of x-rays entering the detector. In modern instruments, the detector has a positive 'take-off' angle, normally ~20°. It is also sensible to tilt the specimen towards the detector so as to increase the total take-off angle to about 40°. Tilting the specimen in this way, however, has the disadvantage that the specimen then interacts with its own continuum radiation.

Despite a positive take-off angle, there will still be regions such as A in figure 4 from which the x-rays are seriously attenuated. The special holders supplied for analysis are normally made from a material with a low atomic number such as beryllium or carbon to reduce the number of backscattered electrons and to minimize the effect of spurious characteristic x-ray peaks. One side-effect of such design is that the x-ray spectrum from an area such as A in figure 4 suffers severe absorption of its low-energy peaks, while the higher energy peaks remain unaffected. It is therefore wise to analyze only from the region of the specimen that is on the side furthest from the detector. It is clear from figure 4 that the specimen should be at the correct (eucentric) height if attenuation problems are to be minimized.

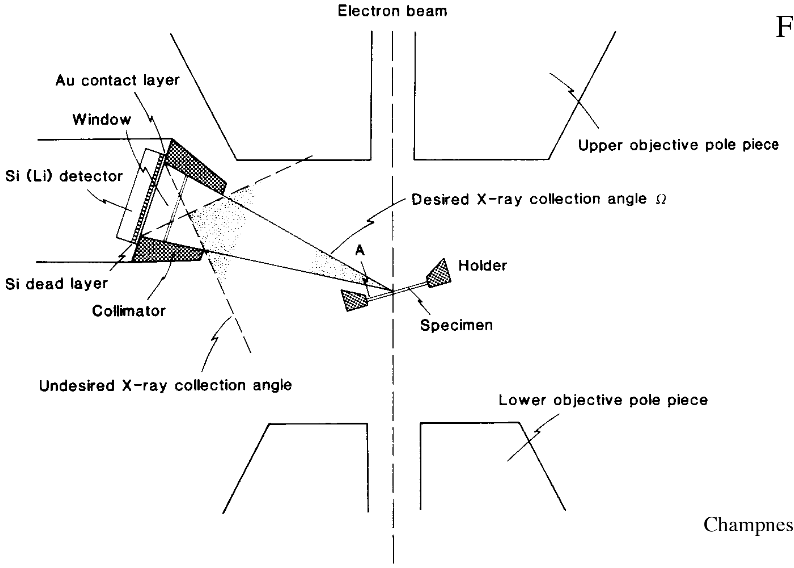


Figure 4

Champness, 1995

Spurious x-rays. X-rays that are not generated in the region of interest in the specimen, but do reach the detector represent serious problem. As is apparent from figure 9, the detector 'sees' a large volume of the stage and its environment and collects x-rays (and electrons) from all these regions. There are many sources of spurious x-rays and the ultimate aim is to remove all of them. They include:

Hard x-rays generated in and transmitted through the condenser aperture. These x-rays can cause fluorescence in the specimen grid and elsewhere in the area around the specimen.

Un-collimated electrons and those scattered from the bore of the C2 aperture can excite x-rays in areas of the specimen remote from the probe and from components below the specimen (e.g. the objective aperture and objective pole piece). Such spurious radiation can be minimized by the following measures, most of which are now standard practice:

- Removal of the objective aperture during analysis.
- The use of an extra-thick, 'top hat' C2 aperture.
- The insertion of extra ('spray') apertures in the column above the specimen.
- The use of materials of low atomic number for the specimen holder and support grid.

Alternatively, the specimen grid can be made of a material that is not contained in the specimen; copper is suitable for most silicate analyses. Nickel or gold may be suitable for the analysis of sulfides.

Another source of spurious x-rays involves the specimen itself and is therefore extremely difficult to eliminate completely. It accounts for the well-known observation that, even if the 'hole count' has been eliminated, Cu x-ray lines invariably appear in the spectrum of a specimen supported on a Cu grid, even if the primary beam is many micrometers from any grid material. The two main effects are:

(i) Backscattering of the high-energy incident electrons first from the specimen and then from bulk material such as the objective pole-pieces. These electrons can generate continuous and characteristic x-rays from the specimen, its support grid, and the specimen holder.

(ii) Continuum x-ray radiation produced in the specimen at the region being analyzed will fluoresce distant regions of the specimen, the support grid, etc.

Choice of accelerating voltage.

Theoretical treatments show that the peak-to-background ratio should increase with kV and therefore the sensitivity of AEM should improve. It is, therefore preferable to operate at the maximum voltage, with the added advantage that the spatial resolution is improved and, for minerals and other non-metals, radiation damage is minimized. However, it should be emphasized that the 'thin-film criterion' cannot be assumed to hold for analyses at high voltage and correction for absorption, and possibly fluorescence, may have to be made, even for elements $Z \sim 11$.

Contamination of the specimen.

Contamination manifests itself as conical carbonaceous deposits that build up on both sides of the thin foil when the electron beam is focused on the specimen during analysis. Although the contamination spots have useful applications, such as in measuring the thickness of the foil and in indicating the occurrence of drift of the probe or the specimen during analysis it has three main undesirable consequences:

1. It will preferentially absorb low-energy x-rays emanating from the specimen. This effect is particularly important if a thin-window or windowless detector is used to detect light elements.
2. It will increase the x-ray background and hence reduce the peak-to-background ratio.
3. Scattering within the cone may cause more spreading within the specimen than would otherwise occur and thus the analyzed volume will increase.

Modern AEMs have relatively clean vacuum systems, with residual hydrocarbons in the specimen area being $<10^{-10}$ torr. The analyst can 'fix' most of any residual contamination by flooding the specimen for about 15 min before analysis with a completely defocused beam with the C2 aperture removed. It is always advisable to use the cold trap that is located below the specimen when performing analyses; use of a specimen cooling stage will also restrict diffusion of the hydrocarbons to the site of analysis.

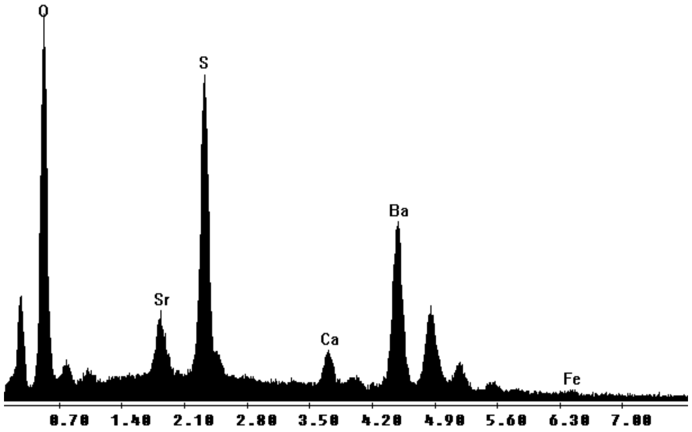
Diffracting conditions

Anomalously high x-ray intensities are generated when the specimen is close to the Bragg condition for diffraction. This enhanced emission of x-rays forms the basis of the technique of ALCHEMI (atom location by channeling-enhanced microanalysis). As the problem may not be entirely eliminated by taking the ratio of two elements, it is advisable to avoid Bragg contours in the image when performing analyses. The use of a large convergence angle, as occurs in the STEM mode with a focused probe also minimizes the problem.

Qualitative X-ray analysis

The first stage in the analysis of an unknown is the identification of the elements present, i.e., the qualitative analysis. Qualitative x-ray analysis is often regarded as straightforward, meriting little attention. It is clear that the accuracy of the final quantitative analysis is meaningless if the elemental constituents of a sample have been misidentified. As a general observation, the major constituents of a sample can usually be identified with a high degree of confidence, but when minor or trace level elements are considered, errors can arise unless careful attention is paid to the problems of spectral interferences, artifacts, and the multiplicity of spectral lines observed for each element.

Figure 5



Because the EDS limit of detection is about 0.1 weight %, the following arbitrary working definitions for elemental concentrations are used: major - 10 wt% or more; minor, 1 - 10 wt%; trace, less than 1 wt%.

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 (Fig. 5). 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 Kα and Kβ 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 Lα(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), Lλ(0.04), and Lη(0.01). The observable M series consists of Mα(1), Mβ(0.6), Mγ(0.05), Mζ(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 Kα and Kβ peaks appear to be nearly Gaussian (because of the decrease in the relative height of the Kβ peak to about 0.01 of the height of the Kα), 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.

Guidelines for EDS Qualitative Analysis

a) Only peaks, which are statistically significant should be considered for identification. The minimum size of the peak (P) after background subtraction should be three times the standard deviation of the background at the peak position, i.e., $P > 3(N_B)^{1/2}$

b) The maximum total spectrum input count rate should be kept below 3000 cps. An alternative criterion is that the dead time should be kept below 30%.

c) The EDS spectrometer should be calibrated so that the peak positions are found within 10 eV of the tabulated values. Note that, because of amplifier drift, the calibration should be checked frequently.

d) Suitable x-ray lines to identify the elemental range from beryllium to uranium are found in the energy range from 0.1 keV to 20 keV. To provide an adequate over-voltage to excite x-ray lines in the upper half of this range, a beam energy in the range 20-30 keV should be used. The beam energy especially for EDS analyses in the SEM should be increased to give at least over-voltage (U) ~ 1.5 and long spectrum accumulation times are used, then these high-energy x-ray lines can prove valuable.

e) 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.

f) 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.

Pathological Overlaps in EDS Qualitative Analysis

The limited energy resolution of the EDS frequently causes the analyst to be confronted with serious peak overlap problems. In many cases, the overlaps are so severe that an analysis for an element of interest cannot be carried out with the EDS. Problems with overlaps fall into two general classes: the misidentification of peaks and the impossibility of separating two overlapping peaks even if the analyst knows both are present. It is difficult to define a rigorous overlap criterion, owing to considerations of statistics. In general, however, it is very difficult to unravel two peaks separated by less than 50 eV no matter what peak-stripping method is used. The analyst should check for the possibility of overlaps within 100 eV of a peak of interest. When the problem involves identifying and measuring a peak of a minor constituent in the neighborhood of a main peak of a major constituent, the problem is further exacerbated, and overlaps may be significant even with 200 eV separation in the case of major versus minor constituents. When peaks are only partially resolved, the overlap can actually cause the peak channels for both peaks to shift by as much as 10-20 eV from the expected value.

Automatic Qualitative EDS Analysis

Most modern computer-based analytical systems for energy dispersive x-ray spectrometry include a routine for automatic qualitative analysis. Such a routine represents an expert system in which the guidelines described in the preceding sections for manual qualitative analysis are expressed as a series of conditional tests to recognize and classify peaks.

The success with which such an expert system operates depends on several factors:

1. Has the analyst accumulated a statistically valid spectrum prior to applying the automated qualitative analysis procedure?
2. Are the complete x-ray families included in the look-up tables?
3. Have x-ray artifacts such as the escape peaks and sum peaks been properly accounted for?

Can the results reported by an automatic qualitative analysis system be trusted? Generally it is difficult to assign a quantitative measure to the degree of confidence with which a qualitative identification is made. Common sense is one of the most difficult concepts to incorporate in an expert system. It is therefore really the responsibility of the analyst to examine each putative identification (major constituents included) and determine if it is reasonable when other possibilities are considered. As always, an excellent procedure in learning the limitations of an automatic system is to test it against known standards of increasing complexity. Even after successful performance has been demonstrated on selected complex standards, the careful analyst habitually checks the suggested results on unknowns.

X-Ray Peak and Background Measurements

Qualitative analysis is based on the ability of a spectrometer system to measure characteristic line energies and relate those energies to the presence of specific elements. Quantitative analysis, on the other hand, involves measuring the intensity of spectral peaks corresponding to pre-selected elements for both samples and standards under known operating conditions, calculating intensity ratios (k values), and converting these k values into chemical concentration.

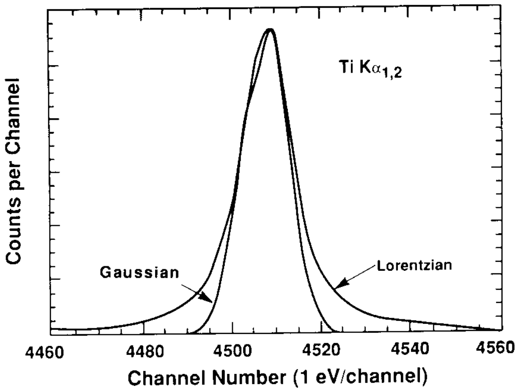
Since quantitative analysis can now be performed with relative accuracy approaching 1%, great care must be taken to ensure that the basic measurement of the characteristic x-ray intensity is accurate to at least the 1% level, and preferably better. Accurate background measurements become increasingly important at lower concentrations as peak-to-background ratios get smaller. For example, a 100% error in a background measurement of a peak 100 times larger than the background introduces a 1% error in the measured peak intensity, whereas the same error in the case of a peak twice background introduces a 50% error.

Peaks in EDS spectra are described by Gaussian distribution

$$Y_i = A_c \exp\left[-\ln(2)\left(\frac{E_i - E_c}{\gamma}\right)^2\right]$$

Y_i is the amplitude in the ith channel, γ is the 1/2FWHM, A_c is the amplitude at the center of the peak, E_c is the energy at the center of the peak, E_i is the energy at the ith channel. The relative shape of this distribution is shown on Fig. 6 which is compared to the Lorentzian distribution characteristic for the peaks obtained by WDS.

Figure 6



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.

Peak Overlap Correction

To measure the intensity of an x-ray line in a spectrum, we must separate the line from other lines and from the continuum background. The separation relies on successful modeling of the shape of individual peaks. The natural energy distribution of characteristic x-rays of a single line is well described by the Lorentzian probability distribution. The experimental measurements introduce additional broadening especially for the energy-dispersive detector the broadening is large. Typically the FWHM at the energy of Mn Kα is 135-165 eV, while the natural width at Mn Kα is just a few eV. Consequently, the Gaussian shape of the energy-dispersive detector dominates the Lorentzian shape of the natural x-ray line.

Quantitative x-ray analysis of thin specimens

Background subtraction

The x-ray spectrum recorded by the EDS consists of the characteristic peaks superimposed on the continuum background. It is necessary to remove the background in order to obtain the integrated intensities. This is achieved by direct calculation or by mathematical filtering using a 'top hat' function, or by scaling and subtracting a reference background from a material such as carbon. Once the background has been removed the peak intensities are obtained either by fitting a Gaussian profile or by using reference spectra that have been acquired previously and stored in the computer.

The ratio technique

In a sample that is sufficiently thin for transmission of 100 keV electrons, the incident beam looses only a small amount of energy and the ionization cross-section is constant along the electron path. To a first approximation, as noted above x-ray absorption and secondary x-ray fluorescence within the specimen can be ignored. Under these conditions the 'thin-film' criterion applies.

The absolute x-ray intensity is a function of the thickness of the specimen, as well as of the composition but the ratio of the measured x-ray intensities I_A/I_B for two elements A and B, is independent of thickness. This ratio can be simply related to the corresponding ratio of the weight fractions (or to the atomic ratios) of the elements, C_A/C_B, by the equation:

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

where k_{AB} is a factor that accounts for the relative efficiency of production and detection of the x-rays. At a given accelerating voltage, k_{AB} is independent of specimen thickness and composition. If peaks of many elements are measured simultaneously, as is usual with an EDS, the measurements are independent of variations in the probe current. The k_{AB} factor is not a fundamental constant because it depends upon such things as the composition and thickness of the detector window and, it will change if contamination builds up on the window. However, k_{AB} values for a particular instrumental arrangement can be stored and used long after they have been measured to obtain concentrations in unknowns. Thus, no standardization is normally necessary at the time of analysis.

As absolute x-ray intensities are not used in the quantification, there is no internal check on the quality of the AEM analysis provided by the analysis total and an assumption must be made about normalization, e.g. $\sum C_n = 1$ if all the elements can be detected, as in sulphides. For silicates such as olivines or pyroxenes, in which x-rays from all the elements except oxygen can be measured quantitatively, the normalized concentration of an element A as a proportion of the total cations is given by:

$$\frac{C_A/C_{Si}}{C_A/C_{Si} + C_B/C_{Si} + ..C_n/C_{Si}} = C_A$$

These concentrations can then be converted to oxide weight percents and totaled to 100%. The chemical formula can be calculated in the usual way to a suitable number of oxygens. The resulting number of cations in each site may give an indication of the quality of the analysis. Problems arise in cases where there are elements other than oxygen that cannot be detected. For hydrated samples assuming that all the cations can be detected an oxide analysis total appropriate to the mineral type can be assumed or the formula can be normalized to an appropriate number of oxygen atoms

In the general case it is recommended that, where possible, normalization be carried out on the basis of the known number of cations in a particular crystallographic site, e.g., the tetrahedral site in feldspars. Apparent cation deficiencies in another site could indicate either that an undetectable element such as Li was present, or that mass loss had occurred during analysis.

Determination of k_{AB} factors

The k_{AB} factors are usually determined experimentally from well-characterized, homogeneous standards, the reference element, B, being Si for silicates and S for sulphides. Because the quality of analyses obtained is critically dependent on the accuracy of the k_{AB} values, it is vitally important that these values are measured with care and it is advisable to use several standards for each element. If the ratio C_A/C_B is plotted against I_A/I_B the slope of the line gives k_{AB}. For elements with $Z>12$ k_{AB} factors can now be measured with an error in the range 1-4% relative. The determination of k_{AB} factors for light elements presents particular problems.

If a suitable standard containing the two elements of interest cannot be found, k_{AB} factors can be obtained from two standards, e.g.

$$k_{ASi} = k_{AB} \times k_{BSi}$$

In cases where no suitable standards are available, the k_{AB} factors must be calculated from:

$$k_{AB} = \frac{Q_B w_B a_B A_A \varepsilon_B}{Q_A w_A a_A A_B \varepsilon_A},$$

where Q is the ionization cross-section for x-rays, i.e. the probability that an electron will excite an atom, *w* is the fluorescence yield (x-rays emitted per ionization), *a* is the relative transition probability, A is the atomic weight and ε is the efficiency of the detector for the X-rays from the particular element. Of the terms in the above equation Q and ε are the most difficult to calculate. Currently, the calculation of k_{AB} values for K lines above 1.5 eV in energy is in error by ~10-15%, mainly because of the uncertainty in Q. Calculation of k_{AB} values is therefore not recommended for light elements $Z < 11$. Calculation of k_{AB} values is not recommended for L lines either.

Breakdown of the thin-film criterion; absorption in the specimen

When the thin-film criterion breaks down, it is usually because the effects of absorption are significant. For any set of two elements A and B an absorption correction is necessary if:

$$\left[(\mu/\rho)_{sp}^{B} - (\mu/\rho)_{sp}^{A}\right]\rho.(t/2).\mathrm{cosec}\alpha > 0.1$$

where ρ is the density, t is the thickness and (μ/ρ) is the mass-absorption coefficient and α is the take-off angle for the detector (assuming zero tilt of the specimen). The maximum thickness for which an absorption correction is unnecessary is thus:

$$t_{max} = \frac{0.2}{\left[(\mu/\rho)_{sp}^{B} - (\mu/\rho)_{sp}^{A}\right]\rho.(t/2).\mathrm{cosec}\alpha}$$

Notice that it is the difference in the absorption coefficients for the two elements that is the important factor. If two elements are adjacent in the periodic table, their values of (μ/ρ) will be very similar (except near an absorption edge) and the ratio of the intensities of their x-ray lines will be little affected by absorption, whatever the thickness of the specimen.

As it happens, the maximum thickness for which microstructures in silicates can be observed using l00 keV electrons is about 200 nm for elements $Z \geq 11$. For higher voltages or lighter elements, this rule of thumb cannot be used and care must be taken to work in suitably thin areas or, alternatively, to correct for absorption.

The effects of absorption can be calculated if the thickness of the sample is known.

$$\frac{I'_A}{I'_B} = \frac{I_A}{I_B} \times \frac{\left[(\mu/\rho)_{sp}^{A}\right]\left[1 - \exp - \{(\mu/\rho)_{sp}^{B}.\rho t.\mathrm{cosec}\alpha\}\right]}{\left[(\mu/\rho)_{sp}^{B}\right]\left[1 - \exp - \{(\mu/\rho)_{sp}^{A}\,\rho t.\mathrm{cosec}\alpha\right]}$$

where I is the measured intensity. This correction is usually available within the software supplied with the AEM; only the appropriate k_{AB} value and the thickness of the specimen: need to be input.

Fluorescence in the specimen

In thicker specimens, the characteristic x-ray intensity emitted by an element A may be enhanced by secondary x-ray fluorescence from the characteristic x-rays emitted by a second element B. This phenomenon leads to an apparent increase in the concentration of A, but is rarely a problem in practice, particularly in silicates, because fluorescence efficiencies are low for $Z < 20$ and tend to be negligible, except for heavier elements of almost adjacent atomic number (e.g. Cr excited by Fe). The correction factor for fluorescence in thin foils is proportional to *t lnt*. This correction factor is available in most software packages supplied with AEMs, but the effects of absorption are almost always much more serious than those of fluorescence in specimens of similar thickness.