

Selected References on Microanalysis in TEM

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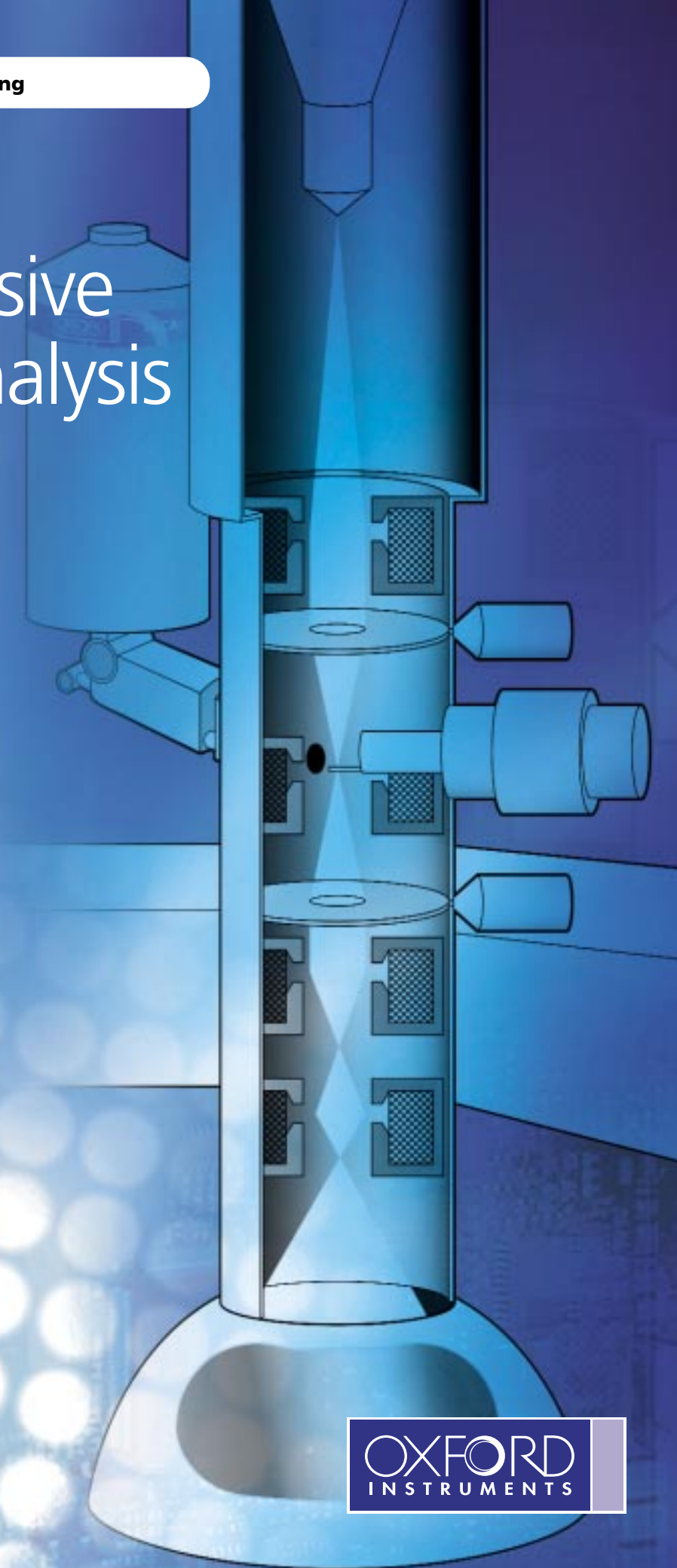
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Oxford Instruments Analytical – technical briefing

Energy Dispersive X-ray Microanalysis for the TEM

Explained



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Introduction

X-ray microanalysis of thin specimens in the Transmission Electron Microscope (TEM) offers nano-scale information on the chemistry of materials.

However, the complexity of TEM designs means that the application of energy dispersive X-ray spectrometers (EDS) to the TEM is a serious technical challenge. This guide explores some of the major issues which have influenced the evolution of EDS on the TEM. It also looks at the current state of instrumentation, and the important requirements for doing successful EDS on this instrument.

Examples of microanalysis in the TEM are used to demonstrate the standard of data that can be routinely collected in a TEM with today's instrumentation. This data is normally equivalent to that collected in the more common SEM, although with higher spatial resolution to study much smaller chemical features.

Fundamentals of the TEM technique

In a TEM, like an optical microscope, a beam is passed through a series of lenses to form a magnified image of a sample that has been inserted in the area of the objective lens (Figure 1). This image is viewed through projection onto a viewing screen. However, electron beams are easily scattered by air molecules and TEM columns must be kept under high vacuum. In addition, electrons cannot be focussed by glass lenses and electromagnetic lenses are used instead. Just as in their optical counterpart the machining of these lenses are critical, as aberrations can have a major effect on resolution. However, electromagnetic lenses do have the advantage that astigmatism can be corrected electronically and magnification can easily be changed by adjusting the lens current. Because the TEM is a multiple lens system, different analytical conditions can be obtained by adjustment of lens and alignment conditions. Computer control of contemporary microscopes

helps significantly in the ease of operation of these complex instruments.

Resolution of TEMs is far superior to that of optical microscopes due to the fact that electrons are used for the source of illumination rather than visible or ultra-violet light. Optical microscopes are limited to a resolution in the order of 100nm whereas modern TEMs demonstrate resolutions approaching 0.1nm. This has proved extremely valuable in the examination of biological ultra-structures such as DNA and viruses, and the structure of materials such as grain boundary properties in metallic specimens, and failures in semiconductor devices.

Quite early in the development of TEMs it was observed that, due to their short wavelengths, crystalline materials diffract electrons. A parallel beam of electrons passing through a regular spaced crystal lattice in the sample holder of a TEM will form a diffraction pattern in the back focal plane of the objective lens. This can be projected onto a viewing screen or recorded on film for measurement. Study of these diffraction patterns helps explain the structure of materials.

By adding a set of scan coils to the electron optic column, a focussed electron beam can be scanned over a sample. The scanning transmission electron microscope (STEM) uses this facility to control the beam for microanalysis (e.g. X-ray mapping). STEM systems also include electron detectors for collecting images of electrons transmitted or scattered back from the sample.

TEMs have been equipped with elemental analysis capabilities since the 1960s. The earlier incarnation of this mode of analysis was the Electron Microscope Micro-Analyser or EMMA developed by AEI Instruments. This was unique in that primary analysis was performed by Wavelength Dispersive Spectrometry (WDS) rather than Energy Dispersive Spectrometry (EDS). Although the WD spectrometers gave better spectral resolution than EDS, collection efficiency was poor and spectrometer stability was a problem. Energy Dispersive Spectrometers

were installed on Transmission Electron Microscopes in the early 1970s, and provided much better collection efficiency along with the ability to acquire a range of elements between Na and U simultaneously. This, in conjunction with improved ability to produce higher energy probes with spatial resolution down in the nanometer range, was instrumental in the formation of the first analytical TEM/STEMs.

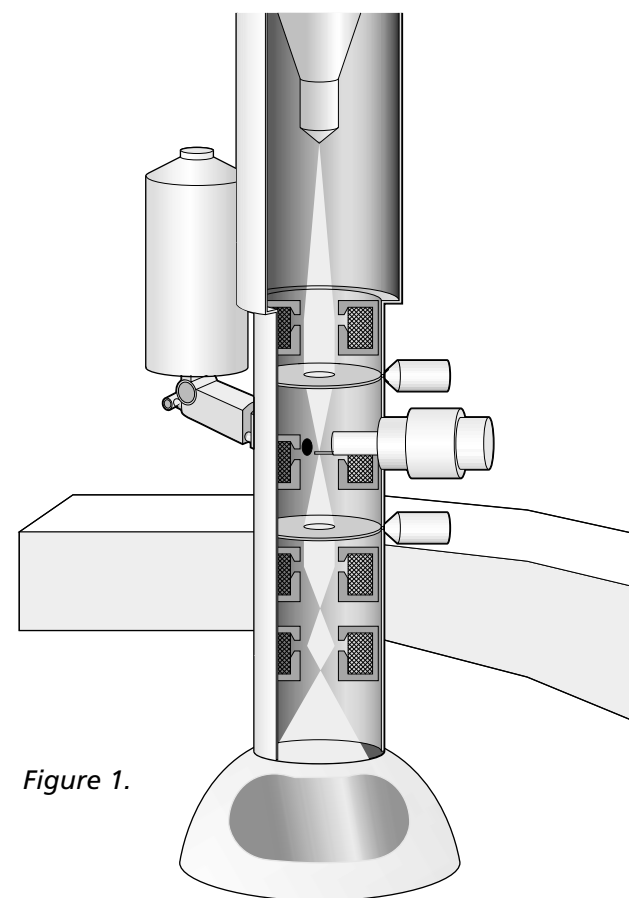


Figure 1.

Basics of electron beam-sample interaction in the TEM

While the overall concept remains the same, Energy Dispersive X-ray Analysis in Transmission Electron Microscopy reveals some marked differences from EDS analysis in the Scanning Electron Microscope (SEM). Normally, SEM samples are thick enough for the focussed probe to be contained within the sample, i.e. complete

absorption of the primary beam. This causes the beam to spread within the material and leads to a number of different phenomena that affect the analytical treatment of raw X-ray counts obtained from the material. These include atomic number (Z), absorption (A) and fluorescence (F) effects, which are dealt with by applying matrix corrections. The incident beam energy, material density and take off angle therefore have a profound affect on X-ray intensity and quantitative results in the SEM.

In contrast, TEM samples should be thin enough to be beam transparent, so the ionization volume formed by a focussed probe is much smaller and, therefore, there is much less electron scattering (Figure 2). High beam energies (commonly between 100kV - 400kV) utilized in the analytical TEM also reduce beam scattering. However, due to the relatively small ionization volume, X-ray generation is much lower than for thick samples. When analyzing thicker samples in TEM, absorption corrections may be made if the material density and thickness at the point of analysis are known, whereas these corrections are not always necessary in thin samples.

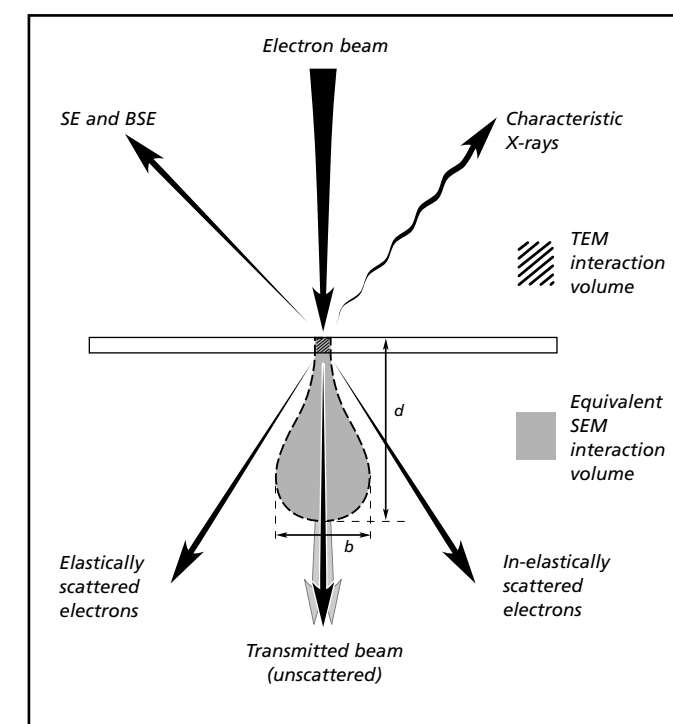


Figure 2.

The Analytical TEM (AEM)

Analytical TEMs are commonly equipped with a variety of detectors for sample analysis. The most important tools are bright field and dark field imaging, electron diffraction, electron energy loss spectroscopy (EELS), and EDS. Due to the confined space in the sample – polepiece region, EDS detector positioning and collimation are of utmost importance. The electron column must be designed to minimize stray radiation passing down the column and generating X-rays from microscope components that may cause artefacts in the EDS spectrum. Analytical TEMs are equipped with special apertures to eliminate hard X-rays being generated in the column and polepiece.

The presence of stray X-rays can be determined by performing a “hole count test”. This is performed by positioning the focussed electron beam in such a way that it is transmitted through a hole in the specimen. The specimen itself may scatter electrons and increase the stray radiation so the hole count test doesn’t represent the true conditions during analysis. Therefore, an even better test is to use a specially prepared standard sample (e.g. NiOx) and check the level of spurious contributions to the spectrum.

Detector geometry for TEMs presents a special challenge for designers due to the inherent space limitations in the objective polepiece area where the sample resides (Figure 3). Ideally, the detector should be able to view X-rays from above the specimen so that the sample can be analyzed in a horizontal or near horizontal position. The position of the

detector is usually described by the take off angle (TOA) relative to the horizontal specimen plane. Care should be taken to limit the entry of backscattered electrons, as magnetic electron traps cannot be used in the TEM, due to the fact that they would cause astigmatism in the objective lens. Consequently, design of the collimator is very important. The solid angle of collection can be improved by increasing detector area although this tends to worsen the resolution of the detector. Alternatively the detector can be moved closer to the specimen but this presents severe challenges for a design that also has to minimize the pickup of stray radiation. TEM detectors are often fitted with a 30mm² area detector that gives reasonable resolution performance and 0.1-0.3sr solid angle when positioned 10-20mm from the specimen. This is significantly higher than the solid angle in a typical SEM. The solid angle is most important in AEMs as the volume of the material being analyzed is much smaller than that in a typical SEM analysis, hence far less X-rays will be generated. This is especially important in the analysis of biological materials. Peaks from the light elements B,C,O,N will often be overlapped by the L and M peaks of heavier elements. This overlap can be corrected by software if the peak shapes are well known. However, incomplete charge collection (ICC) in the detector can distort low energy peak shapes and it is therefore vital to determine what performance the detector will achieve in this low energy range if light elements are to be successfully detected. This is typically measured using the ISO 15632:2002 recommendation of measuring resolution at $FK\alpha$ and $CK\alpha$.

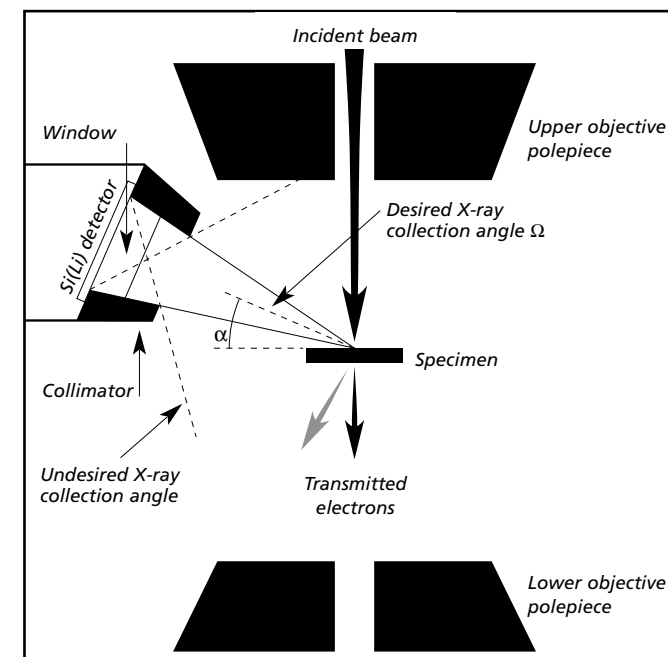


Figure 3. After Williams and Carter (1996)

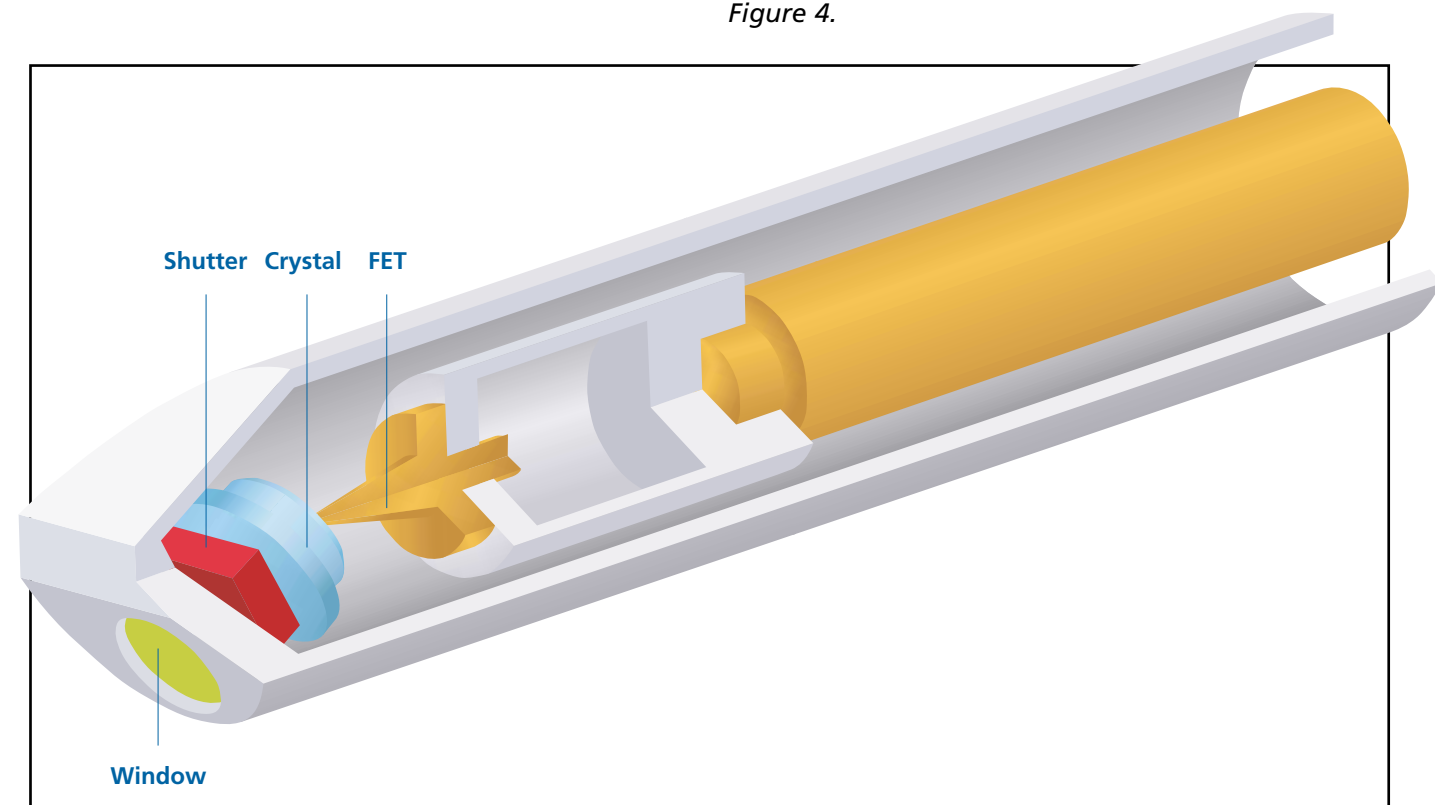
Detector Protection

If a specimen support grid passes under the beam or the sample is viewed under low magnification conditions where the whole grid is exposed to

high beam currents, a large flux of backscattered electrons is generated. The close proximity of the detector to the sample can cause an excess of these backscattered electrons to enter the detector. This not only overloads the electronics but may also deposit excess charge in the detector. As a result, the detection system is effectively paralyzed and may take many minutes to recover.

It is possible to initiate automatic detector withdrawal if counts exceed an acceptable value. However, this can cause vibration and image distortion, and due to the fact that the detector actually protrudes into the polepiece, it may also change the stigmation conditions of the microscope at high magnifications. Another option is to use a shutter between the sample and the crystal that closes when a high count rate is exceeded (Figure 4). The shutter does not cause the mechanical disturbance or stigmation problems associated with withdrawal and will prevent overload of the detection system. The detector is therefore ready to use immediately on return to normal analysis conditions and analysis throughput is improved.

Figure 4.



Qualitative Analysis In The AEM

Many analytical observations in the AEM are qualitative. Often, it is only necessary to distinguish between phases and it is not necessary to calculate elemental concentrations. Spectra may be collected at up to 0 - 40 keV range as this aids in the identification of *K* lines of elements that may have overlapping *L* or *M* peaks in a lower range e.g. Pb and Mo. It is easier to detect small peaks from minor elements when the background is smooth. Counting for longer periods of time increases total counts, which reduces statistical scatter in the background. Increased counts can also be achieved by increasing probe current or analyzing thicker parts of the specimen, although this involves some sacrifice in spatial resolution. Peak visibility is improved by having good detector resolution, which improves peak to background. To avoid false identifications, spurious peaks need to be eliminated by good collimation and design of sample holder.

The limit of detectability for an element, expressed as the minimum mass fraction (MMF), depends on the other elements present in the sample, microscope kV, detector resolution and the number of counts recorded in the spectrum. The MMF is usually calculated as the largest concentration that could be attributed to statistical fluctuations alone. By reducing statistical fluctuations, the MMF is improved. In a TEM, the total volume of material analyzed is determined by the probe diameter and specimen thickness. Therefore the total mass of material excited by the probe can be very small and masses as small as 10^{-19} g can be measured with EDS.

Quantitative Analysis In The AEM

The corrections normally associated with the analysis of thick SEM specimens do not apply to thin TEM specimens. Consequently, quantitation may be performed by using a simple ratio technique first developed by Cliff and Lorimer at the University of Manchester Institute of Science and Technology (UMIST) in the early 1970's (Cliff and Lorimer 1975).

Cliff and Lorimer observed that matrix corrections are not needed when analyzing very thin films because self absorption in the film is negligible. In this case, peak intensities are proportional to concentration and specimen thickness. They removed the effects of variable specimen thickness by taking ratios of intensities for elemental peaks and introduced a "k-factor" to relate the intensity ratio to concentration ratio:

$$C_A/C_B = K_{AB} \cdot I_A/I_B$$

Where I_A = Peak intensity for element A and C_A is concentration in weight % or mass fraction. Each pair of elements requires a different k-factor which depends on detector efficiency, ionization cross section and fluorescence yield of the two elements concerned.

An individual k-factor relates the concentration of two elements to their X-ray peak intensities. Where more than two elements are to be analyzed, a number of k-factors may be derived by using external standards to relate known concentrations with measured intensities. If all ratios are taken with respect to a single element (this is called the ratio standard element), a sensitivity response curve may be drawn for any given detector/ microscope analytical system (Figure 5).

Theoretical k factor values may be determined using the X-ray line type (K series, L series, etc) for the ratio standard you select. For a given X-ray line, A, and ratio standard line, R, the k factor k_{AR} is calculated as follows:

$$k_{AR} = A_A w_R Q_B a_R e_R / A_R w_A Q_A a_A e_A$$

where **A** = atomic weight; **w** = fluorescent yield; **Q** = ionisation cross section; **a** = the fraction of the total line, e.g. $K\alpha / (K\alpha + K\beta)$ for a *Ka* line, and **e** = the absorption due to the detector window at that line energy.

Once k factors are known relative to the ratio standard, any other k factors can be calculated using the formula

$$k_{AB} = k_{AR} / k_{BR}$$

Any element can be selected as the ratio standard element (R) if theoretically derived k factors are employed. Conventionally, Si is selected, but other elements such as Fe may be used

instead. This selection usually depends upon the type of sample that is commonly analyzed in the microscope.

k factors may also be derived experimentally. A variety of standards have been used to generate these curves and it is important that the composition of the materials used is accurately known, that they are insensitive to the electron beam, and thin enough to conform to the requirements of thin film analysis. It is also necessary to make a number of measurements per standard to take into account sample inhomogeneity and statistical variation in counts.

It must be noted that empirically derived k-factors are system specific in the sense that they are derived for specific beam energy and EDS window thickness. Also, both theoretically and empirically derived k-factors are kV dependent.

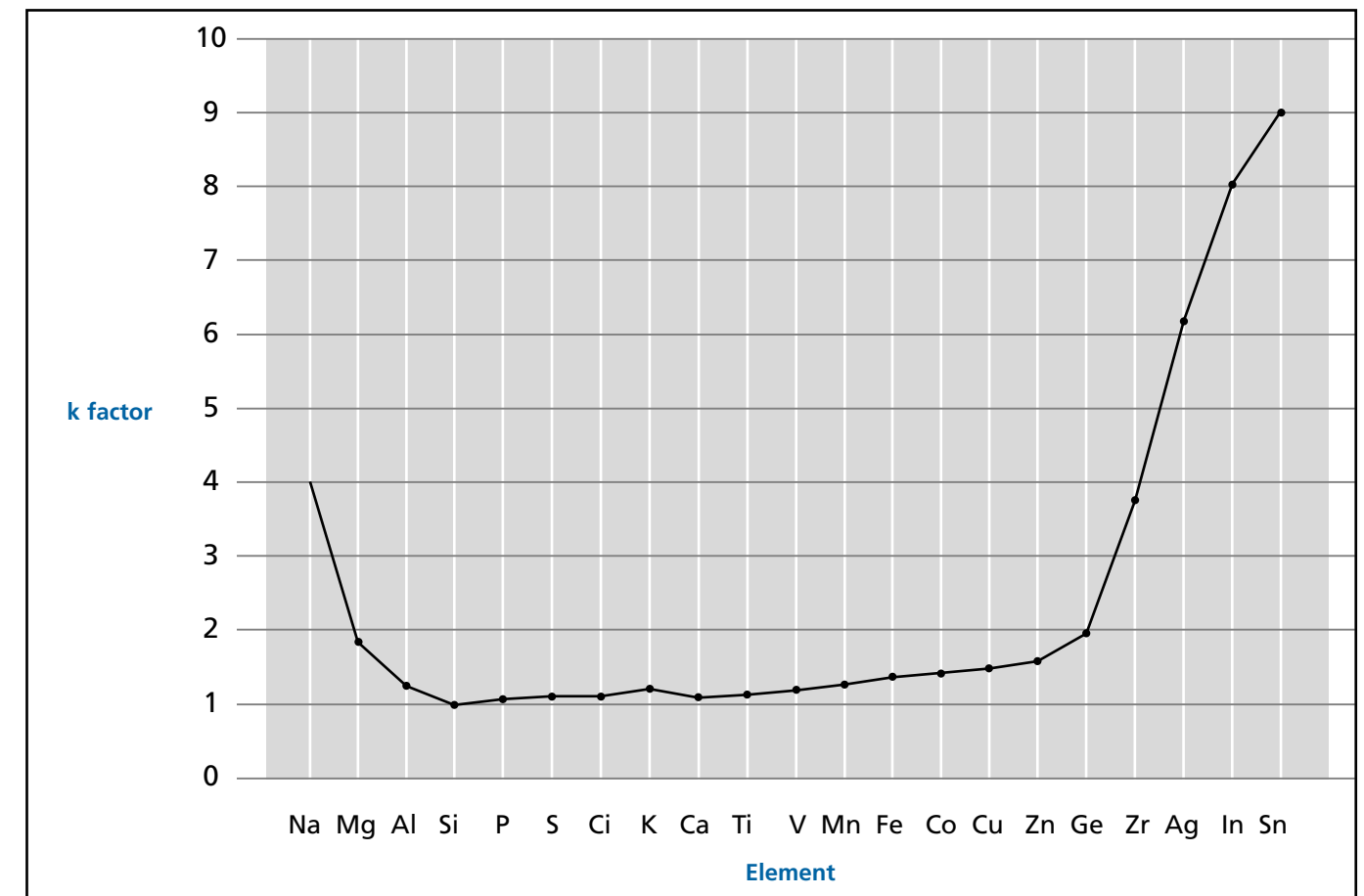


Figure 5. Typical k_{ASi} curve for $K\alpha$ lines for a Be window detector (after P. J. Sheridan [1989])

Examples of Microanalysis in the TEM

Quantitative Analysis of areas of varying film thickness

When analysing samples, a number of practical issues arise.

- Samples are often inhomogeneous and it is advisable to take measurements at more than one point.
- Sample self absorption can usually be neglected for X-rays greater than 1.5keV in energy but may be significant for low energy peaks from B,C,O,N,F,Na.
- Therefore, it is expected that if the sample is of a thickness where matrix corrections need to be applied, it is important to enter thickness and density values into the **INCA** TEM quant set up. Thicknesses may be calculated by a number of imaging, diffraction or EELS techniques in the AEM (see Williams and Carter).
- Some materials are beam sensitive. In these cases, it is necessary to adjust beam current and count times accordingly.
- Any spectral artefacts caused by the microscope, sample holder and sample grid should be taken into consideration.

As an example, **Figure 6** shows data collected from an aluminium oxide film of varying thickness. When a spectrum taken from a thin area (fig 6a) is analyzed, it gives a concentration ratio close to that expected from the stoichiometry of the compound. Data collected from a thicker area (fig 6b) shows the effect of increased absorption of the O K α peak. The analysis result would suggest that the composition has changed, whereas this is purely a consequence of not making a correction for specimen thickness. If a sample does have variable thickness then it is important to determine the likely effects of absorption by trying different thickness and densities in the correction program.

Table 1 shows quantitative analysis from an aluminium alloy (Ti-47% Al "A") analysis using an **INCA**Energy TEM system. It can be seen that the results from different points are consistent

and the mean value of several point analyses can be used to improve the precision if the material is expected to be homogeneous. A single point would not show whether the analysis was representative of the sample.

Figure 6a.

Spectrum acquired in thin specimen. Analysis Al 44%, O 56%. Results expressed as atomic percents.

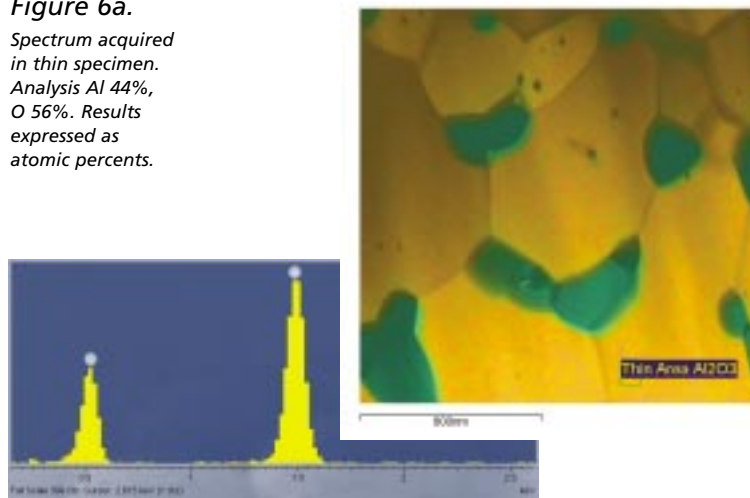
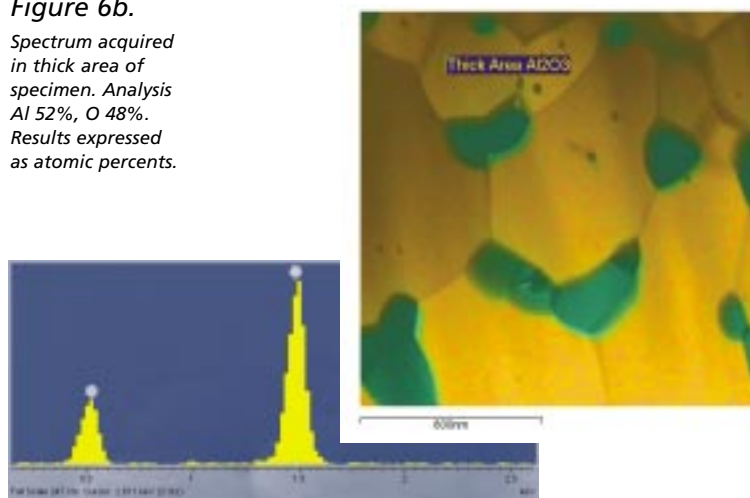


Figure 6b.

Spectrum acquired in thick area of specimen. Analysis Al 52%, O 48%. Results expressed as atomic percents.



Spectrum	Al	Ti	Nb	Mo	W	Total
Spectrum 1	47.09	49.86	2.13	0.43	0.48	100
Spectrum 2	47.83	49.04	2.14	0.66	0.32	100
Spectrum 3	47.33	49.46	1.96	0.59	0.67	100
Spectrum 4	48.72	48.38	2.08	0.25	0.58	100
Mean	47.74	49.19	2.08	0.48	0.51	100
Standard dev.	0.72	0.63	0.08	0.18	0.15	
Maximum	48.72	49.86	2.08	0.66	0.67	
Minimum	47.09	48.38	1.96	0.25	0.32	

Sample: Ti-47% Al "A".
Data from M Phaneuf, L. Weaver, G Carpenter. (Fibics Inc.)

Table 1.

Drift Correction using **INCA**SiteLock™

In a thin AEM sample, analytical resolution is governed by the size of the focussed probe which may be as low as 10nm. Therefore, X-ray maps can be collected at high magnifications with excellent spatial resolution. However, the X-ray signal is very weak and visibility of features will be totally masked by statistical noise unless enough counts are recorded in the map. Therefore, if small features or elements present in low concentrations need to be studied, then very long acquisition times will be required to obtain sufficiently good counting statistics. Signal strength can be improved by increasing the beam current with a field emission gun microscope but even so, long counting times are often required.

A major limitation of X-ray mapping at such high magnifications is image drift caused by movement of the sample or the AEM stage. This will either cause distortion of the image if long dwell times are used in a single scan over the field of view, or will cause blurring of the X-ray map data if multiple scans are performed with a short dwell time per pixel.

For this reason, it is useful to correct for drift using compensation software that continually moves the analysis point to track any movement in the specimen during acquisition. The software periodically obtains high resolution electron images and uses sophisticated image processing algorithms to detect movement between successive images, and thus generate an appropriate correction x-y deflection to be used during X-ray acquisition. If the drift between successive electron image acquisitions is less than the required analytical resolution, then the compensation technique can be used for point analysis, linescans and X-ray maps.

A typical application for X-ray mapping in the AEM is the study of semi-conductor layer cross-sections for failure analysis. Figure 7a shows the results of mapping a semi-conductor cross-section when drift occurs. The X-ray maps (Al-red, Si-green and Ti-blue) are overlaid on the STEM image. Oxford Instruments SiteLock™ drift correction software has been used to

correct for this drift (Figure 7b). The program first collects a digital STEM image of the site of interest and this can be used to define discrete points or lines or grids of points for analysis. During acquisition of the data, STEM images are acquired at predetermined intervals and compared with the original image of the site using a correlation algorithm. Even with a noisy STEM image, small shifts can be determined and used to correct the deflection voltages so that the site of interest is effectively "locked" to the same position on the specimen, even if the stage is drifting.

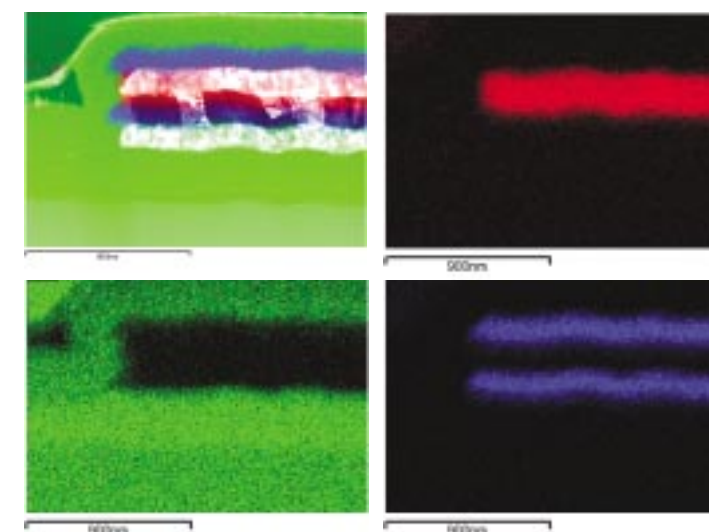


Figure 7a.

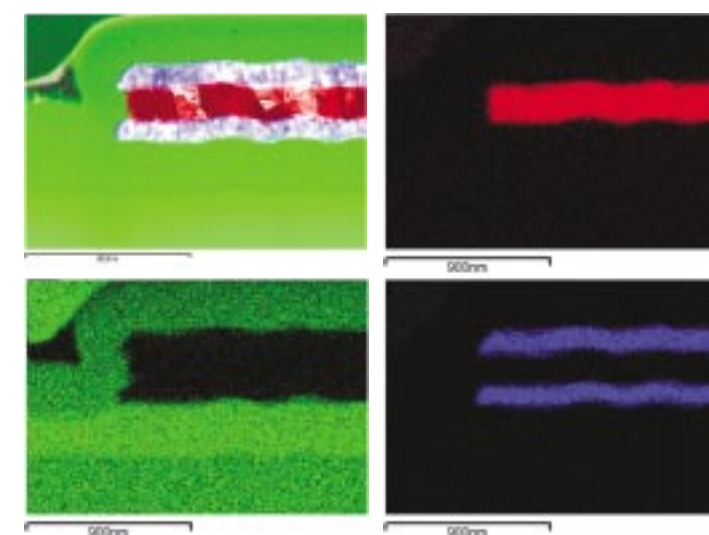


Figure 7b.

Spectrum Imaging Using SmartMap™ in INCAEnergyTEM

Modern EDS systems offer spectrum imaging, where all X-ray information detected during an X-ray map collection is saved. In this way a full X-ray spectrum is acquired and stored for every pixel in the map and used to investigate further aspects of the chemistry of the sample during or after the acquisition. The main advantage of analyzing samples in this fashion is that minimal knowledge of the sample composition is required prior to X-ray analysis since all X-ray data is collected. For example, there is no need to define specific energy windows for mapping before collecting the data as this can be done during or after the acquisition. It is important that X-ray maps are dead time corrected, so any changes in count rate due to variation of sample thickness or

beam intensity are correctly represented and no associated artifacts are created in the maps. The spectrum image data in INCAEnergyTEM is referred to as a SmartMap and the software provides a series of tools for reconstructing spectra, linescans and maps from a single SmartMap. For example, a SmartMap has been collected from a two phase ceramic sample consisting of aluminium oxide and titanium carbide. The collected datacube contains 2.5 million X-rays and was acquired for 30 minutes. Data from the SmartMap file has been used to reconstruct X-ray maps for the major elements in the sample: including titanium (orange), and aluminium (green) (Figure 8a). Representative spectra describing the different phases clearly identify the aluminum oxide (Figure 8b) and titanium carbide (Figure 8c).

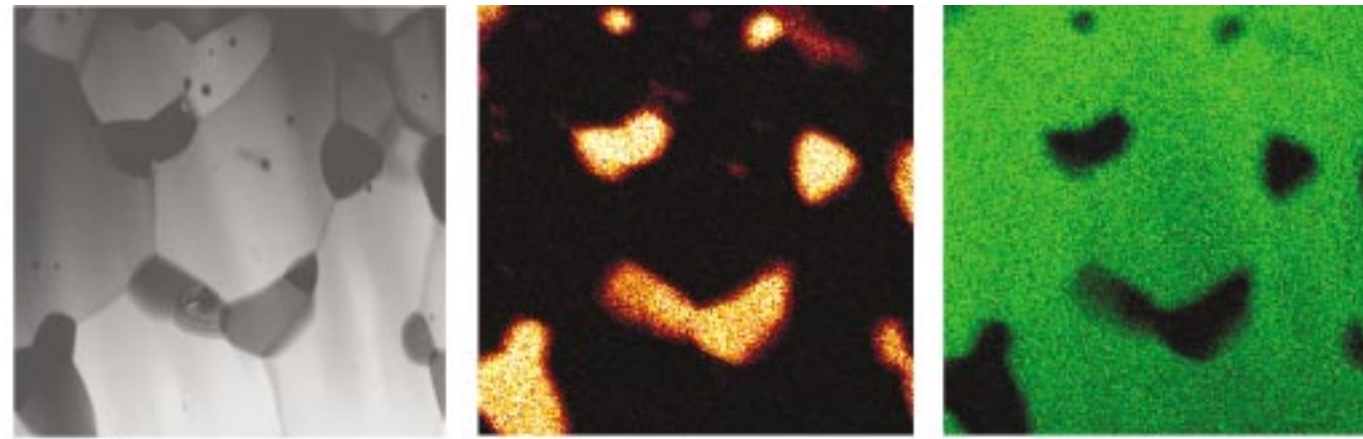


Figure 8a.

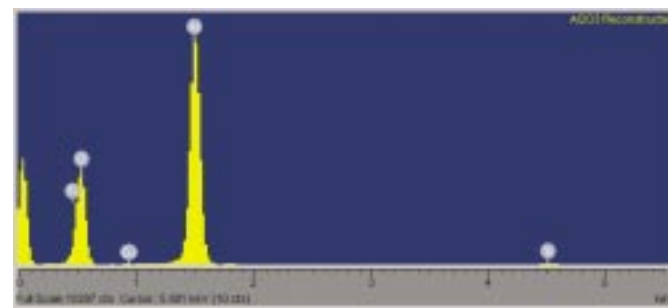


Figure 8b.

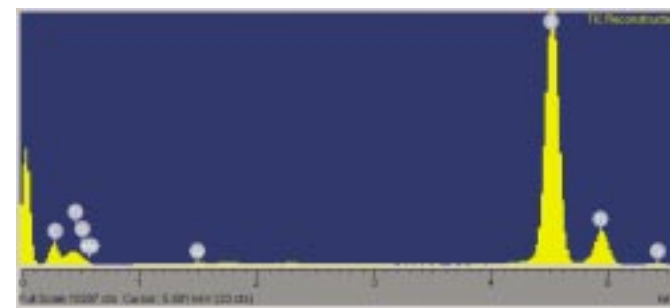


Figure 8c.

Spectra have been reconstructed from 20nm square areas across a TiC grain to study the chemistry at grain boundaries in this ceramic material (Figure 9). Using the quantitative linescan software in INCAEnergyTEM, the chemistry variations across these grain boundaries can be determined (Figure 10).

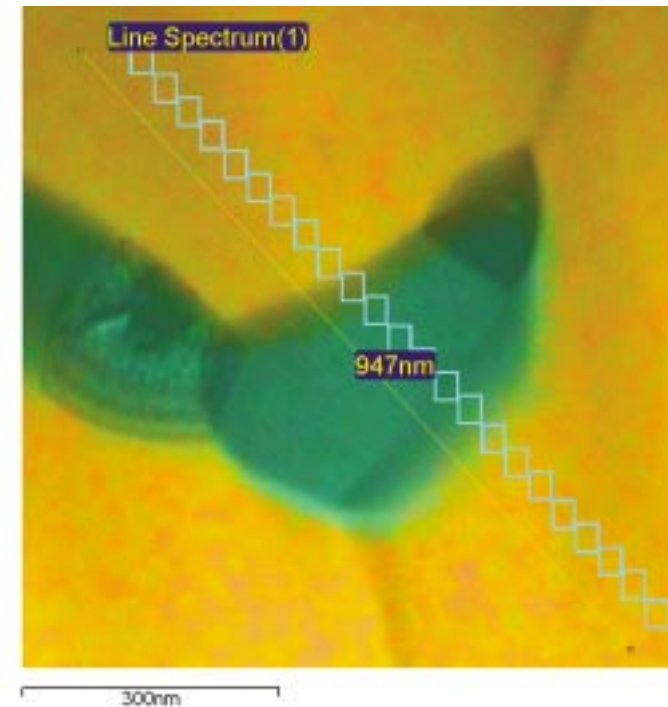


Figure 9.

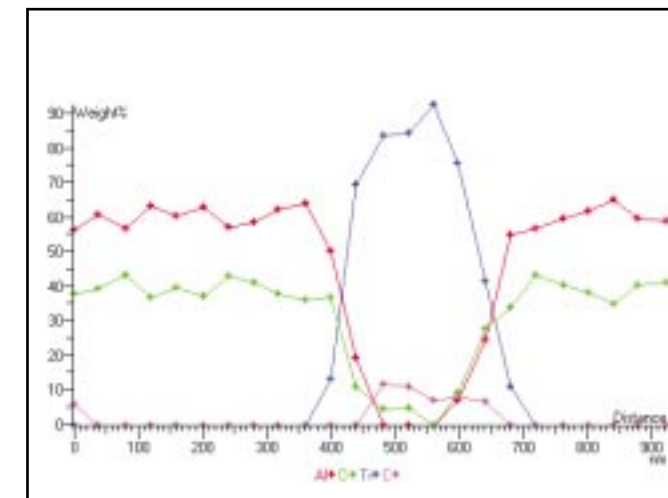


Figure 10.

Summary

EDS offers a routine microanalytical solution for determining nano-scale chemical variations in the TEM. By looking at a very thin specimen at high accelerating voltage, the electron-sample interactions are minimized, which means that X-rays are only generated from a volume of similar diameter to the electron beam. This allows the study of chemical features which are much smaller than can be studied in the SEM.

The complex construction of the TEM, combined with the energetic and varied nature of radiation generated by the beam, offers a challenge to the designers of EDS systems. An EDS detector for the TEM is a compromise which offers the best combination of solid angle, take-off angle, spectral performance and overload protection. Software for the TEM must account for the specialized requirements of analysis in the TEM including, quantitative analysis of thin films, drift correction, long dwell time acquisitions, and high kV excited lines.

Combining these functions, an EDS system can provide the same detailed information on the nm scale that is provided on the μm scale in the SEM. This includes the ability to do accurate identification of constituent elements, or determine elemental concentrations, and collect drift corrected spectrum image datacubes for complete data reconstruction of maps, linescans, and spectra.