X-ray Microanalysis and Electron Energy Loss Spectrometry in the Analytical Electron Microscope: Review and Future Directions

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ABSTRACT

This paper reviews and discusses future directions in analytical electron microscopy for microchemical analysis using X-ray and electron energy loss spectroscopy (EELS). The technique of X-ray microanalysis, using the ratio method and $k_{\text{abs}}$ factors, is outlined. The X-ray absorption correction is the major barrier to the objective of obtaining 1% accuracy and precision in analysis. Spatial resolution and minimum detectability limits (MDL) are considered with present limitations of spatial resolution in the 2 to 3 nm range and of MDL in the 0.1 to 0.2 wt. % range when a field emission gun (FEG) system is used. Future directions of X-ray analysis include improvement in X-ray spatial resolution to the 1 to 2 nm range and MDL as low as 0.01 wt. %. With these improvements the detection of single atoms in the analysis volume will be possible. Other future improvements include the use of clean room techniques for thin specimen preparation, quantification available at the 1% accuracy and precision level with light element analysis quantification available at better than the 10% accuracy and precision level, the incorporation of a compact wavelength dispersive spectrometer to improve X-ray spectral resolution, light element analysis and MDL, and instrument improvements including source stability, on-line probe current measurements, stage stability, and computerized stage control.

The paper reviews the EELS technique, recognizing that it has been slow to develop and still remains firmly in research laboratories rather than in applications laboratories. Consideration of microanalysis with core-loss edges is given along with a discussion of the limitations such as specimen thickness. Spatial resolution and MDL are considered, recognizing that single atom detection is already possible. Plasmon loss analysis is discussed as well as fine structure analysis. New techniques for energy-loss imaging are also summarized. Future directions in the EELS technique will be the development of new spectrometers and improvements in thin specimen preparation. The microanalysis technique needs to be simplified and software developed so that the EELS technique approaches the relative simplicity of the X-ray technique. Finally, one can expect major improvements in EELS imaging as data storage and processing improvements occur.

1. INTRODUCTION

In the last 20 years the analytical electron microscope (AEM) has allowed investigators to obtain chemical composition and structural information from <100 nm diameter regions in thin samples of materials. The critical factors that have accompanied the development of this instrument are the ability to focus the electron beam of a conventional transmission electron microscope (TEM) to <100 nm, to scan the focused electron probe in order to obtain an image, and to measure the electrons and X-rays emitted from the sample. The increased spatial resolution of the instrument and microchemical analysis capability have allowed investigators to explore problems where reactions occur at boundaries and interfaces or within small particles or phases in bulk samples.

This paper reviews X-ray and electron energy loss spectroscopy as performed in the AEM and provides some suggestions for future directions. Any complete review of the
AEM would explore additional analytical techniques such as electron diffraction, Z contrast, surface analysis, and STEM imaging. These topics have been discussed by other authors (Joy et al., 1986; Williams, 1984; Tanaka et al., 1988) and will not be referred to further in this article.

2. DEVELOPMENT OF THE AEM FOR MICROANALYTICAL MEASUREMENTS

Some 25 to 30 years ago Duncumb (1966) recognized the advantage of using thin samples as specimens for X-ray microanalysis. Both the X-ray spatial resolution could be improved and the analysis procedure for chemical analysis simplified. Figure 1 contrasts electron beam–sample interactions for solid and thin samples bombarded by a focused high energy electron beam. In a thick-bulk sample, normally analyzed in the scanning electron microscope (SEM) electron probe microanalyzer (EPMA), the electron beam produces X-rays to a depth within the specimen of 1 to 5 μm. In addition, generated X-rays are often heavily absorbed by the specimen and X-ray fluorescence occurs (ZAF correction). Thus, the spatial resolution of the technique is limited to the micrometer scale. In a thin-foil sample, analyzed in the AEM, the electron beam passes through the sample and X-rays are generated in a volume dictated by the size of the focused probe and the extent of electron scattering, which is a function of the thickness (t) of the sample. For a very thin sample (t <10 nm) X-ray spatial resolution can approach the size of the focused probe as long as the current in the probe excites a sufficient amount of X-rays for chemical analysis. Because the specimen is thin (t <100–200 nm), X-ray absorption and fluorescence are minimal and the measured intensity is often the same as the generated intensity (Z correction).

In the mid 1960s, Duncumb developed the first AEM using a 100 keV TEM fitted with wavelength dispersive X-ray spectrometers (WDS). Figure 2 shows a schematic cross section of the instrument, EMMA, which was developed by Duncumb (1966) and Cooke and Duncumb (1969). Unfortunately, the efficiency of detection for the WDS was quite low, owing mainly to the necessity, at that time, of mounting the WDS far from the X-ray source. To overcome the low X-ray flux into the WDS, a higher current was required in the electron probe, which unfortunately increased the focused probe size to 100 nm or more.

Fortunately, the energy dispersive X-ray spectrometer (EDS) was developed in the early 1970s and was added to the AEM to measure the sample X-ray spectrum. The EDS detector was placed within 1 to 2 cm of the focused probe and the measured X-ray flux was sufficiently large so that electron probes less than 10 nm in diameter produced by a W or LaB₆ filament gun could be employed in the AEM. These instrument developments are the basis for the modern AEM instrument.

Figure 3 illustrates the type of data obtained from the early AEM instruments. Figure 3a shows a bright field electron microscope image of a lamellar taenite (ordered fcc-γ-tetataenite) platelet in the Dayton iron meteorite (Goldstein et al., 1976). The platelet is about 4 μm wide and contamination spots left from the EMMA analysis, shown in Figure 3b, are visible. The EMMA-4 was operated at 100 kV and the Ni analysis was obtained using an EDS detector. In this analysis the spatial resolution was ~200 nm. Figure 3c shows a Ni concentration profile measured on an Fe-30.7 Ni alloy heat treated at 450°C for 120 days (Romig and Goldstein, 1980). A Philips EM300 STEM, operating at 100 kV, was used to obtain the concentration data. For the operating conditions used, the X-ray spatial resolution was ~50 nm. Modern FEG instruments now allow spatial resolutions approaching 2 nm, as discussed later in this paper.

The characteristic X-rays used for microanalysis arise from the ionization of inner-shell (core) electrons by the primary beam electrons. The beam electrons lose energy as a result of ionization, but also through a whole range of inelastic processes. Electron energy-loss spectrometry (EELS) separates these inelastically scattered or energy-loss electrons from those that have lost no energy (zero-loss electrons). Historically, the technique of EELS predates X-ray spec-

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3. X-RAY MICROANALYSIS

**Ratio Method** If one assumes that the specimen is infinitely thin with respect to X-ray absorption and fluorescence, the intensity ratio, \( I_A/I_B \), of the characteristic X-rays of two elements, A and B, in the sample is directly proportional to...
the ratio of the two element concentrations, \( C_A/C_B \) (Cliff and Lorimer 1975). Equation 1 gives the Cliff-Lorimer relationship:

\[
\frac{I_A}{I_B} = k_{AB} \frac{C_A}{C_B}
\]

where \( k_{AB} \) is the Cliff-Lorimer \( k \) factor,

which is independent of the concentration of A and B in the specimen and is only a function of the operating voltage of the AEM. Equation 1 is the basis of the ratio method, which is currently used for X-ray microanalysis. If the concentrations of the elements present in a sample are known, the \( k_{AB} \) factor can be determined by measuring \( I_A \) and \( I_B \) in the EDS spectrum. Figure 4a shows the first measurement of \( k \) factors for various elements for an operating voltage of 100 kV (Cliff and Lorimer, 1975) using well-characterized silicates.

In this study element B is Si and the \( k_{AB} \) factor for Si in Si is 1.0. The errors in the measurement of \( k_{AB} \) in the original Cliff and Lorimer study are 10% or more and these errors limit the accuracy of the analysis.

**Measurement and Calculation of \( k_{AB} \)** The \( k_{AB} \) factor, assuming no absorption or fluorescence, is an atomic number (\( Z \)) correction which can be calculated in terms of fundamental parameters of X-ray generation (Goldstein et al., 1977) as:

\[
k_{AB} = \frac{(Q_0 a / A)A \epsilon_A}{(Q_0 a / A)B \epsilon_B}
\]

where \( Q \) is the ionization cross section for X-rays, \( \omega \) is the fluorescence yield (X-rays per ionization), \( \alpha \) is the relative transition probability \( [Ka/(Ka + KB)] \), \( A \) is the atomic weight, and \( \epsilon \) is the EDS detector efficiency.

To obtain \( k_{AB} \) directly, the various terms in the brackets for Equation 2 must be calculated. Of these terms the EDS detector efficiency and the ionization cross section are the most difficult to calculate. The detector efficiency depends on the thickness of the beryllium window, the gold contact layer, the silicon dead layer, and the active silicon layer. These thicknesses vary from one detector to another and even change with time for one detector. The detector efficiency term is particularly difficult to establish for X-ray energies (<1.5 keV), where detector absorption is significant. The ionization cross section is the most difficult term to calculate, and many forms of equations for \( Q \) are available in the literature (see Joy et al., 1986, Williams et al., 1984, and Zaluzec 1984). Currently, the calculation of \( k_{AB} \) for K lines above energies of 1.5 keV is in error by ~10% to 15%, mainly due to the uncertainty in the cross section (Joy et al., 1986, Williams et al., 1984). Below 1.5 keV for the light elements, detector efficiencies are difficult to calculate because of major differences in window materials and thicknesses.

**FIGURE 4.** Experimental \( k \) factors.

a. Experimental \( k \) values for 100 kV plotted as a function of X-ray energy (keV) for \( K\alpha \) lines (Cliff and Lorimer, 1975). Experimental error limits are given in the figure.

b. Experimental \( k_{AR} \) factors for 120 kV plotted as a function of X-ray energy (keV) for \( K\alpha \) lines (Wood et al., 1984).
Calculations of $k_{AB}$ for L lines have a much larger uncertainty and are not recommended for use in obtaining compositional data.

At the present time it is necessary to measure $k_{AB}$ using standards if analyses with errors of $<10\%$ (rel.) are desired. Since $k_{AB}$ is not a function of composition, at least for elements with atomic numbers 11 and above, stoichiometric minerals, intermetallic compounds, or precipitates of known composition will serve the purpose of the needed standard for each element combination AB. The $k_{AB}$ factors can now be measured with an error in the range of 1% to 4% rel. (see, for example Wood et al., 1984, Sheridan, 1989). Figure 4b shows an experimental plot of $k_{AF}$ factors obtained by Wood et al. (1984) at 120 kV operating potential. Measurement errors are in the range $\pm 1\%$ to $\pm 4\%$. If no standards are available, calculated $k_{AB}$ factors must be used.

Absorption and Fluorescence Correction  The effects of X-ray absorption, $A$, and fluorescence, $F$, cannot always be neglected. Fortunately, the fluorescence correction (Nockolds et al., 1979) is usually small (less than a few percent) in most specimens. The current accuracy level of X-ray microanalysis in the AEM is determined by the counting statistics and the error in $k_{AB}$ and is $\sim 3\%$ rel. Therefore, fluorescence can usually be safely ignored.

The absorption correction, on the other hand, is often significant, particularly if elements with X-ray lines of an energy less than 1.5 keV (Al, Na, C, N, O, etc.) are measured. Based on the original work of Tixier and Philibert (1969) and Konig (1976), Golstein et al. (1977) have derived an equation to calculate the absorption factor, $A$, and to correct the $k_{AB}$ factor for the preferential absorption of X-rays from elements A and B:

$$A = \frac{\mu / \rho^A_{\text{SPEC}}}{\mu / \rho^B_{\text{SPEC}}} \cdot \frac{1 - \exp[-\mu / \rho^A_{\text{SPEC}} \csc(\psi) \rho t]}{1 - \exp[-\mu / \rho^B_{\text{SPEC}} \csc(\psi) \rho t]} \quad (3)$$

where $\rho$ = the density, $t$ = the thickness of the film, $\mu / \rho^A_{\text{SPEC}}$ = the mass absorption coefficient for X-rays from element A or B in the specimen, and $\psi$ = the X-ray takeoff angle.

The term $t \csc \psi$ is the path length for X-ray absorption in a parallel-sided thin foil of thickness $t$ when the thin foil is normal to the incident electron beam. The absorption factor is multiplied by the value of $k_{AB}$, where there is no absorption or fluorescence, to obtain the $k_{AB}$ factor used in Equation 1.

Equation 3 is currently used in X-ray analysis in the AEM to correct for absorption. The correction is applicable as long as X-ray generation is uniform throughout the specimen and the X-ray generation with depth or mass thickness ($\rho t$), for element A and B, $\phi_A(\rho t)$, $\phi_B(\rho t)$, equals 1.

Using Equation 3 we can calculate, for a specific amount of absorption for elements A and B, the maximum thickness that a specimen can have for a given takeoff angle before an absorption correction is necessary. We can use the current accuracy level of X-ray microanalysis in the AEM of $\sim 3\%$ rel. as a guide to the point at which one must consider the absorption effect. For some element combinations, the maximum foil thickness is very small (NiAl, 9 nm; Al2O3, 14 nm; SiC, 3 nm), assuming a takeoff angle of 20°. These thicknesses are not often achieved during the specimen preparation process. Because of the high mass absorption coefficients when a low energy X-ray line (<1.5 keV) is measured, the absorption correction is often necessary in materials containing these elements.

To calculate the correction factor for absorption, the values of $\mu / \rho$, $\rho$, and the absorption path length, which involves the takeoff angle $\psi$ and the film thickness $t$, must be accurately known. Of these factors, the measurement of thickness is the most difficult to make and can vary substantially in a wedge-shaped thin foil. There are several ways to measure $t$, as is reported in the literature. The contamination spot separation method first used by Lorimer et al. (1976) is universally applicable if contamination can be generated. The technique, however, tends to overestimate the thickness of the specimen. An accurate method of determining thin-foil thickness for crystalline materials is that of measuring the spacing of the Kossel-Mollenstedt fringes in convergent beam diffraction patterns (Kelly et al., 1975). This method requires that the required diffraction conditions can be obtained at the point of interest on the specimen. These conditions are often not available, for example at points of local deformation, when analyzing most specimens. Other techniques include measuring both K and L X-ray intensity from a given element to deduce the absorption path length or measuring several spectra from the same analysis point at different tilt angles (Morris et al., 1979). Both of these techniques are difficult to use in practice. Finally, two other techniques have been proposed to measure the foil thickness, the EELS log-ratio technique (Malis et al., 1988) and the standards technique (Porter and Westengen, 1981).

The EELS log-ratio technique is an effective and convenient method to measure the local specimen thickness because there is a very simple relationship between the specimen thickness and the ratio between zero energy-loss electrons and total incident electrons (see Equation 15 later in this paper). The technique depends on the calibration of thickness inherent in the method and the ability to measure EELS spectra "on-line" at each data point. The standards technique uses a thin foil or region of thin foil of known mass thickness (usually determined by CBED techniques) and of known composition to calibrate X-ray intensity in terms of foil thickness. In this case, one measures the intensity of the whole EDS X-ray spectrum entering the EDS detector. The intensity of the EDS X-ray spectrum is a direct function of foil thickness for a constant takeoff angle until absorption effects become significant. One can therefore use the linear variation of EDS X-ray intensity versus thickness as calibrated by the standard specimen. The standard speci-
men is usually of similar composition to the specimen of interest. This technique should be quite useful as it does not rely on the direct measurement of thickness at each analysis point. However, the technique requires that the beam current remain constant as measurements from the standard specimen and sample are made or that the beam current be measured on-line in the AEM and appropriate adjustments made to take account of the varying beam current.

A technique has been developed by Horita et al. (1987) in which the absorption correction can be eliminated. In their simplification of the X-ray absorption correction, the intensity ratios of elements A, B, C, etc., in a homogeneous phase are plotted versus X-ray intensity from one of the elements, A or B or C, etc., which is not absorbed significantly as the specimen increases in thickness. An extrapolation of the nonabsorbed X-ray intensity to zero provides the intensity ratio of elements in which the absorption (A) factor is 1.0. From these measurements, \( k_{AB} \) can be determined directly. This technique holds great promise. However, it cannot be used in some of the more important analysis situations, where the concentration varies throughout a phase or region of the sample or the sample is relatively thick.

As is shown in this section, there are numerous cases where the effect of absorption is significant and must be taken into account to calculate an accurate \( k_{AB} \) factor for the ratio method. Measurement of sample thickness, which is needed for the calculation of absorption, is not yet a routine procedure and sample geometries must also be considered. As more accurate \( k_{AB} \) factors are measured, and the accuracy of the method improves, the need for a more accurate calculation of the absorption correction will increase.

**Spurious X-rays** In analyzing a specimen using the EDS spectrum, precautions have to be taken to ensure that the detected X-rays come only from the region of interest. AEM instrumental problems arise because of pre-specimen illumination system effects and post-specimen effects in the AEM stage region. In the AEM either uncollimated primary electrons hit the specimen away from the point of interest or, more probably, continuum radiation from the illumination system floods the specimen, fluorescing it, as shown in Figure 5. These two sources are instrument-dependent, since AEM illumination systems differ. This problem has been recognized for a long time, and several reviews detail the solutions (Goldstein and Williams, 1978; Bentley et al., 1979; Williams and Goldstein, 1981; Allard and Blake, 1982). Currently all manufacturers of modern AEMs attempt to minimize the effects of the illumination system by offering extra-thick, beam-defining apertures or nonbeam-defining “spray” apertures, or both. These options are essential if the AEM is to be used for quantitative X-ray microanalysis.

Assuming that the illumination system problems are removed, it is still not certain that all the detected characteristic X-rays are generated solely from the point of interest. The primary reason for this is that the thin specimens allow both transmission of high keV electrons and scatter of electrons in both the forward and backward directions. As summarized by Williams et al. (1986), the major post-specimen interaction sources are (a) incident high energy electrons backscattered into the microscope column, generating X-rays from this region (e.g., cold trap, upper polepiece, EDS collimator); (b) incident high energy electrons transmitted, scattered, or diffracted into the specimen chamber below the specimen, generating either X-rays or backscattered electrons, and (c) characteristic X-rays and high energy continuum from the point of interest on the specimen and fluorescing of the specimen environment. Using low atomic number materials for the microscope surfaces and self-supporting specimens or grids of low atomic number materials will minimize these additional X-rays generated from other than the point of interest on the specimen.

Instrument manufacturers have attempted to minimize illumination and thin specimen effects, and most instruments have acceptable background levels as determined by measuring the “hole count” from a specimen where the electron beam is passed through a hole in the specimen and the EDS X-ray spectrum is measured. In the last few years attempts have been made to develop a hole count standard (Lyman et al., 1989; Lyman and Ackland, 1991) that is independent of instrument configuration and can be used by the AEM community to determine the presence and severity of spurious X-ray generation. It appears that a standard configuration such as...
a uniform 30 nm thick Cr film sputtered onto a holey carbon film supported on a 400 mesh Au grid and backed by a Au or Mo washer would prove useful. This configuration allows the spurious X-ray counts, which are measured when the focused probe is placed in the hole in the carbon film and are produced by excitation of the thick Au or Mo washer, to be ratioed to a standard Cr peak generated in the uniform Cr film.

**Spatial Resolution and Minimum Detectability Limit** The spatial resolution of X-ray microanalysis in a thin foil is determined by the size of the beam–specimen interaction volume. This volume is a combination of the incident electron beam diameter, \( d \), and the beam broadening, \( b \), due to elastic scatter within the specimen. Definitions of spatial resolution have been proposed by several authors (Goldstein *et al.*, 1977; Reed, 1982; Michael *et al.*, 1990). The average size of the interaction volume \( R \), midway through the thin foil (Figure 6) can be given by

\[
R = \sqrt{d^2 + (d^2 + b^2)^{1/2}}/2 \quad (4)
\]

This definition of \( R \) ignores the effects of diffraction and fast secondary (FS) electrons. Recent Monte Carlo calculations show that FS are only significant for elements below atomic number 13 (Al), (Williams *et al.*, 1991a,b). It has been shown by Michael *et al.* (1990) that Equation 4 is in agreement with experimental measurements, so long as both \( d \) and \( b \) are consistently defined. Many models exist to describe the resultant beam broadening, \( b \), but are all basically variations on the original single-scattering model (Goldstein *et al.*, 1977) given by

\[
b \approx (p/A)^{1/2} (Z/E_0)^{1/2} \quad (5)
\]

where \( p \) = the density,

\( A \) = the atomic weight,

\( Z \) = the atomic number,

\( E_0 \) = the beam energy, and

\( t \) = the specimen thickness.

In order to minimize \( R \) according to Equations 4 and 5, one should use as thin a specimen as possible, as high an electron beam energy as possible, and as small a beam diameter as possible. High brightness guns, such as a field emission gun (FEG), produce the smallest probe diameters (\( d \)) for the same beam current and clearly provide for the highest spatial resolution (\( R \)) as long as beam broadening (\( b \)) is not a dominant factor.

Figure 7 shows a calculation of \( R \) for a Cu specimen as a function of foil thickness and electron beam energy, using \( d = 1.8 \) nm full width tenth maximum (FWTM), typical of a field emission gun (FEG) in a VG STEM (Williams *et al.*, 1991a,b). Both Monte Carlo simulations (closed symbols) and calculated values of \( R \) (open symbols), from Equations 3 and 4, agree well for all values of \( E_0 \). In this calculation, the spatial resolution improves with increasing \( E_0 \) and decreasing foil thickness as predicted by the beam-broadening equation (4). For the 50 nm foil, \( R \) decreases only slightly with increasing beam energy because the value of beam broadening is approaching that of the beam diameter, for example 3 to 4 nm at 300 keV. Therefore, for very thin specimens (\( t < 50 \) nm), the major contribution to \( R \) is the beam diameter, \( d \). Figure 8 shows a Ni composition profile across a planar 10 nm precipitate in the plessite region of the Grant iron meteorite (Zhang *et al.*, 1988). A spatial resolution of 2.5 nm was obtained from a 20 nm thick sample analyzed in a VG HB 501 FEG AEM at 100 keV (probe diameter 1.8 nm, FWTM). X-ray spatial resolution in the 2 to 3 nm range can be obtained with current instrumentation using a FEG. For a
larger beam diameter (e.g., 10 to 15 nm [FWTM], which is typical for a LaB₆ thermal emission electron gun) the effect of beam broadening in Cu is only important when thicker foils (>100 nm) are analyzed.

The minimum mass fraction (MMF) represents the smallest concentration of an element that can be measured in the analysis volume as defined by the spatial resolution, $R$. The MMF can be decreased (improved) by increasing the peak X-ray intensity ($P$) for the element of interest, the peak-to-background ratio ($P/B$) for the element of interest, and the analysis time ($\tau$) (Ziebold, 1967). In general

$$\text{MMF} \sim (P \cdot P/B \cdot \tau)^{-1/2}$$

The MMF can be improved by increasing the current in the focused probe, increasing the electron beam energy to increase $P/B$, and by increasing the analysis time. Currently MMF values of 0.1 to 0.2 wt. % can be achieved using an EDS detector. As is discussed in Section 5, Future Directions in X-ray Microanalysis, improved MMF can be achieved if the necessary beam stability is obtained so that longer counting times (>~100 s) are practical.

The X-ray spatial resolution, $R$, and the MMF are not independent of one another (Goldstein et al., 1990). In order to improve the spatial resolution, one can minimize the probe current to improve $d$ and use a thinner specimen to minimize $b$. Both of these improvements will degrade MMF because less X-ray intensity, $P$, will be generated. The trade-off between spatial resolution and MMF is clearly shown in Figure 9 for measurements of Ni in an Fe-25 wt. % Ni alloy (Goldstein et al., 1990). For the data shown in Figure 9, the electron probe current and the probe diameter for each of 3 AEM instruments is held constant. The thickness of the alloy specimens is varied from 20 to 250 nm. The spatial resolution, $R$, approaches the beam diameter, $d$, in the thinnest specimens. The usefulness of the FEG is clearly illustrated in Figure 9, where spatial resolution, $R$, can be improved by almost an order of magnitude from ~15 to ~1.8 nm for the same MMF and electron beam energy (100 keV). The MMF decreases (improves) continuously as the specimen thickness and spatial resolution increases. For all 3 AEM instruments, the MMF is approximately the same and is optimized at about two to five times the minimum spatial resolution.

**X-ray Imaging** The AEM has the capability of producing high resolution X-ray images that show the distribution of various elements in a specimen. Unfortunately, the volume of material excited by the focused probe in the thin foil is small, and the analysis time per picture point is also small. The low X-ray yield coupled with the low peak to background ratio of the EDS detector has made X-ray imaging in the AEM difficult using traditional thermionic guns. However, the use of AEMs with field emission guns combined with digital imaging has allowed for useful X-ray images at magnifications approaching 1 million times (Lyman, 1986). The conditions for optimum X-ray imaging are high current (>1 nA) in a small probe (<2 nm), high X-ray collection efficiency, a focused electron probe the size of a single pixel, and long dwell times per pixel (Lyman, 1986). Total acquisition times from about 1 hour to 10 or more hours (overnight running) may be needed. The problem of image drift will cause distortions of the X-ray image at high magnifications. In such cases an image drift correction is critical.

### 4. ELECTRON ENERGY LOSS SPECTROMETRY (EELS)

**The EELS Spectrometer** The spectrometer is usually a compact magnetic prism that offers sufficient energy resolution (~1 eV) to distinguish spectral peaks from all the ele-
FIGURE 9. Relationship of spatial resolution and MMF measured for Ni in Fe-25 wt. % Ni alloy by three AEM instruments (Goldstein et al. 1990). Operating conditions are (1) Philips EM400T: 120 kV, LaB6 gun, spot size 4, 0.09 nA beam current, 15.5 nm probe diameter (FWTM); (2) Philips EM430T: 300 kV, LaB6 gun, spot size 4, 0.26 nA beam current, 11.8 nm probe diameter (FWTM); (3) VG HB501: 100 kV, FEG, 0.3 to 0.35 nA beam current, 1.8 nm probe diameter (FWTM). Counting time, 120 s.

ments in the periodic table and so is ideal for microanalysis. Also, electrons in the energy range 100–400 keV, typical of AEMs, can be dispersed sufficiently to detect the spectrum electronically, without limiting the energy resolution.

There are two ways in which the spectrum can be acquired. Either electrons of a given energy range (e.g., 0–1 eV) are accumulated at one time, followed by the next energy range (1–2 eV) and so on, which is known as serial EELS, or electrons of all energies are detected simultaneously, which is termed parallel EELS. Serial EELS is the most common but least efficient method of acquisition. The spectrometer system scans or "ramps" the spectrum across a slit in the dispersion plane of the spectrometer, leaving the spectrum for a fixed "dwell time" (τ) at each energy loss. After each dwell time, the total signal is assigned to a channel corresponding to a specific energy loss, ΔE, in a multichannel analyzer (MCA).

Parallel EELS gathers the whole energy spectrum simultaneously through a scintillator coupled via fiber optics to a semiconductor photodiode array in the dispersion plane of the spectrometer. After integration, the whole spectrum is read out via an amplifier through an A/D converter and into an MCA system. The advantage of parallel EELS is that all regions of interest are gathered for the whole integration time and not just some fraction of the acquisition time as in serial EELS. Reasonable spectra can be acquired in a fraction of a second.

The Energy-Loss Spectrum There are three principal regions of the energy-loss spectrum. The first is the zero-loss peak, which is primarily elastic forward-scattered electrons that ignored the specimen. The second, the low-loss region up to an energy loss of > 50 eV, contains information about weakly bound outer-shell electrons, which control the dielectric properties of the specimen. The third, the high-loss region of < 50 eV, contains information about the more tightly bound core-shell electrons and thus reflects the nature of the atoms in the specimen. In addition there is fine structure information about how the atoms are bonded and the atomic distribution around a specific atom. The energy-loss spectrum is far more useful than a simple X-ray spectrum, but it is also far more complex. A typical spectrum is shown in Figure 10.

Microanalysis with Core-Loss Edges The ionization of a core-shell electron produces an ionization edge in the spectrum with a threshold onset equal to the ionization energy. It is possible to quantify either a single element (N^A) or a ratio of two elements (N^A/N^B) in the spectrum (Egerton, 1986). First, the appropriate K, L, or M edges must be selected for quantification and the background intensity subtracted. Next, the collection semiangle (θ) must be measured and the intensity in the core edge (I_K, l_K) integrated over an energy window (Δ). Finally, the partial ionization cross section (e.g., for a K shell ionization, σ_K(β, Δ)) for elements A and B must be determined. (Note that it is customary to use σ for the ionization cross section in core-loss spectroscopy, while the same ionization cross section is termed Q in X-ray spectroscopy, e.g., Equation 2). The following equation then gives the ratio of A to B:

\[
\frac{N^A}{N^B} = \frac{I_K^A(\beta, \Delta)\sigma_K^A(\beta, \Delta)}{I_K^B(\beta, \Delta)\sigma_K^B(\beta, \Delta)}
\]
The standard approach to background subtraction is to use linear least squares fitting of the background before the edge to an expression termed a power law:

\[ I = AE^{-r} \]  

(8)

where \( I \) = the background intensity at an energy loss \( E \), and \( A \) and \( r \) are fitting parameters.

Because of the dependence on the value of \( E \), different edges in the same spectrum will have different power-law fitting parameters. The power-law fit is not a good approximation in the low-loss region of the spectrum (below ~100 eV), and other polynomial functions may offer a better fit. By differentiating spectra (Shuman and Kruit, 1985) it is possible to amplify ionization edges with respect to the background in a similar manner to the processing of Auger spectra. This process removes slowly varying parts of the spectrum (i.e., the background), converting the intensity to zero, but leaves rapidly varying parts essentially unchanged (i.e., the edges). With a parallel EELS, the simplest way to carry out such an operation is to record two spectra separated by a small energy shift, then subtract one from the other, which gives a first difference spectrum, such as the one shown in Figure 11. Because of its simplicity in comparison with the power-law approach, this procedure is becoming much more common as parallel EELS becomes more widely available. The difference spectrum easily reveals the presence of very small ionization edges such as the Li K edge shown in Figure 11, and also has the advantage that it suppresses spectral artifacts arising from variations in the efficiency of individual detector diodes. Difference spectra appear less susceptible to specimen thickness changes than spectra processed using a power-law background fit.

After background subtraction, the edge intensity has to be determined. This can be done either by simple integration of the remaining intensity in the window \( \Delta \) or by multiple least squares (MLS) methods. The MLS method requires the generation of standard reference spectra, which are compared to the unknown. A similar procedure is carried out in X-ray microanalysis after digital filtering, but unlike the current situation in X-ray analysis, the MLS routines are not yet commercially available.

The ionization cross section is usually calculated with the hydrogenic models of Egerton (1986) called \( \text{Sigmak and Sigmal} \) for K and L edges respectively. These models approximate the ionized atom to a hydrogen atom and produce a simple triangular-shaped fit to the ionization edge, neglecting any near-edge and post-edge fine structure. It is only necessary to feed in a value of the collection semiangle \( (\beta) \), the integration window \( (\Delta) \), and the accelerating voltage.

Parametric approximations and \textit{ab initio} calculations have also been used to determine \( \sigma \), but it is now becoming common to use experimental approaches, essentially identical to the \( k \) factor method for X-ray analysis (Hofer, 1991). Quantification of core losses permits light element microanalysis of elements undetectable or unquantifiable by X-ray techniques, such as lithium, as was already shown in Figure 11 (Liu and Williams, 1989).

**Limitations of Core-Loss Microanalysis**

(a) The Beam Convergence: The semiangle of convergence, \( \alpha \), is assumed to be negligibly small in TEM image or
diffraction mode, since it is usually $< 10^{-4}$ radians. In STEM mode however, $\alpha$ can be equal to or greater than $\beta$, and in this case the value of $\sigma(\beta, \Delta)$ substituted into the quantification equations must be modified. When $\alpha > \beta$, Joy (1986) recommends a correction factor $R$ be determined:

$$
R = \frac{\ln(1 + \alpha^2)\theta_E^2\beta^2}{\ln(1 + \beta^2)\theta_E^2\alpha^2} \quad (9)
$$

where $\theta_E$ = the characteristic scattering angle corresponding to the mean energy loss.

This correction factor $R$ modifies $\sigma(\beta, \Delta)$ by a factor $<1$. Alternatively, an effective collection semi-angle $(\beta)$ can be calculated and substituted in the quantification equation.

(b) Specimen Thickness: Ideally, the specimen should be so thin that all electrons undergo only a single-scattering event. In practice the specimen is usually much thicker and plural scattering occurs. Under these circumstances, corrections are needed to get the best quantitative analysis. First, the thickness, $t$, needs to be determined to see if correction procedures are required. Second, the ideal single-scattering spectrum has to be deconvoluted from the experimental plural-scattering spectrum. Deconvolution is often essential, and typically either a Fourier-log or a Fourier-ratio approach is used (Egerton et al., 1985). Deconvolution, however, may introduce artifacts into the spectrum, so it is best always to start with the thinnest possible specimen.

Spatial Resolution In contrast to the situation in X-ray microanalysis, beam spreading is not a major factor in determining the source of the EELS signal, so the many factors that influence beam spreading for X-rays are mainly irrelevant. As shown in Figure 12, because the spectrometer only collects those electrons emanating from the sample in a narrow cone, energy-loss electrons that are widely scattered by elastic scattering are excluded from contributing to the spectrum. In contrast, these same high angle electrons generate X-rays some distance from the incident probe position, and these X-rays would be detected by the X-ray spectrometer.

In the absence of a contribution from beam spreading, the spatial resolution of core-loss microanalysis depends on the mode of analysis. The factor controlling the spatial resolution in STEM mode (or in a probe-forming mode on a TEM) is principally the size of the probe, and one can easily get data with probe sizes $<10$ nm. In TEM mode, the spatial resolution is a function of the selecting aperture, that is, the spectrometer entrance aperture and its effective size at the plane of the sample. Under these circumstances lens aberrations usually limit the spatial resolution (Egerton, 1986).

![Figure 11. Creating a first difference spectrum: By acquiring two spectra displaced by 1 eV on the diode array and subtracting one from the other, a first difference spectrum is created in which the background is reduced to zero and the small Li K and Al L\textsubscript{2,3} core-loss edges are amplified. (Courtesy J. A. Hunt)](image)

![Figure 12. The reason for improved spatial resolution in EELS compared with X-ray microanalysis: the EELS spectrometer only collects those electrons emanating from the hatched region of the specimen, defined by the entrance aperture to the spectrometer, while the X-ray detector collects X-rays from the larger dotted region, where elastic-beam spreading occurs. (From Egerton, 1986. Reproduced courtesy of Plenum Press.]}
Because the EELS signal isn't affected by beam spreading and one can easily limit the source of the signal to a few nanometers with an FEG, there have been correspondingly fewer studies of the limits of spatial resolution. Most work on defining the spatial resolution has been pursued in France by Colliex and coworkers (see, for example, Colliex, 1985). Because the primary factor when operating in STEM mode is the incident probe diameter, one is concerned about the problems of spherical aberration broadening the probe (Colliex and Mory, 1984), and careful selection of the beam defining aperture is required.

One factor that is often considered in EELS but ignored in X-ray microanalysis (although it also occurs in X-ray generation) is the phenomenon of delocalization. Delocalization is the ionization of an inner-shell electron by the passage of a high energy electron some distance from the atom. The scale of this wave-mechanical effect is small, in the range 2–5 nm, and it is inversely proportional to the energy loss. It appears that except in rare cases delocalization will not limit the spatial resolution, and the practical factors such as probe aberrations, signal to background in the EELS signal, and specimen damage are much more important. So we can conclude that EELS spatial resolution will be somewhat better than the spatial resolution of X-ray analysis under equivalent conditions of kV and thickness. Experiments seem to indicate that this indeed is the case (Colliex, 1985), although with FEG instruments the improvement is small (Titchmarsh, 1989).

**Detectability Limits** To get the best detectability limits for ionization loss spectrometry requires optimization of the edge intensity, the signal to background ratio, the efficiency of signal detection, and the time of microanalysis. EELS has an inherently higher efficiency than X-ray microanalysis but a correspondingly poorer signal to background because of the higher background in the spectrum. Joy (1986) has attempted to compare the two techniques in some detail using calculations based on a thermionic source. Minimum mass fractions of the order of 1% to 10% in a 50 nm thick Si foil are calculated, which is somewhat worse than the experimental data for X-ray microanalysis in similar samples.

For an FEG the situation is further improved, since the time of collection, which strongly influences the detectability limit, will be decreased if a high brightness FEG source is used. The time of collection also depends on whether serial or parallel collection is used. Colliex (1985) argues that a factor of 10 improvement in all EELS performance criteria is to be expected if parallel collection is used, and shows the detection of less than 0.1% of a solute element as possible in a few tenths of a second using parallel EELS and an FEG. Such results would not be achievable using serial EELS. The best results combining sensitivity and spatial resolution will be obtained with an FEG source. Shuman and Kruit (1985) have used an FEG AEM, parallel detection, and sophisticated data processing to detect approximately 0.01% of Ca in biological tissue, with a spatial resolution of 200 nm. More recently, Mory and Colliex (1989) have shown the possibility of single atom detectability for thorium atoms on a carbon support film, and Leapman and Newbury (1992) have demonstrated a sensitivity of <10 ppm from some standard reference material (SRM) glasses prepared by the National Institute for Standards and Technology (NIST) from specimen regions ~10 nm in size. Leapman and Hunt (1991) have also shown that under similar ideal conditions (i.e., a heavy element in a carbon film) EELS has the advantage over X-ray microanalysis for most elements. In less ideal conditions, particularly for materials science samples where the matrix is heavier, this conclusion may not apply.

![Al - Plasmon Energy as a Function of Lithium Content](image-url)
In conclusion, microanalysis using ionization edges, although considerably more difficult to perform than X-ray microanalysis, appears to offer both improved spatial resolution and analytical sensitivity. Parallel collection is significantly better than serial collection in both aspects, and as was the case for X-ray microanalysis, an FEG source is required for the best performance.

**Plasmon Loss Analysis** Plasmon loss analysis detects shifts in the plasmon peak position caused by changes in the electron density of the specimen as a result of alloying. The shift in the peak energy $\Delta E$ is proportional to the square root of the free electron density $n$ through the relationship:

$$E_p = \hbar \omega_p = \hbar \left(\frac{ne^2}{m}\right)^{1/2}$$  \hspace{1cm} \text{(10)}$$

where  $2\pi\hbar = $ Planck’s constant,
$e = $ the electron charge,
$m = $ the electron mass, and
$\epsilon_0 = $ the dielectric constant (permittivity of free space).

The advantages of plasmon loss microanalysis over ionization loss techniques are (1) specimen thickness is not a limitation, (2) it does not require knowledge of a cross section, (3) it does not require background subtraction, and (4) the spectrum intensity is high. The disadvantages are (1) it is not a generally applicable technique, and (2) the theory is not well known and the approach relies on empirical calibration.

As is shown in Figure 13 there is a measurable change in the plasmon peak shift of pure Al as a function of Li content, and similar relationships hold for several other solid solution additions (Williams and Edington, 1976).

**Fine Structure in the EELS Spectrum** The high energy resolution of EELS ($\sim 1 \text{ eV}$) compared with X-ray energy dispersive spectrometry ($\sim 130 \text{ eV}$) reveals spectral information other than the basic elemental chemistry of the beam-specimen interaction volume (Egerton 1986). This information can’t be obtained by other techniques if high spatial resolution ($< 100 \text{ nm}$) is also essential. There is fine structure around the ionization edge, which can be divided into energy-loss near-edge structure (ELNES) and extended energy-loss fine structure (EXELFS). In addition there is fine structure in the low loss region of the spectrum associated with the weakly bound valence electrons.

(a) Energy-Loss Near-Edge Structure (ELNES): There is a range of possible energy levels above the Fermi level, and the distribution of these energy levels is termed the density of states. Simplistically the ionized electron can reside in any of the unoccupied states above the Fermi level, and therefore the ELNES changes with changes in the density of states, as shown in Figure 14. For example, if the nature of the atomic bonding changes, the ionization energy may be measurably different. Figure 15 shows the change in the oxygen K near-edge structure across an interface between ZrO$_2$ (top three spectra) and NiO (bottom three spectra) (Hunt and Williams, 1991). The different oxygen bonding in the two ceramics accounts for the changes.

Many attempts have been made to compare the fine structure around the ionization edge with calculations of the density of states in simple oxides, carbides, and nitrides (Rez et al., 1991). Although the experimental and calculated spectra show reasonable agreement in terms of the energy of the spectral features, there are still discrepancies in the measured
and calculated intensity (Figure 16). At present our understanding of the electronic structure of the atom is insufficient to allow a complete model of the ELNES to be developed. It is not possible to extract a complete picture of the electronic structure of an atom in an unknown sample by analyzing the ELNES, although in principle such information is present.

(b) Extended Energy Loss Fine Structure (EXELFS). If the ionized electron is given more energy (E) than it needs to escape the attractive field of the nucleus (E\textsubscript{K}), this excess energy appears as an electron of wavelength determined by \( E - E\text{K} \). This wave is scattered by the surrounding atoms. The scattered waves interfere with one another, and this interference effectively changes the cross section. The interference between the radiating and the scattered waves is possible because the ionization process is slow compared with the wave velocity. The interference manifests itself as small modulations in the post-edge intensity visible in the Be K edge spectrum above energy loss of ~140 eV (Figure 17). These modulations, which start several tens of eV after the threshold, each cover an energy range from 20–50 eV and continue for several hundred eV. EXELFS modulations are analogous to the oscillations seen in extended X-ray absorption edge fine structure (EXAFS) in synchrotron X-
ray spectra (Teo and Joy, 1982).

EXELFS is important because of the structural information contained in the intensity oscillations. To extract this information, one has to ensure that the spectrum contains single-scattering information only, otherwise the plural scattering intensity may mask the EXELFS peaks. Therefore, deconvolution is required. Next, one has to remove the background. Then the intensity spectrum is converted to an electron wave function in k-space (reciprocal space) where, as shown by Joy (1986),

\[ k = \frac{2\pi}{\lambda} = \left[ 2m(E - E_p) \right]^{1/2} / h \]  

where \( m \) = the effective mass of the electron and
\( h \) = Planck’s constant.

This is because the electron wave interference gives periodic intensity maxima in k-space when

\[ 2\pi(2\alpha / \lambda) + \Phi = 2\pi n \]  

where \( \alpha \) = the distance from the ionized atom to the first nearest neighbor, and
\( \Phi \) = the phase shift that accompanies the scattering.

So periodic maxima occur for \( n = 1, 2, \) etc., and for different interatomic spacings. Thus, it is possible to determine the local atomic environment if the various interferences can be discriminated. The atomic spacing is obtained by a Fourier transform of the k-space modulations to give a radial distribution function, originating at the ionized atom. Peaks in the RDF indicate the probability of an atom occurring a certain distance from the origin.

Although the technique is potentially extremely powerful, offering enormous improvements in spatial resolution (and cost and convenience) when compared with synchrotron-source EXAFS, it has yet to become widely accepted. There have been few structural determinations made with EXELFS that were not previously known, and often the EXELFS results do not compare well with the results from other techniques such as diffraction, except for the first nearest neighbor spacings. But if EXELFS does progress, its major role may well prove to be in the study of amorphous or quasicrystalline structures, or in detailed high spatial resolution studies of such phenomena as crystallographic channeling.

(c) Low-loss Fine Structure: In addition to the fine structure around the core edge, the valence spectra may contain fine detail superimposed on the dominant bulk plasmon peak. The most common extra peak is a surface plasmon peak. Surface plasmon studies can reveal the presence of local interface effects not visible in TEM images (Walls and Howie, 1989). In some specimens such as polymers, small peaks due to interband transitions can be seen in the low-loss spectrum.

In summary, there is detail in the energy-loss spectrum beyond the basic chemistry of the sample. To extract this information a single-scattering (deconvoluted) spectrum is needed, as well as sophisticated mathematical analysis. Often interpretation of the data is limited by lack of knowledge of the physics of the electron–specimen interactions, and to a large extent these techniques offer more promise than hard results.

**Dielectric Constant Determination** The energy-loss process can be viewed as the dielectric response of the specimen to the passage of a fast electron, and as a result the energy-loss spectrum contains information about the (frequency-dependent) dielectric constant or permittivity (\( \varepsilon \)). The single-scattering spectrum intensity, \( I(\omega) \), is related to the imaginary part of the dielectric response function by the expression

\[ I(\omega) = (I_0 / k) \text{Im}(-1/\varepsilon) \ln \left[ 1 + (\beta/\theta_p)^2 \right] \]  

where \( I_0 \) = the intensity in the zero-loss peak,
\( \beta \) = the specimen thickness,
\[ k = \text{a constant incorporating the electron momentum and the Bohr radius}, \]
\[ \beta = \text{the spectrometer collection semiangle, and} \]
\[ \theta_E = \text{the characteristic scattering angle}. \]

Since a single-scattering spectrum is essential, deconvolution is the first step. The energy spectrum is then subjected to a Kramers-Kronig analysis (Egerton, 1986) to extract the real part of the dielectric constant from the imaginary part in Equation 13. The Kramers-Kronig analysis gives the energy dependence of the dielectric constant and other information usually obtained by optical spectroscopy. The advantage of EELS is the improvement in spatial resolution over light-based techniques, and also the extended frequency range. The low-energy plasmon part of the spectrum out to ~20 eV is of most interest, and corresponds to optical analysis of the dielectric response from the visible through the ultraviolet frequency range. So in a single EELS experiment one can in theory substitute for several optical spectroscopy techniques.

Physicists are most interested in the low frequency range around 1 eV, since this is less accessible to optical spectroscopy. For this measurement one needs an FEG system and a high resolution spectrometer so that the zero-loss peak tail does not mask the low energy intensity.

**Thickness Determination** It is possible to measure thickness \( t \) directly. From a well-defined plasmon peak \( t \) can be determined if the plasmon mean free path \( \lambda_p \) is known since, if single scattering occurs (Joy, 1986),

\[
t = \lambda_p l_p / l_0
\]

where \( l_p \) = the intensity in the first (and only) plasmon peak and

\( l_0 = \text{the intensity in the zero-loss peak.} \)

Since plural scattering usually occurs, we have to modify equation 14 thus (Egerton, 1986) to give the log-ratio thickness equation already mentioned:

\[
t = L \ln (l_T / l_0)
\]

where \( l_T = \text{the intensity in the total spectrum above the zero-loss and} \]

\[ L = \text{an average mean free path for the total energy-loss spectrum}. \]

Malis et al. (1988) have given a parameterized expression for \( L \) based on many experimental thickness measurements over a wide range of materials. This approach gives a value for \( t \) with an accuracy of \( \pm 20\% \). While a more accurate value of \( t \) would be desirable, this approach is still very useful for analytical microscopists because it is rapid. It can be used for calculation of X-ray absorption and spatial resolution.

**Energy-loss Imaging**

(a) Digital Spectrum Imaging: Spectrum imaging uses high density magnetic media to collect and store a complete spectrum at each pixel in a digital STEM image. The term “spectrum imaging” was coined by Jeanguillaume and Colliex (1988), who first applied the concept to EELS in a STEM. The original approach, which only stored and mapped a few channels of the spectrum at each pixel, has been expanded to give complete spectrum storage (Hunt and Williams, 1991). Sophisticated software allows the stored spectra to be accessed rapidly and sectioned in “spectrum space” so that any feature in the spectrum may be mapped. Because the data are always stored, any kind of post-analysis interrogation is possible. Thus, a map of any detected element, even one unsuspected prior to analysis, can be produced. Different quantification routines can be applied to the same data and the results compared. Information such as thickness, plasmon peak shifts, and fine structure details can all be mapped quantitatively, in addition to the simple elemental distributions. Figure 18 shows examples of spectrum imaging in an aluminum-lithium alloy aged to produce spherical \( \text{Al}_x\text{Li} \) particles with a nominal composition of 25 at. \% Li. Each image is formed from different information available in the energy loss spectrum. Figure 18a shows the variation in the position of the zero loss peak as a function of time and thus represents a map of the stability of the source and the spectrometer magnet. Figure 18b is an image of the first plasmon loss peak position and shows the shift in the plasmon peak as a function of the position of the beam on the specimen. The plasmon peak shifts as a result of changes in the free electron density, which are linearly related to the amount of lithium in the specimen. Figure 18c is the difference between Figures 18b and 18a, that is, a plasmon energy shift image. Figure 18d is a thickness map of the sample produced by applying the Egerton-Malis equation to the low loss portion of each spectrum. Figure 18e is an absolute Li content map, and Figure 18f is a relative Al content map. These latter two figures were produced by multiplying Figure 18c by the thickness plane. The gray scale look-up table along the base of the image can be used to quantify the intensity variation in each image. For example, the maximum Li content (white pixels) in Figure 18e is 1,056 atoms/nm², the maximum Al content in Figure 18f is 5,425 atoms/nm², and the maximum thickness in Figure 18d is 99 nm.

(b) Analog Energy-Filtered Imaging: For analog imaging we have to insert a spectrometer into the imaging system of the TEM. The only commercial systems are the Zeiss energy filtered TEMs in which a Castaing-Henry mirror-prism spectrometer sits between the intermediate and projector lenses. Until recently, the instrument was not available with a goniometer stage and was limited to 80 kV, so it only saw substantial applications in the biological sciences. Now these limitations have been overcome in the latest Zeiss TEM (Bihl et al., 1991); increased usage in the materials sciences is expected.
To select the electrons for imaging, the spectrum is shifted relative to a slit that is positioned after the prism but before the final lens. The shift is made by increasing the accelerating voltage of the microscope by \( +E \) to keep the energy loss electrons of interest (\(-E\)) on the optic axis. Either an image or diffraction pattern can be filtered by changing the strength of the intermediate lens preceding the prism-mirror system. In addition the energy-loss spectrum can also be displayed on the TEM screen showing the angular distribution of the energy-loss electrons. The intensity has to be determined by digitizing the spectrum or using a microdensitometer (Reimer and Rennekamp, 1989). The energy window is adjusted by varying the slit width. With a 20 eV window it is possible to obtain images with a chromatic aberration resolution of \( \pm 0.5 \) nm, which compares well with normal TEM chromatic-aberration limits. Resolution may be \( \pm 0.5 \) nm under ideal conditions.

In summary, EELS applications in materials science still emphasize microanalysis using core edges and occasionally plasmon shifts. Imaging is the preferred way to carry out microanalysis, since it tends to give the full picture rather than isolated spectra, often from operator-biased selections of the region of interest.

5. FUTURE DIRECTIONS IN X-RAY MICROANALYSIS

**X-ray Spatial Resolution and Minimum Detectability Limits**

The best compromise in terms of improving X-ray spatial resolution and MMF is to use high operating voltages (300 to 400 kV) and thin specimens. The loss of X-ray intensity, \( I \) in Equation 6, a consequence of using thin specimens, can be compensated in part by the higher voltages and the high brightness FEG source, where a small spot size of 1 to 2 nm can still be maintained. Under these circumstances, optimum MMF and spatial resolution can be obtained by using a high brightness, intermediate voltage source with thin foils, perhaps of the order of 10 nm in thickness. Under these circumstances MMF values \( < 0.1 \) wt. % will become routine.

Of interest is the ultimate ability of the AEM to detect the presence of only a few atoms in the analysis volume. For the SEM-EPMA with 1 \( \mu m^3 \) excitation volume in Fe and a 0.01 wt. % MMF, \( \sim 10^7 \) atoms are detected in the analysis volume. Using data from Figures 8 and 9, for an Fe-Ni alloy analyzed in a VG HB501 FEG AEM operating at 100 kV, with a beam diameter of 1.8 nm (FWTM), a spatial resolution of 2.5 nm (FWTM), a foil thickness of 20 nm, a counting time of 120 s and a MMF of 0.4 wt. % Ni using an EDS detector, \( \sim 350 \) atoms of an element of interest are detected in the analysis volume. If the counting time is increased by a factor of 10 using a more stable sample stage and instrument electronics and if the operating voltage is increased to 300 kV, with a beam diameter of \( \sim 1.0 \) nm (FWTM) and the foil thickness reduced to 10 nm, the spatial resolution would improve to \( \sim 1.5 \) nm (FWTM) and the MMF would improve to \( \sim 0.1 \) wt. %. In this situation, \( \sim 1 \) to 2 atoms of an element of interest could be detected in the analysis volume. In other words, with expected improvements in AEM instrumentation to reduce background and to improve peak to background and in the preparation of thin foils, it will be possible to detect the presence of single atoms in the analysis volume. Potential applications of this capability will be in nanometer segregation problems, semiconductor doping measurements, examination of nucleation theory, the analysis of growth steps, and the analysis of surface reactions in situ. Most of these potential applications can only be pursued in a UHV system.
It is important to note that single-atom analysis will not be possible in larger analysis volumes (spatial resolution $>1.5$ nm). The MMF of the EDS detector is not low enough to detect the X-ray signal generated from a single atom. The lower MMF of the parallel EELS technique, using the FEG AEM instrument, is an advantage for single-atom analysis for larger analysis volumes as demonstrated by Leapman and Newbury (1992). As is discussed in a later section, the use of a WDS detector in a FEG AEM, with the capability of handling high peak intensities and of obtaining higher peak-to-background ratios, should yield improved MMF and therefore single-atom analysis in larger analysis volumes.

One potential problem with achieving a spatial resolution approaching 1 to 2 nm is the effect of fast secondaries, as has been pointed out by Gauvin and L'Esperance (1989) and Williams et al. (1991a,b). For example, Monte Carlo simulations using a parallel supercomputer (Williams et al., 1991a,b) showed that the major effect of fast secondary electrons is to cause non-Gaussian beam tailing in carbon and presumably other light elements but is insignificant for $Z > 13$. The beam broadening causes an increase in the spatial resolution far beyond that predicted by Equations 3 and 4. Experimental measurements have not been obtained to date but may be expected to show that light element matrices will yield an X-ray source size well beyond that expected from a calculation using a simple beam-broadening model.

**Specimen Preparation and Clean Room Techniques**

The preparation of thin foil specimens is, in many ways, more of an art than a science. Nevertheless, if the goal is to improve spatial resolution and MMF to the single-atom analysis region, one must obtain thin foil samples approaching 10 nm in thickness. The two major methods, jet electropolishing and ion beam thinning, subject the thin regions of the sample to either severe mechanical stress combined with rapid electrochemical dissolution or intense ion-beam heating, differential sputtering, and surface damage. It is critical, however, that the thin foils continue to have the same composition and other characteristics of the bulk sample.

As has been discussed by Williams and Goldstein (1991), there is ample evidence that both electropolishing and ion-beam thinning can change the surface chemistry and introduce severe heating effects. Unfortunately, the thinner the sample, the more severe the problem becomes. The easiest way to see the surface effect is to measure the composition variation with thickness in a homogeneous sample. If surface chemical changes have occurred, instead of a constant composition, a change in composition of one or more elements is often detectable as the $I_A/I_B$ ratio is measured as a function of specimen thickness. If such an effect is observed, it is necessary to change the specimen preparation method, or to clean the sample surface in some way. At the present time, a short "dusting off" is carried out for only a few minutes in the ion beam thinner to clean the surface.

To handle the thin specimens required for high spatial resolution microanalysis, more careful specimen-handling techniques will need to be developed. Typical clean room techniques will be adopted so that specimens and sample holders are cleaned and handled in laminar flow hoods. More often than not specimens will have to be heated using infrared techniques to remove water and residual hydrocarbon films from prior thinning as well as "dusted off" in an ultra high vacuum specimen preparation chamber attached directly to the AEM. Because the surface layer of the thin foil specimen represents a significant proportion of the foil thickness, surface analysis preparation techniques now used for Auger, XPS, and other surface analysis techniques will need to be employed. These sample preparation techniques will, however, enable the investigator to employ surface analysis techniques on the same specimens prepared for AEM, perhaps even in the same instrument. In any event, analytical electron microscopy must be pursued in a UHV environment.

The ultimate limitation to microanalysis in the AEM is beam damage. In the AEM, particularly in 300 to 400 kV instruments, knock-on damage or sputtering effects can occur that may change the local chemistry of the specimen. Voltages for knock-on damage of most elements are well known, and surface atom sputtering has been studied (Zaluzec and Mansfield, 1987). In either case, the obvious solution is to operate below the critical threshold voltages, although this will remove many of the attractive aspects of operating at the highest available voltage. As we seek more intense electron sources, the power-input capabilities of modern AEMs are very large. Fortunately, in the AEM most electrons ignore the sample completely; otherwise the specimen would be vaporized. Nevertheless, in the future the analyst must consider that we are rapidly approaching the limits of the technique in terms of the ability of the sample to remain unchanged in the microscope.

**Quantification and Light Element Analysis**

In order to obtain precision and accuracy approaching 1% rel. in thin film X-ray microanalysis, as obtained in the EPMA, it will be necessary to measure $k_{AB}$ factors to within 1% rel. This goal can only be achieved when X-ray counting statistics approach those available with the EPMA. The limit with present AEM instruments is the relatively low X-ray yield from thin foils and the relative instabilities in the stage and electron beam current, which prevent X-ray counting times that exceed ~100 s. The further development of high brightness FEG instruments will provide higher electron current in the focused probe. Coupled with more stable instruments, the ability to measure beam current during analysis, and the use of more than one EDS detector, it should be possible to obtain enough X-ray counts from elements A and B (roughly 50,000 counts for $I_A$ and $I_B$) to approach 1% counting statistics. Using homogeneous alloy standards, it should be possible to measure $k_{AB}$ factors in X-ray microanalysis to 1% rel.

In practical analysis, measurements of foil thickness must be made at each analysis point unless absorption effects are $<1\%$. The EELS log-ratio or standards technique (see Section 3) can provide thickness measurements approaching
10% to 20% accuracy. In the future it should be possible to make these thickness measurements on-line as long as specimen stage stability is improved and on-line beam current measurements can be made to compensate for changes in electron beam current with time. The extrapolation technique (Horita et al., 1987) eliminates the need for measuring foil thickness but cannot be applied when concentration gradients are measured or when the foil is relatively thick. With improvements in the measurement of foil thickness or in cases where the sample is relatively homogeneous, it should be possible to measure X-ray generation through the \( k_{AB} \) factor and absorption using foil thickness measurements and approach the goal of AEM X-ray microanalysis at the same 1% accuracy level as in the EPMA. More accurate analysis of interfaces, diffusion gradients, and of differences in phase composition will be available with spatial resolutions better than 100 times those of the EPMA.

The optimistic outlook for X-ray microanalysis at the 1% accuracy level must be tempered when considering X-ray analysis for the light elements, that is, elements with characteristic X-ray lines with energies less than 1.5 keV (e.g., Kα lines for Al, Mg, Na, O, N, C, etc.). In the last few years, EDS detectors have been constructed with ultrathin windows or used without an X-ray window in order to measure X-rays with energies <1.5 keV. This improvement in X-ray detection for the light elements allows for quantitative analysis of the light elements. However, the relatively poor resolution of the EDS detector produces peak overlaps from more than one light element or, even worse, from the overlap of L lines of heavier elements such as Ti, Cr, Fe, Ni, and Cu. Assuming that such overlaps do not occur or can be handled by software techniques, there are also severe absorption effects (see Section 3) where even 20 nm thin foils can cause significant problems for the analysis. A recent paper by Westwood et al. (1992) shows that quantitative light element analysis can be performed using the extrapolation technique to obtain light element k factors (\( k_{OA} \), \( k_{NM} \)).

One of the main assumptions in the ratio technique is that the normalized distribution of characteristic X-ray intensity with mass depth, \( \phi(\rho t) \), is constant with mass depth, \( \rho t \), and equals a value of 1.0. If this assumption is violated, the X-ray generation must be calculated as a function of mass depth, and the standard absorption term (Equation 2) must be modified. Measurements of \( \phi(\rho t) \) curves for thin specimens have been determined only for a limited number of elements because of the difficulty in performing such experiments.

Recently, Monte Carlo electron trajectory simulations have been performed to calculate \( \phi(\rho t) \) and \( k_{AB} \) factors (Gauvin and L’Esperance, 1989, and Michael et al., 1991) and include effects of fast secondary (FS) electrons. Michael et al. (1991) have shown that for Al Kα X-rays generated in a 50 nm thin foil of pure Al bombarded by 300 keV electrons, the \( \phi(\rho t) \) value is 1.0 without considering FS, but is about 1.013 with FS. This relatively small effect is much larger for lower energy X-rays, for example for N Kα X-rays in TiN, the generated X-ray intensity is increased by about 7% for 300 keV electrons and \( \phi(\rho t) \) is not constant with \( \rho t \). Figure 19 shows the generated and emitted (after absorption in the thin foil is considered) N Kα \( \phi(\rho t) \) curves in a 50 nm thin foil of TiN excited by 300 keV electrons. The effect of absorption is very important, particularly when coupled with a varying \( \phi(\rho t) \) in the thin foil. In a system containing a light and a heavy element, the enhanced X-ray emission from the light element due to fluorescence by fast secondary electrons leads to a compositionally dependent \( k_{AB} \) factor (Gauvin and L’Esperance, 1989). Figure 20 shows the variation of \( k_{AB} \) as a function of B concentration in B-N, B-Fe, and B-Nd calculated by Monte Carlo techniques for 100 keV electrons and for 100 nm thin foils. As has been shown by Westwood et al. (1992), measurements of \( k_{AB} \) factors of the light elements approaching the 10% accuracy level are now available. However, X-ray microanalysis for the light elements in the AEM will require further development before 1% rel. accuracy can be approached.

**WDS Possibilities** The advantages of the wavelength dispersive spectrometer (WDS) are high-energy resolution (<40 eV), high peak-to-background ratios (over 10 times greater than the EDS), high input (output) count rates (up to 50,000 cps), and the ability to detect and measure the light elements more efficiently than EDS. Clearly then, the addition of a WDS detector to the AEM would improve MMF and the analysis of the light elements and the overlap of characteristic X-ray peaks in the EDS. The clear disadvantage of the WDS, as was discussed earlier in this paper, is the low X-ray flux into the detector (10^2 to 10^3 worse than the EDS) owing to the large size of the spectrometer (see Figure 2). Other problems include the need to measure or control beam current while two separate peak measurements are made, the mechanical instability of the WDS, and the low efficiency of some diffracting crystals.

Goldstein et al. (1989) have proposed the addition of a small horizontal WDS unit to the AEM (Figure 21). In this unit the analyzing crystal of the WDS is brought as close to the specimen as for the EDS detector (1 to 2 cm). A design is proposed in which crystal and detector are moved independently by computer-controlled mechanical motors placed within the vacuum of the AEM. A doubly bent diffracting crystal would be used to focus the X-rays and a solid state detector would take the place of the conventional flow proportional detector. Alternative WDS designs are now being developed that will ultimately help to improve MMF in the instrument, resolve peak overlaps, and detect the light elements without interferences from the L lines of the transition elements.

**Instrument Development** From the standpoint of X-ray microanalysis, the AEM is still in the development stage. At the present time it is not an instrument optimized for microanalysis. Using well-developed EPMA concepts, a true "electron-probe nanoanalyzer" will undoubtedly be available in the near future. The instrument improvements necessary for an optimized instrument include (i) electron source stabil-
ity, (2) in situ probe-current measurement, (3) multispecimen capability, (4) high detector takeoff and collection angle, (5) maximum peak-to-background ratio and minimum hole count, (6) stage stability and computerized stage control, and (7) ultra high vacuum stage environment and sample preparation assembly. Most of these instrument development areas were discussed by Williams and Goldstein (1991).

1. Source stability: In the EPMA high levels of probe-current stability are achieved by feedback mechanisms from isolated condenser aperture drives. With FEG sources, particularly cold FEG systems, the emission behavior is notoriously unstable and a stabilizing feedback mechanism would appear to be very important even for imaging purposes.

2. On-line probe-current measurements: This requires a Faraday cup in the column below the final probe-limiting aperture. Such a measurement capability is necessary if on-line foil thickness measurements are to be achieved and a WDS is to be effectively used on an AEM.

3. Multispecimen capability: The majority of AEMs can still examine only one sample per specimen exchange, and thus require that the beam be turned off between sample viewings. If instrument development areas 1 to 3 were available and on-line thickness determination a possibility, X-ray microanalysis in the AEM could be carried out using thin-film pure-element standards in entirely the same manner as in the EPMA. Ultimately this will provide more accurate analysis than the conventional Cliff-Lorimer ratio approach.

4. High detector takeoff angle and collection angle: The detector takeoff angle is constrained owing to the confined stage region of the TEM-based system. A compromise takeoff angle of ~20° permits reasonable absorption path lengths and higher collection angles (>~0.1 sr.). With careful design, collection angles closer to 0.3 sr. should be possible when the takeoff angle is ~20°, and this aspect is most critical in the AEM where low count rate from thin samples and fine probe sizes limits the analytical sensitivity. Another approach to increasing the collection angle is to use two detectors or a WDS-EDS combination.

5. Peak-to-background and hole-count ratio: Part of the problem with confined AEM stages and very high voltage electron beams is that electron scatter and high-energy continuum X-rays within the illumination system and stage combine to excite additional X-rays from regions other than the primary excited region. One of the results of this process is to lower the P/B ratio in the X-ray spectrum. Commercial AEMs show a wide range of P/B (Williams and Steel, 1987), and considerable work is required before the stage area is shielded sufficiently to minimize extraneous radiation and to produce a maximum P/B ratio. The availability of a standard hole-count specimen will greatly help to characterize the spurious X-rays and to provide a specimen for measurement of P/B ratios.

6. Stage stability and computerized stage control: Because X-ray analysis is performed at high magnifications, small amounts of specimen drift are large enough over long time periods to be the major limitation to unattended microanalysis. Recently, in combination with digital
image-storage and image-matching programs, on-line drift correction has become available, and unattended micro-
analysis is possible (Vale and Statham, 1986). In combina-
tion with digital storage, computerized traversing, and tilting, it now becomes feasible to project that all operations currently possible on the EPMA at the micron level will soon be reproducible on the AEM at the sub-10 nm level.

7. Ultra high vacuum stage environment and sample prepara-
tion assembly: Because of the potential for surface modifi-
cation during sample preparation and analysis, it becomes more important to provide an environment in which inter-
face reactions with the atmosphere will not occur. Surface analysis equipment already contain specimen preparation chambers, and it is not too difficult to predict that these chambers will become a necessity as microanalysis moves toward one-atom detection.

**X-ray Imaging**  This aspect holds great promise for the future. The ability to store the entire EDS spectrum at each pixel in a digital STEM image removes many of the barriers to complete materials characterization. With on-line probe current measurements, high voltage FEG AEM instruments, high detector takeoff angle and collection angle and enhanced stage stability, it should be possible to take >10 hour digital scans and be able to to obtain quantitative analyses at each pixel. Such analysis capabilities are now available with the EPMA (Newbury et al., 1990). Typical storage requirements for digital spectrum imaging are in the range from 4 MB to 1 GB and require significant processing time.

**6. FUTURE DIRECTIONS IN EELS**

**Spectrometers**  The advent of parallel EELS was a major step forward, and the availability of UHV-compatible spectrometers will help in the analysis of very thin specimens in clean microscopes. Although energy resolution is excellent in comparison with EDS, it still remains well above the mil-
livolt level available in low-energy surface reflection EELS. The combining of high energy resolution with the capability to handle 300–400 keV electrons would be a big advance (Krivaneck et al., 1991). Scintillators capable of handling the intense zero-loss peak in the spectrum would avoid the cur-

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**TABLE 20.** $k_{AB}$ factor as a function of B concentration in B-N, B-Fe, and B-Nd calculated by Monte Carlo techniques for an electron beam energy of 100 keV for a 100 nm thick foil (Gauvin and L'Esperance, 1989).

**FIGURE 21.** Schematic design of a compact wavelength disper-
sive spectrometer fitted within the electron column of a Philips EM 420 AEM (Goldstein et al., 1989).
rent problem of overloading the parallel EELS diode array. Increased dispersion through more post-spectrometer lenses would be required if the energy resolution improves much beyond the current best value of ~0.2 eV (Batson, 1989). The Wien filter spectrometer remains a minor alternative to the magnetic prism spectrometer, for high energy resolution, and the Ω filter may become more popular, particularly if electron spectroscopic imaging in energy-filtered TEMs finds more applications.

**Specimen Preparation** A good thin specimen is even more critical to EELS than to X-ray microanalysis. The discussion in Section 5 on clean specimen preparation is also applicable to EELS. UHV microscopes and clean specimens will make surface EELS a powerful tool to probe the surface chemistry and bonding effects, perhaps with the same kind of energy resolution as ESCA but with a spatial resolution at the few nanometers level.

**Microanalysis** Unlike the situation with X-ray microanalysis, the spatial resolution and minimal detectability limits of EELS are not of major concern. As was already noted, the detection of single atoms is a possibility, and the limits of spatial resolution, set by the physical localization of the ionization event, are being approached in modern FEG AEMs. The future of EELS microanalysis remains with core-loss spectral quantification. In this area the fundamental limits remain our understanding of the ionization cross section and the background subtraction procedure. Substantial work needs to be done to turn the process of quantification into a “turnkey” approach, wherein the operator input to the software is minimal, as in the case of thin film X-ray microanalysis. Currently, too many variables affect the quantification, and a whole range of errors can thus creep into the quantification. The number of variables has decreased with the advent of PEELS, but the operator must still be aware of the many experimental factors such as beam convergence, the angular distribution of the loss electrons (which varies with ΔE), the importance of thin specimens and the need for deconvolution, the microscope parameters, the pros and cons of carrying out analysis in image mode or diffraction mode, the effects of chromatic and spherical aberration on the spatial localization of the spectra, all of which conspire to confound the uninitiated (Egerton 1986). The progress in digital filtering and difference spectra is a major advance but is not generally available. To condense the number of variables into a manageable software package is essential if EELS is ever going to find the general application that X-ray microanalysis enjoys, but there is no major commercial thrust in this direction.

**Fine Structure** ELNES is limited by the energy resolution of the spectrometer, but its interpretation is also limited by the lack of a complete theoretical understanding of the electronic structure interactions. ELNES is explainable by a simple model of the density of states, but is equally amenable to a model based on wave interference phenomena analogous to EXELFS. In both cases, although the energy of the fine structure modulations is well matched between theory and experiment, the intensity comparison is poor. Further theoretical work is required, along with improvement in spectral processing and thin specimen production to minimize plural-scattering effects. EXELFS has remained a laboratory curiosity for years, and despite the spatial resolution advantages it offers over synchrotron-based EXAFS, there is not a flood of new users abandoning the high intensity X-ray sources for the electron microscope. EXELFS is likely to remain this way in the near future.

**EELS Imaging** This aspect holds great promise for the future. The ability to store all the spectrum at each pixel in a digital STEM image removes many of the barriers to complete materials characterization. It is possible to analyze for all elements a posteriori, even if their presence was not suspected beforehand. Different analysis routines can be tried on the same data and the results compared. However, this approach puts the onus on the operator to select the initial image area from which all the spectral data are to be obtained. This chosen area must clearly be a critical region of the specimen and be representative of the bulk specimen both in terms of its microstructural and microchemical characteristics. Otherwise much memory and computer processing time will be wasted. Typical storage requirements for digital spectrum imaging are in the range from 4 MB to 1 GB, and processing times for specific images vary from a few minutes for a 128 × 128 pixel plasmon loss image to almost 1 hour for a Kramers-Kronig dielectric response image of 128 × 128 pixels.

7. SUMMARY

The past and present state as well as future directions of analytical electron microscopy for microchemical analysis using X-ray and electron energy loss spectroscopy (EELS) were discussed. The technique of X-ray microanalysis, using the ratio method, kAB factors and the X-ray absorption correction, was outlined. Spatial resolution and minimum detectability limits (MDL) were considered with present limitations of spatial resolution in the 2 to 3 nm range and of MDL in the 0.1 to 0.2 wt. % range when a field emission gun system is used. Future directions of X-ray analysis include improvement in X-ray spatial resolution to the 1 to 2 nm range and MDL as low as 0.01 wt. %. With these improvements the detection of single atoms in the analysis volume will be possible. Other future improvements include the use of clean room techniques for thin specimen preparation, quantification available at the 1% accuracy and precision level with light element analysis quantification available at better than the 10% accuracy and precision level, the incorporation of a compact wavelength dispersive spectrometer to improve X-ray spectral resolution, light element analysis and MDL, and instrument improvements including source stability, on-line probe current measurements, stage stability and computerized stage control.

The EELS technique has been slow to develop and still
remains firmly in research labs rather than in applications labs. Consideration of microanalysis with core-loss edges was given along with a discussion of the importance of beam convergence and specimen thickness. Spatial resolution and MDL were considered along with the recognition that single-atom detection is already possible. Plasmon loss analysis was discussed along with the use of the fine structure in the EELS spectrum. Future directions in the EELS technique include the developments of new spectrometers and improvements in thin specimen preparation. The microanalysis technique will be simplified and software will be developed so that the EELS technique approaches the relative simplicity of the X-ray technique. Finally, one can expect major improvements in EELS imaging as data storage and processing improvements occur.

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