Artifacts Encountered in Energy Dispersive X-ray Spectrometry in the Analytical Electron Microscope

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ABSTRACT

The analytical electron microscope, consisting of an energy dispersive spectrometer interfaced to a scanning transmission electron microscope, produces its own particular spectral artifacts. These artifacts are due specifically to the use of high kV electrons, and thin foil specimens. The detection of these artifacts, the identification of their source and the minimization of their effect are discussed. It is concluded that an ideal microanalytical configuration for an AEM exists and that now it is possible to reduce the effect of spectral artifacts to the level where they do not limit quantitation of the X-ray data.

1. Introduction

The interfacing of an X-ray energy dispersive spectrometer (EDS) to a scanning transmission electron microscope (STEM) is one of the principal configurations for analytical electron microscopy (AEM). Ideally in the AEM the measured characteristic X-ray intensity above background is related to the specimen composition directly through a known constant of proportionality. For this to occur the source of X-rays measured by the EDS must be the region of the specimen interacting with the primary 100 kV electron beam. This is not routinely the case in AEM where X-rays generated from other sources are often detected. This undesired signal is the major artifact in the EDS and is sometimes called the spurious X-ray signal.
These spurious X-rays are insidious because they are often part of the desired spectral information, and are thus not immediately obvious. Unless very specific precautions are taken, AEM X-ray microanalysis is not quantitative under these conditions and therefore the applications of AEM are limited.

The problem of spurious X-rays has received much attention recently.\textsuperscript{(1-2)} It appears that the spurious X-ray signal is caused by two major effects, 1) stray radiation in the AEM illumination system and 2) specimen interaction with the primary electron beam. The resultant spectral artifacts are specific to AEM because the system uses high kV electrons and the specimen is transparent to the high kV beam. These points contrast with other instruments (e.g., scanning electron microscope and electron microprobe) in which EDS is used, where bulk specimens are typically irradiated by $\leq 30$ kV electrons.

This paper summarizes the present state of knowledge and describes how the instrument-specific sources can be identified and eliminated or minimized. In the ideal configuration that concludes the paper, it is considered that AEM X-ray microanalysis using EDS can be free of quantitation-limiting spectral artifacts and that quantitation is then a straightforward process.

2. Sources of Spurious X-rays

A. Artifacts Due to Stray Radiation in the AEM Illumination System

The existence of this type of spurious X-rays is easy to determine. Figure 1a shows a typical EDS spectrum obtained in ~60 secs. from a thin Ag disc specimen in a Philips 300 TEM-STEM operated at 100 kV. Figure 1b shows a similar spectrum obtained when the primary beam was placed down a hole in the foil. Since it can be assumed that the primary beam continued
uninterrupted down the microscope, it is clear that something other than the primary beam is exciting specimen-characteristic X-rays. This and similar phenomena have been reported by many investigators and the effect ascribed to both uncollimated electrons \(^{(3-5)}\) and stray X-rays \(^{(6-8)}\). However it is possible to distinguish between the two sources because the Ag spectrum contains high and low keV X-ray lines \((K_\alpha \text{ at } 22.2 \text{ keV and } L_\beta \text{ at } 3.0 \text{ keV})\) and the relative height of the lines is a useful indicator of the source of the spurious X-rays \(^{(2)}\). By performing this type of experiment and observing the 'hole-count' spectral artifact, it is possible to identify unambiguously the sources of the spurious X-rays, from the illumination system as described below.

The use of 100 kV electrons in STEM gives rise to detected X-rays from areas other than the point of interest on the specimen principally by the following two ways, shown schematically in Figure 2:\(^1\):

1. The STEM electron optical system is not always designed to collimate the electron beam completely. In normal TEM and STEM imaging and diffraction operation, it is of little consequence if stray electrons hit the specimen and holder at distances well away from the point of interest. However this is clearly undesirable in an AEM when the EDS can detect X-rays from a wide area of the specimen chamber.

2. 100 kV electrons generate continuum (bremsstrahlung) and characteristic X-rays from various apertures as they are collimated by the illumination system. If these X-rays reach the specimen chamber, they can act as efficient sources of fluorescent X-rays from large areas of the specimen, and its surrounds.

The two problems outlined above are instrument dependent, since illumination systems differ. Therefore solutions to eliminate 'hole count'
spectra are instrument dependent. The first problem is to determine the existence of the spurious X-rays and identify their source(s). After that one can attempt to minimize the effect.

In the Ag spectrum (Fig. 1a) obtained with the primary beam incident on a thin region of the disc, it is assumed that the $L_\alpha$ to $K_\alpha$ peak height ratio is primarily characteristic of an electron-induced spectrum. Thus, observing the hole spectrum (Fig. 1b), a similar conclusion might be drawn. Thus in this instrument (a Philips EM300) some of the uncollimated electrons are not stopped by the $C_2$ aperture and are focused onto the specimen. This effect is particularly acute in that series of Philips instruments and was first determined in 1976. A simple solution to stop uncollimated electrons (which are in fact scattered around the beam defining apertures) is the insertion of a spray aperture or plug beneath the variable $C_2$ aperture. If this is done, the hole count spectrum is as shown in Figure 3. The reduction in scale (x 4) compared with Figure 1b indicates that a substantial proportion of the spurious contribution to the specimen spectrum has been eliminated.

However there is still a detectable hole count but, as shown in Figure 3, the $K_\alpha$ peak is now substantially higher than the $L_\alpha$ (compare with Figs. 1a and 1b). The remaining source of stray radiation is the hard X-rays generated in the illumination system. A simple calculation shows that even conventionally thick Pt apertures (~25 μm in the vicinity of the hole) allow through substantial fractions of the continuum X-rays generated. Figure 4 shows the calculated spectrum of continuum X-rays which would travel down the column through increasing thicknesses of a Pt aperture. Since the efficiency of X-ray fluorescence depends on the energy of the fluorescing X-rays, it is clear that the continuum X-ray intensity coming down the column
will excite the high energy Ag K$_\alpha$ line more efficiently than the low energy Ag L$_\alpha$ line. This explains the hole spectrum shown in Figure 3.

This problem of fluorescence by continuum X-rays is inherent in all AEMs, but will be reduced if thin film specimens are used, since X-ray absorption is minimized. However in metallurgical and ceramic specimens, which are usually thick discs with a central electron transparent zone, the fluorescence problem will always be significant.

Two ways to combat the fluorescence problem have been proposed. First the source may be removed by using extra thick, (9) or cylindrical (no taper) (10) apertures. Figure 5 shows a SEM image of a 200 $\mu$m thick, 20 $\mu$m wide aperture designed for this application and produced by Microengineering.* In this case the hole count is further reduced using both a spray aperture and an extra thick $C_2$ aperture by a factor of 4 as shown in Figure 6 (compare scale with Fig. 4). Extra thick apertures are now available for Philips EM300 and 400 series AEMs. The second approach to the hard X-ray problem is to insert non beam-defining apertures further down the column. (7) This has the effect of cutting down substantially on the area fluoresced. This solution is incorporated into all JEOL 100CX and 200CX 'hard X-ray kits.'

With all the modifications to the illumination system discussed above, the problems of spurious X-rays from electron and X-ray sources can be reduced to acceptable levels. Two criteria of acceptability have been defined, (2,11) but they have the same aim--i.e., to ensure that these spurious X-rays are not the limiting factor in the accuracy of X-ray quantitation. Given a reasonable microanalysis situation, if the spurious hole count for a given element is less than the continuum background generated when the beam is on the specimen, then at least the spurious contribution to

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the spectrum is of the order of the detection limit of the characteristic line of interest. For example, selecting a thin region of a specimen, such that 10,000 counts (statistically significant) can be accumulated in ~60 secs (reasonable time) with a typical probe size (70-100Å) used for microanalysis, then the characteristic X-ray hole count, using the same probe for the same time, should be less than the background for all peaks of interest in the specimen spectrum.

With the latest AEM instruments the modifications described above are currently being incorporated. However, all earlier first generation AEMs suffered from the problem of spurious X-rays induced by stray radiation and the individual user should check his instrument in the way outlined above and correct the problem accordingly.

B. Artifacts Due to Beam Interaction with the Specimen

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 transmission of high kV electrons, and also scatter electrons in both the forward and backward directions.

The sources of X-rays that can reach the EDS due to this effect are summarized in Figure 7a,b. These problems can be identified as follows.

1. Incident high kV electrons are backscattered into the microscope specimen chamber and generate X-rays from this region (e.g., cold trap, upper pole piece, EDS collimator). The possibility of direct backscatter into the EDS itself also cannot be discounted, although the strong prefieid of upper objective polepiece should prevent this.

2. Incident high kV electrons are transmitted, scattered or diffracted into the specimen chamber (or specimen support grid if it is very
close to the region of interest), and generate a) characteristic and continuum X-rays, b) backscattered electrons from e.g., lower objective polepiece, objective aperture drive.

3. Characteristic and high energy bremsstrahlung from the point of interest on the specimen fluoresce the specimen environment. This is probably the most important problem. If the specimen is a disc and is tilted to some non-horizontal angle to enable detection of the characteristic X-rays, then the possibility of self-fluorescence exists (Fig. 7a). This of course depends on the specimen shape, thickness, and microstructure, and the actual energy and intensity distribution of the bremsstrahlung X-rays. If a specimen support grid is used (Fig. 7b), then this radiation will fluoresce the grid. This probably accounts for the observation of Cu peaks in otherwise 'clean' STEM systems, when a Cu support grid is used. Figure 8 which is a spectrum from a 2000Å particle of Fe-Ni sulphide in a silicate matrix illustrates this problem. A Cu Kα peak is still clearly visible although the primary beam is confined totally within the particle and the grid bar is ≥ 200 μm away from the focused beam. The use of Be support grids will remove the Cu Kα peak in the spectrum since a) there will not be efficient fluorescence of Be, and b) Be X-rays cannot be detected by the EDS anyhow. However, even using Be support grids, there is still a danger of backscatter of scattered (diffracted) 100 kV electrons from this grid into the bulk of the specimen, if the grid is very close to the region of interest.

The minimization of problems 1 and 2 above, will again be somewhat instrument dependent. For example, the JEOL 100C generated system counts from pole pieces, anticontaminator and the guard tube in the stigmator coils. All of these contributions to the spectrum may be minimized by
suitable light element inserts which either reduce the backscatter, or produce X-rays which are not detectable. Conversely, in some instruments, no such systems peaks have been detected.

The use of thin foil specimens rather than discs may cut down the possibility of specimen self-fluorescence. Furthermore, the development of high take-off angle detectors (standard on some STEM/AEMs and being developed on others) is an essential step. Specimen interaction with its own bremsstrahlung is thus minimized. There is, however, the possibility of increased backscatter directly into the detector in this configuration, but to date, no conclusive evidence exists for this effect. The use of Be grids, when grids are necessary, is of paramount importance, but even in this case, microanalysis should be performed at least 0.1 mm away from any grid bars to minimize any backscatter of diffracted or scattered electrons. Electron backscatter and X-ray production from the lower objective polepiece can be minimized by covering it with a low Z element such as C, B, or Be. The same could be done to minimize X-ray production from the upper objective polepiece and/or anticontaminator. Taking all these points into account, an ideal microanalysis situation from the specimen chamber point of view is shown in Figure 9.

3. Summary

To the unwary operator, spectral artifacts due to spurious X-rays in EDS in the AEM can contribute significantly to errors in quantitation. The spurious X-rays unique to AEM are insidious in their effect because more often than not, the signals they generate are similar to that expected from the point of interest, although often originating from far away on the specimen. Careful operation and ideal microanalytical configurations have now been identified and it is possible to reduce spurious contributions.
to the specimen spectrum to levels at which they do not limit the accuracy of quantitation. It is considered that at this stage of development EDS in the AEM is fully quantitative and may be confidently applied to a whole range of materials problems awaiting the advent of the superior spatial resolution of this technique.

Acknowledgements

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References

5. J. C. Russ, 1977, SEM (IITRI), 1, 335.
Fig. 1a  Typical spectrum from the thin region of a Ag dıse (FS = full scale).

Fig. 1b  Spectrum obtained when the primary beam is placed down a hole in the same Ag specimen as Fig. 1a.
Fig. 2 Principal sources of spurious X-rays in the illumination system of an AEM.
Fig. 3 The hole-count spectrum obtained after the contribution of uncollimated electrons has been removed by a spray aperture. Compare the F.S. with Fig. 1b.

Fig. 4 Calculated spectrum of bremsstrahlung X-rays generated by 100 kV electrons at the final beam-defining C2 aperture. The reduction in intensity due to absorption by increasing thickness of Pt is shown as well as the relative position of the ArKα and Lα X-ray lines.
Fig. 5 SEM image of extra-thick Pt C₂ variable aperture. The aperture is cylindrical, no regions being < 200 μm thick.

Fig. 6 The hole-count spectrum obtained using both a spray aperture and extra thick C₂ aperture. There is still a small amount of Ag Kα and Lα due to residual stray radiation.
Fig. 7a Sources of spectral artifacts due to electron beam-thin disc specimen interaction in an AEM.

Fig. 7b Sources of spectral artifacts due to electron beam interaction with a thin foil specimen mounted on a support grid.
Fig. 8 Spectrum from an analysis situation as in Fig. 7b. The Cu peak due to the Cu grid bars is clearly visible.

Fig. 9 Ideal microanalytical configuration which minimizes spectral artifacts in an AEM. The configuration shown is attainable in current AEMs, and assumes that any stray radiation from the illumination system has been effectively suppressed.