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X-Ray Microanalysis in the Environmental SEM: A Challenge or a Contradiction?

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Abstract. In this paper, the application of X-ray energy dispersive spectroscopy in the environmental scanning electron microscope is reviewed. Various techniques that have been used to remove the effects of the beam spreading in the gaseous environment are discussed, specifically the pressure variation techniques and the beam-stop method. The results of the application of modified versions, developed at the University of Michigan, are also presented. It is shown that quantitative analysis in the environmental SEM, operating at 30 kV, is possible at short working distances (6 mm to 7.2 mm, gas path length 1.2 mm to 2.2 mm) in the 70 to 350 Pa range.

Key words: Environmental SEM; energy dispersive analysis; beam spreading; pressure variation in ESEM; water vapour in ESEM.

The environmental scanning electron microscope (environmental SEM) has, in recent years, proven to be a powerful tool in a large number of materials laboratories around the world. Full characterization of materials in the environmental SEM usually requires chemical analysis by X-ray energy dispersive spectroscopy (EDS), however, XEDS in the environmental SEM is not as straightforward as in the conventional SEM. Application of EDS in the environmental SEM is complicated simply by the presence of "the environment". The gas pressure in the sample chamber causes significant scattering of the primary electron beam and results in the formation of a "skirt" of electrons, the diameter of which may be many tens, or indeed hundreds, of microns [1]. This phenomenon has been well characterized by two research groups, Bolon [2] and Griffin [3]. Bolon's work revealed that 45% of the primary electron beam was scattered out to more than 25 microns from the incident beam axis when it traversed a working distance of 15 mm in 400 Pa of water vapor at an accelerating voltage of 30 kV. Griffin's work showed that, even at shorter working distances (< 10 mm) and lower chamber pressures (270 Pa), there is a large fraction of the electron beam scattered up to 400 microns from the incident beam axis. Figures 1 and 2 summarize Griffin's findings. They are plots of the intensity of the copper K peak as a function of distance as the electron beam is moved away from a pure block of copper into the Bakelite™ resin in which the copper is mounted. Figure 1 shows the effect of varying pressure at a fixed accelerating voltage of 15 kV and Fig. 2 illustrates the variation with accelerating voltage at a fixed pressure of 530 Pa. The scattering phenomenon has been labeled "beam skirting" because the electrons scattered out from the primary beam form a low profile skirt around the primary beam (see Fig. 3). The presence of the skirt obviously means that there is a significant contribution to the EDS spectrum from outside of the focus of the primary probe. The most obvious way of removing the skirt is to remove the atmosphere from the sample area, however this is not usually an option. If a sample is being examined in the environmental SEM, it is typically because a residual environment is necessary to limit damage to the sample from the vacuum. A technique must be used to correct for, or subtract, the effects of the skirt.

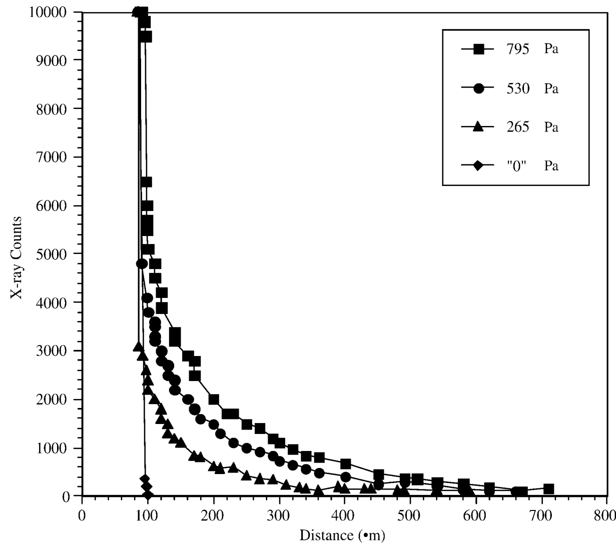

Fig. 1. Data summarised from Griffin (ref. [3]) illustrating how the intensity of the copper K peak varies as the electron beam is stepped away from a piece of pure copper into the polymer of the metallographic mount at four different pressures; 795 Pa, 530 Pa, 265 Pa and high vacuum. Accelerating voltage 15 kV

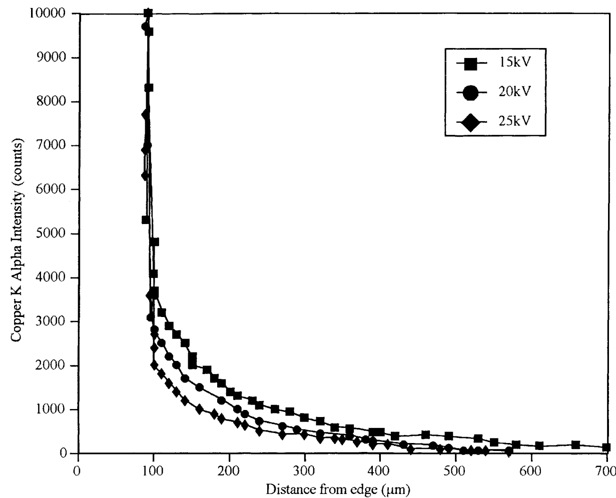

Fig. 2. Data summarised from Griffin (ref. [3]) illustrating how the intensity of the copper K peak varies as the electron beam is stepped away from a piece of pure copper into the polymer of the metallographic mount at three different accelerating voltages; 15 kV, 20 kV and 25 kV. Pressure 530 Pa

Review of Skirt Correction Techniques

There have been a number of attempts to "solve" the skirting problem. Each solution introduces added complexity to the EDS spectrum acquisition and analysis process, however, they do offer at least partial resolution of the problem. The solutions fall into two general categories, the beam-stop methods and the pressure-variation methods.

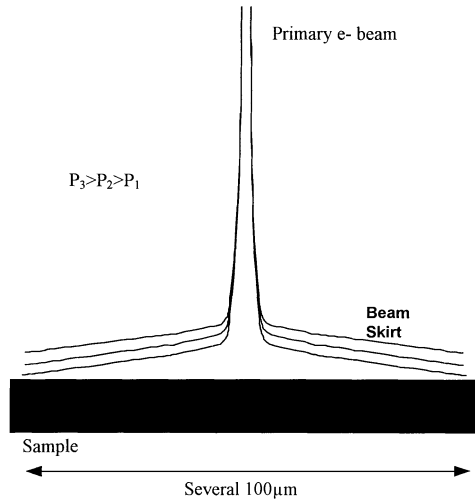

Fig. 3. Simple schematic diagram illustrating the shape of the electron beam intensity that impinges on the sample in the environmental scanning electron microscope

The Beam-Stop Method

The beam-stop method has been reported most extensively by the group from Risø National Laboratory in Roskilde, Denmark [4–8]. The beam-stop is a fine needle of a known element that is not present in the sample. This needle is inserted into the electron beam path by a micromanipulator so as to shadow the area of the sample that is under analysis (see Fig. 4). An X-ray spectrum is recorded with the beam stop in place. This X-ray spectrum contains the peaks from the needle (typically tungsten or platinum) plus the signal generated from the sample areas irradiated by the electron skirt. The beam stop is then removed and

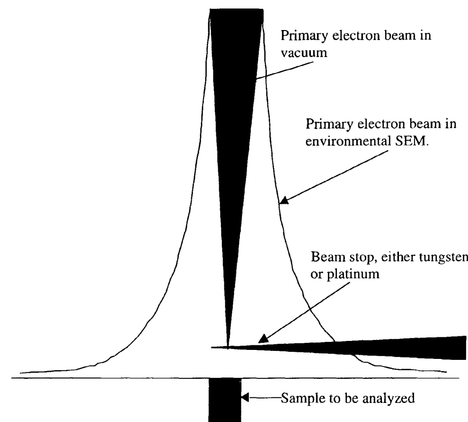

Fig. 4. Schematic diagram of the beam stop system for EDS acquisition in the environmental scanning electron microscope

a second spectrum is acquired. This spectrum contains signal from both the area of interest and the skirt. The characteristic peaks from the needle are stripped from the first spectrum and then that modified spectrum is subtracted from the second spectrum ostensibly to obtain the spectrum of the area of interest alone. It is interesting to note that the subtraction is often not perfect. Bilde-Sorensen and Appel [7] tested the beam-stop technique on a sample of cerium oxide that contained small islands of platinum. They attempted to recover a pure cerium oxide spectrum. The beam-stop in this experiment was tungsten. After processing their "pure" cerium oxide spectrum still contained a platinum peak that was a significant fraction of the intensity of the cerium peak ($\sim 14\%$). Since quantitative analysis of oxygen is difficult in EDS, and almost impossible when it is closely associated with comparatively heavy rare earth elements, Bilde-Sorensen and Appel did not attempt to retrieve the composition of the cerium oxide from their data.

One possible cause for the residual platinum signal is the Bremsstrahlung present in the spectrum recorded from the needle/beam-stop. The Bremsstrahlung signal is heavily atomic number dependent. Although cerium is in the same row of the periodic table as tungsten, the density of tungsten ($19.25\,\mathrm{g/cm^3}$) is over three times that of cerium oxide. The Bremsstrahlung background peaks in the region of the spectrum where the tungsten and platinum M peaks occur and it appears that subtraction of the tungsten peaks, without careful and precise subtraction of the Bremsstrahlung intensity could result in extra spurious intensity left in the platinum M peak.

A variation of the beam-stop method has also been discussed in the reports by the Risø group. In this version, a sheet of aluminum foil is placed over the sample immediately adjacent to the area to be analyzed. Spectra are recorded from the area of interest and from the aluminum foil. It is assumed that the skirt signal from the aluminum foil spectrum is essentially identical to that of the area of interest. The aluminum peaks are subtracted from the first spectrum and the resulting spectrum is subtracted from the spectrum of the area of interest. The final spectrum is taken to be from the area of interest alone. Bilde-Sorensen and Appel's [8] reported data does, however, show that the subtraction is less than complete, between 10% and 20% of the original aluminum K intensity is still visible in the final spectra. Again, it seems likely that this is a Bremsstrahlung/atomic number effect.

The Pressure-Variation Method

Eric Doehne, of the Getty Conservation Institute, has implemented a pressure-variation technique. Doehne records two spectra at different pressures, subtracts them and uses the difference spectrum to calculate peak intensities in the "zero-pressure" regime [9, 10]. The exact procedure that Doehne uses is as follows: a spectrum (A) is acquired under conditions of high pressure (1070 Pa, for example). Another spectrum (B) is acquired under identical conditions, except at a lower pressure (say, 530 Pa). The difference between the two spectra gives information on how the lowering of the pressure reduces the number of X-rays generated by the skirt. Doehne then approximates spectrum C, the spectrum at zero pressure, as:

$$C = B - ((A - B) * D) \tag{1}$$

This expression assumes that the pressure for A is greater than the pressure for B and the changes in the shape of the electron skirt with pressure are less important than the changes in intensity [11]. D is an empirical adjustment factor that is used to correct significant changes in the background shape that may occur when ($A-B$) is subtracted from B.

In the Risø Laboratories in Denmark, Bilde-Sørensen and Appel have also described a pressure-variation technique [4, 5, 7, 8]. They, too, seek to work in the single scattering regime where the shape of the electron skirt is independent of pressure and varies only in intensity [12, 13]. Thus, in the single scattering regime, it can be assumed that each point excited by the electron skirt emits an X-ray signal proportional to the intensity of the skirt. Bilde-Sørensen and Appel then note Danilatos' expression for the fraction of scattered electrons as a function of pressure [14]:

$$\frac{I}{I_0} = \exp\left(\frac{-p\sigma L}{kT}\right) \tag{2}$$

where I/I_0 is the fraction of unscattered electrons, p is the pressure, σ is the scattering cross section for electrons in the gas, L is the path length from the pressure-limiting aperture to the sample surface, k is the Boltzmann constant and T is the absolute temperature. They use Eq. (2) together with the notion that the total X-ray count may be written as the sum of the count from unscattered electrons and the count from the scattered electrons to write:

$$\begin{aligned} C_{\text{total}} &= C_{\text{unscattered}} + C_{\text{scattered}} \\ &= C_0 \cdot \exp(-pN) + C_1 \cdot (1 - \exp(-pN)) \end{aligned} \tag{3}$$

where C_{total} is the total X-ray count, $C_{unscattered}$ is the X-ray count from the unscattered portion of the beam, $C_{scattered}$ is the X-ray count from the beam skirt, C_0 is the X-ray count that would be obtained if there was no scattering of the primary electrons (i.e. the zero pressure regime), C_1 is the count X-ray count that would be obtained if each electron were scattered once and $N = \sigma L/kT$. Equation (3) may be rewritten as:

$$C_{total} = (C_0 - C_1) \cdot \exp(-pN) + C_1 \qquad (4)$$

Bilde-Sørensen and Appel stated that this equation is of the form $y = ax + b$, the equation of a straight line. They then determined that, for a plot of the intensity of an X-ray peak as a function of pressure, they could perform a simple linear regression to extrapolate the peak intensity at zero pressure. They tested their hypothesis with pure elements. The electron beam was placed on a piece of pure nickel 10 μm from the interface with a piece of pure copper. Analysis revealed that the intensity of the copper peak extrapolated to within one standard deviation of zero counts at zero pressure.

Closer examination of Eq. (4) actually reveals that the function is not linear. It may be reduced to a linear approximation if the gas pressure is indeed low enough that the exponential part of Eq. (4) can be expanded as a series and terms in p^2 or higher ignored, then Eq. (4) may be rewritten:

$$C_{total} = (C_0 - C_1)(1 - Np) + C_{1(5)} \qquad (5)$$

which may be written:

$$C_{total} = -(C_0 + C_1)Np + C_0 \qquad (6)$$

A plot of the total X-ray count for a given X-ray line as a function of pressure should yield a straight line with an intercept that equals C_0, the total X-ray count at zero pressure.

The beam-stop method and the two pressure-variation techniques are attractive possibilities for the extraction of quantitative intensity information from environmental SEM XEDS data however, there is still obviously some uncertainty in their application. Therefore, a series of experiments were performed in the ElectroScan E3 environmental SEM located in the University of Michigan Electron Microbeam Analysis Laboratory (EMAL). These experiments were designed to determine:

1. Which, if any, of these skirt correction techniques provide the most reliable EDS data in the environmental SEM, and
2. the optimum range of pressures, working distances, and accelerating voltages, at which they should be applied.

Experimental Procedures and Results

Two series of measurements were performed. One series involved a modified version of the beam-stop method and the second tested the pressure variation method.

Beam-Stop Experiment

For the beam-stop experiment, a sample was fabricated that consisted of a small piece of gallium phosphide cemented with carbon paint into a small hole drilled in a 1 cm diameter copper disc. Gallium phosphide was chosen because it was available in small flakes with a purity of 99.999%, a high stoichiometry, and little or no tendency to decompose or change composition under the electron beam. To test the stability of gallium phosphide under electron irradiation, a sample was exposed to a 30 kV beam in the Philips XL30FEG SEM that is located in EMAL for a period of approximately 30 min. EDS spectra were recorded in two-minute increments and the ratio of the Ga K intensity versus the P K intensity monitored as a function of time. There was no detectable change in the intensity ratio for the duration of the exposure.

In order to eliminate the need for removing the characteristic X-ray peaks of the beam-stop from the EDS spectra, a beryllium beam-stop was chosen. The EDS detector mounted on the E3 ESEM is a UTW Noran model 931C-3SSS. The Norvar window on the front of the detector is slightly thicker than would be found in a conventional SEM to minimize the transport of water vapor into the detector area and therefore the ice formation on the detector. Consequently, it is impossible for the detector to detect the beryllium peak. There is no micromanipulator system fitted to the EMAL ESEM and so the beam-stop was mounted onto the sample by the careful cementing of a 50 μm beryllium wire directly on top of the GaP/Cu sample with carbon paint. A SEM image schematic illustrating how the beam-stop was attached to the manufactured composite sample is shown in Fig. 5. Note that the beam-stop does

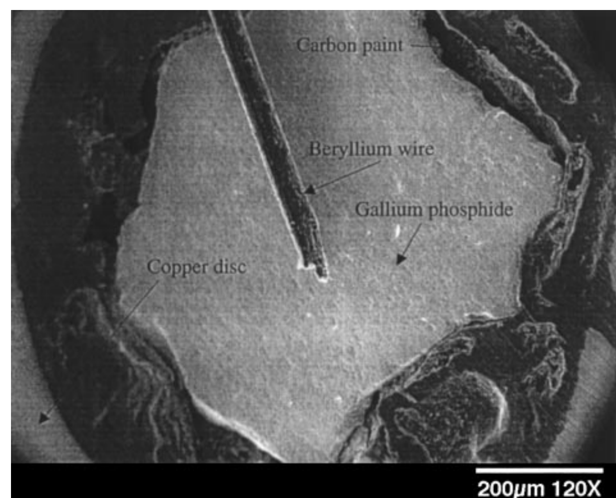

Fig. 5. Micrograph of beryllium beam stop inserted over the test sample of a flake of gallium phosphide cemented into a copper disc

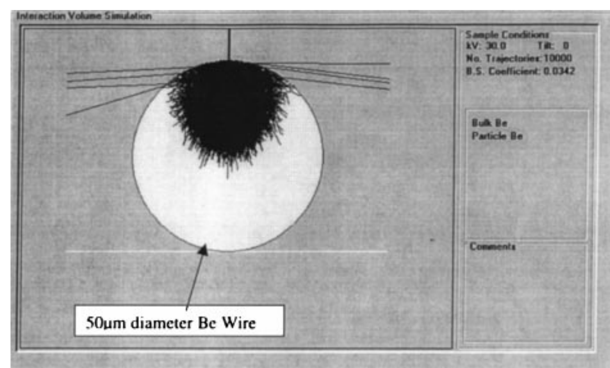

Fig. 6. Electron Flight Simulator Monte Carlo simulation of a 30 kV electron beam impinging on a 50 µm beryllium wire. Note that the beam is entirely absorbed by the wire and the backscatter coefficient is very low

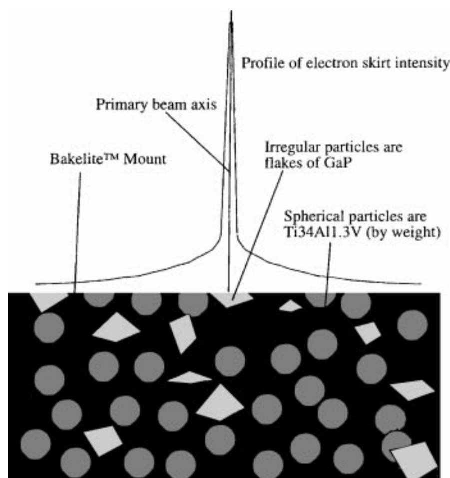

Fig. 7. Schematic diagram of the manufactured composite sample of GaP flakes and TiAlV spheres

not completely cover the GaP flake, since this is not necessary, it only needs to stop the primary beam from exciting the sample. To ensure that 50 µm of beryllium was sufficient to completely stop the electron beam Monte Carlo simulations were performed with *Electron Flight Simulator* [15] (see Fig. 6).

The EDS acquisition system consisted of the Noran detector and a Noran preamplifier and pulse processor, a 4Pi Analysis Spectral Engine II installed in an Apple Power Macintosh 7200/90. The XEDS spectra were recorded with the NIST acquisition program DTSA. The detector is one of the original ESEM configurations and it has a negative take-off angle. The sample must be tilted to at least 35° to ensure reliable collection of the X-ray signal and an unobstructed path for the X-rays from the sample to the detector.

The electron beam was focussed on the middle of the beryllium wire approximately 60 µm from the end of the wire and a series of 100 s acquisitions were recorded at pressures of 800, 530 and 270 Pa. Three spectra were recorded at each pressure. The microscope was then vented to atmosphere and the beryllium wire removed and the series of acquisitions was repeated at the same pressures.

The spectra with the beryllium wire in place were assumed to be the "skirt only" spectra and those without the wire were deemed to be "skirt + sample". To recover the "sample only" spectra, the spectra with the wire were subtracted from the spectra without the wire. The spectra were scaled before the subtractions. The Bremsstrahlung background in the area above the P K peak was used for this scaling to ensure that subtraction would result in positive counts in the peaks of interest. The results were totally inconclusive. Of the twelve sets of data only three resulted in data that had positive counts in the gallium and phosphorus K and gallium L peaks.

Pressure-Variation Experiment

For the pressure-variation experiments, a variation of the gallium phosphide sample was used. Pieces of the gallium phosphide were ground in a mortar and pestle into approximately 5–20 µm pieces. These pieces were mixed with powdered spherical particles of an alloy of aluminum Al-34%Ti-1.3%V. This mixture was then mixed with Bakelite™ resin and cast into a metallographic mount and is illustrated in the schematic diagram in Fig. 7. The sample hence consisted of a crude composite of gallium phosphide, the alloy and the Bakelite™. The alloy and the gallium phosphide components

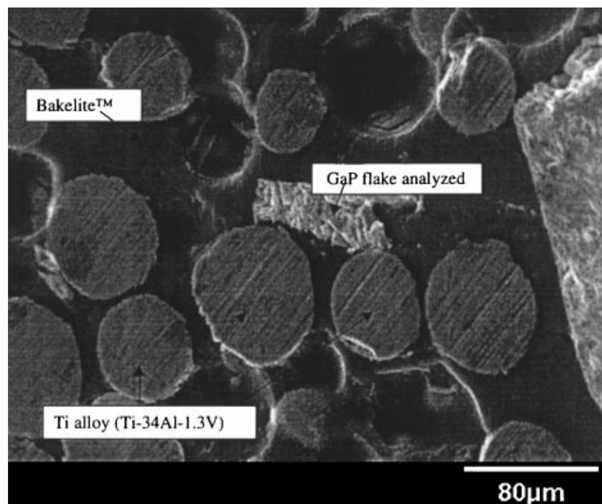

Fig. 8. Micrograph of manufactured composite sample of GaP and Ti-34Al-1.3V

were of known stoichiometry. The sample was mounted in the ESEM and again tilted to 35° towards the X-ray detector.

A large 20 µm particle of gallium phosphide was chosen for the pressure variation acquisitions (see Fig. 8). A series of spectra were recorded at 70 Pa intervals from 70 Pa to 400 Pa. These series were repeated at three working distances, 6.4 mm, 6.7 mm and 7.2 mm. Because the ESEM in question operates with an Environmental Secondary Detector, which extends 5 mm into the chamber, these working distances reflect true gas path lengths of 1.4 mm, 1.7 mm and 2.2 mm respectively. For each working distance a spectrum was also recorded in high vacuum mode at otherwise identical operating conditions for reference.

The background was subtracted from the pressure series spectra and the intensity of the phosphorus K peak and gallium K alpha peak were plotted as a function of pressure (Fig. 9). A straight line was fitted through the data for each element and extrapolated back to zero pressure. The results are shown in Table 1.

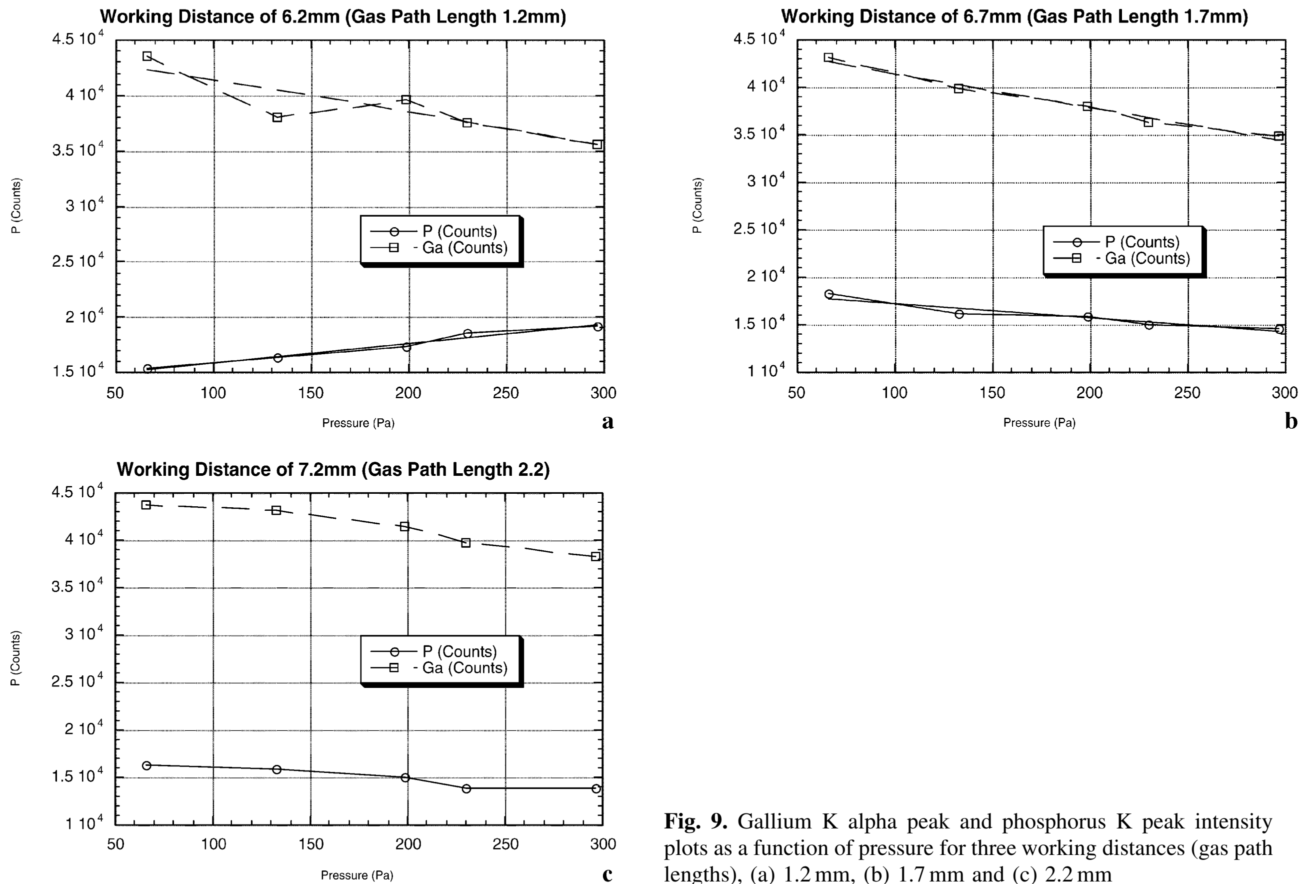

Fig. 9. Gallium K alpha peak and phosphorus K peak intensity plots as a function of pressure for three working distances (gas path lengths), (a) 1.2 mm, (b) 1.7 mm and (c) 2.2 mm

Table 1. Ratios of the intercepts of the P X-ray intensity and Ga X-ray intensity versus pressure plots at three working distances (gas path lengths) as compared to the same intensity ratios for high vacuum

Intercept ratios from pressure series	
Working distance/gas path length	P intensity/Ga intensity
6.2 mm/1.2 mm	0.33 ± 0.05
6.7 mm/1.7 mm	0.38 ± 0.04
7.2 mm/2.2 mm	0.36 ± 0.02
Ratios for zero pressure	
Working distance	P intensity/Ga intensity
6.2 mm	0.33 ± 0.05
6.7 mm	0.34 ± 0.05
7.2 mm	0.35 ± 0.05

Discussion and Conclusions

Beam-Stop Experiment

The beam-stop method for acquiring a ‘‘skirt-only’’ spectrum is an attractive possibility for performing X-ray analysis in the environmental SEM, particularly if the instrument is equipped with a micromanipulator. In addition, the use of a beryllium beam-stop would mean that the characteristic lines of the beam-stop would not appear in the skirt-only spectra and therefore would simplify the spectral processing. However, the results obtained to date are not readily explainable. Negative intensities resulted in the gallium K and L peaks and in the phosphorus K peaks when the skirt-only spectra were subtracted from the skirt + sample spectra. This implies that the intensity of the gallium and phosphorus peaks was greater when the beam was not focussed on the sample. This clearly is not a sensible result and further work is in progress to determine if the effect is indeed real or whether it is simply the result of some large systematic error that has been introduced inadvertently.

Pressure-Variation Method

The results of the pressure-variation studies are encouraging. There is good agreement between the intensity ratios for the gallium phosphide spectra

obtained by zero pressure extrapolation and those obtained in high vacuum mode. Theory shows that the characteristic X-ray intensity plotted as a function of pressure should be an inverse exponential function Eq. (4). However, analysis at relatively low pressures (70 to 330 Pa), high accelerating voltage (30 kV) and short gas path length (1.4 to 2.2 mm) allows the approximation of that part of the inverse exponential function to a straight line Eq. (6).

Quantitative analysis should therefore be possible in the environmental SEM under these conditions. Newer models of the Philips XL30 environmental SEM are optimized to record X-ray spectra at these short gas path lengths and it may be possible to incorporate pressure correction algorithms into the X-ray data acquisition software for these instruments [16]. Further studies are under way to extend the working pressure to greater than 330 Pa and to work at lower accelerating voltages.

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