# Lecture

## Practical Aspects of Charge Compensation in X-ray Photoelectron Spectroscopy

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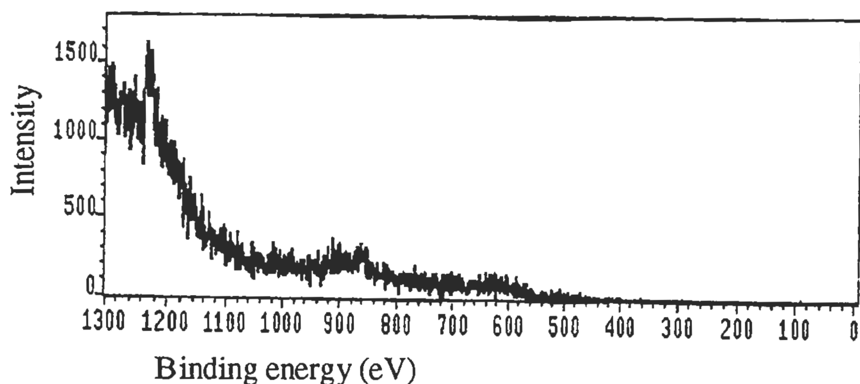
Obtaining reliable chemical information from insulating samples requires effective charge compensation. The development of a positive surface charge on insulating samples can lead to distorted peak shapes and significant shifts in binding energy. The problem is particularly critical when a monochromatic x-ray source is used. Current methods of charge compensation are discussed, and high energy resolution data presented. The problems which can result from differential charging are shown using a variety of samples. Sample mounting and x-ray flux contributions to differential charging problems are emphasized.

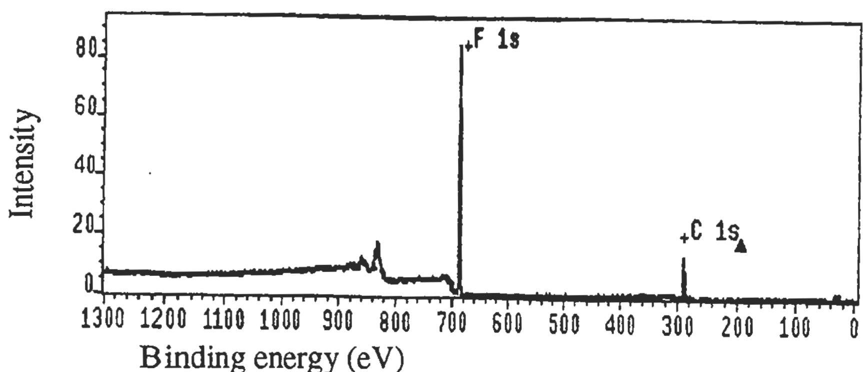
### Introduction

The ability to obtain chemical, in addition to elemental, information is one of the most powerful aspects of XPS analyses. The continuing development of XPS instrumentation has enhanced the analysts' ability to acquire interpretable chemical data from samples of increasing complexity. Recent improvements include stable, high intensity monochromatic x-ray sources, enhanced collection optics, and multichannel detection systems. This combination decreases data acquisition times, which can help to minimize damage in susceptible samples. The ability to routinely acquire small area spectra and photoelectron images has seen dramatic developments in the last five years as well. Along with these developments, come increasing demands for analysis of multicomponent or multilayered samples with ever-decreasing feature sizes.

In routine applications, a successful surface chemical analysis by XPS requires the establishment of a uniform potential within the analysis volume. For conducting samples, this requirement is met by placing the samples in electrical contact with the spectrometer. Samples containing insulating, or isolated conducting regions, will develop a potential gradient across the surface during the analysis if no method of charge compensation is utilized, resulting in a positive surface potential. [1] A method of charge compensation is generally required for the analysis of samples such as glasses, ceramics and polymers. In the most severe cases, no peaks are observed when insulators are analyzed using a monochromatic source. Figures 1a and 1b compare the spectrum observed when a thick PTFE sample is analyzed using a monochromatic x-ray source with, and without, charge compensation. In less extreme cases, differential charging may still be observed. This may be the case for semiconductors, samples that are improperly mounted or when insufficient charge compensation is provided.




a) PTFE survey spectrum acquired with no charge compensation




(b) PTFE with charge compensation

Figure 1: Analysis of PTFE using a monochromatic x-ray source

**Experimental**

The data shown was acquired on either a modified Kratos AXIS HS or a Kratos AXIS Ultra photoelectron spectrometer. Unless otherwise specified, a monochromatic Al K$\alpha$ source operated at 300 W was utilized.

Charge compensation for both imaging and spectroscopy was accomplished using low energy (~2 eV) electrons. Standard conditions were filament current of 2.1A, -1.0 filament voltage and -2.8 eV bias voltage. The operation of the charge compensation system is described within this article. Data demonstrating possible problems with charge compensation was acquired either with the charge compensation off, or by changing the bias voltage. The standard conditions were used for all spectra showing proper charge compensation.

## Methods of Charge Compensation

A variety of methods have been utilized for charge compensation on insulating samples. The most common methods are based upon the use of a low energy electron gun. The ideal system should provide:

- A source of low energy electrons in order to minimize sample damage
- A method for directing the electrons to the sample
- A high flux of electrons to provide a uniform charge density
- Turn-key operation (minimal or no adjustments by the operator when changing samples or analysis conditions)
- Charge compensation on rough surfaces and tilted samples

Charging problems are particularly severe when a monochromatic x-ray source is used, and effective charge compensation using only an electron gun is difficult to accomplish. Early work on the acquisition of high energy resolution spectra from polymers used a screen or mesh above the sample to control the potential development. This method has been shown to produce very good results[2], although it can complicate sample mounting.

Two relatively recent developments have improved charge compensation and come close to meeting the above requirements. One method is based upon directing low energy electrons from both the sample and a heated filament back down to the sample by utilizing the magnetic field from the magnetic immersion lens. In this case the neutralizer system consists of a heated filament, a charge balance plate, and a pair of plates to produce the transverse electric field, as shown in Figure 2. The dashed lines represent the diverging magnetic field from the magnetic lens. Photoelectrons to be analyzed are focused into the optical column, following the paths shown. A heated filament is used to provide a source of low energy electrons. The electron trajectory is shown in Figure 2; the combination of electron and magnetic field lines allows electrons to drift across the magnetic field lines. Low energy electrons can then be repelled down the magnetic field towards the sample by the charge balance plate. If the sample is charged more positive than the source potential, the electron will hit the sample and lower the surface charge. Electrons not accepted by the sample are trapped in the magnetic field and oscillate up and down the magnetic field until a part of the sample is charged positively enough to accept them. This design produces a self-compensating system since there are more trapped electrons than surface charges generated by the x-ray beam.

C 1s spectra from poly(methyl methacrylate) (PMMA) are shown in Figure 3. The two spectra were acquired sequentially, using 150 and 300 W on the monochromatic x-ray source. There was no time delay between the acquisitions, and no adjustments to the charge compensation system were made. The spectra have not been charge-corrected and

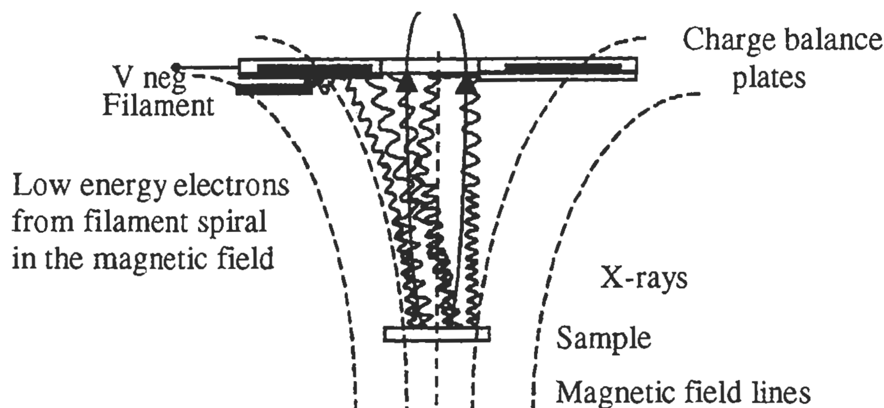
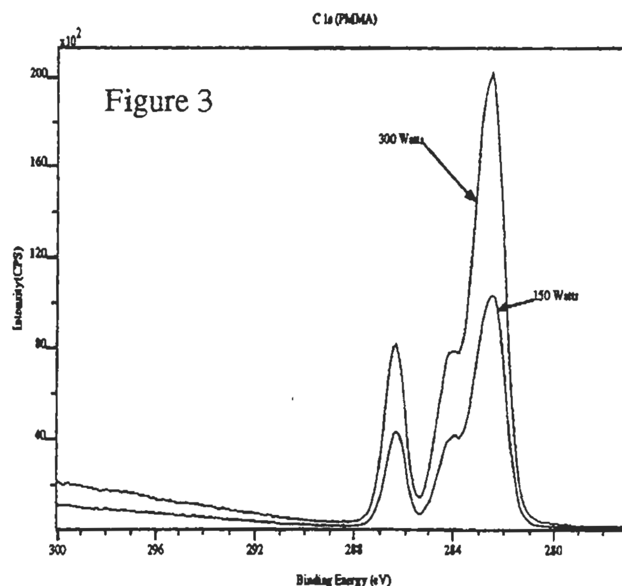



Figure 2: Charge compensation in the Kratos AXIS instruments utilizes a low energy source of electrons and the magnetic immersion lens.

show the ~ 2 eV shift to lower binding energy which is typical for this charge compensation method. The peak shapes and position are comparable, demonstrating that the system responds rapidly to changes in surface charge. As an additional example, Table 1 lists the FWHM of the O-C=O peak in poly(ethylene terpthalate), PET. This peak is routinely used to evaluate the performance of charge compensations systems. The values of ~ 0.68 eV compare favorably with the value of 0.85 eV reported by Beamson and Briggs[3] and 0.80 eV reported by Bryson.[1] The decrease in FWHM is a result of the improved charge compensation provided by the incorporation of the magnetic lens. Table 2 shows only a small decrease in the FWHM as smaller analysis areas are utilized.

Table 2: FWHM of C=O in PET C 1s Spectrum using Kratos AXIS Ultra

| Analysis Area (μm's) | O-C=O FWHM (eV) |
|---|---|
| 27 | 0.678 |
| 55 | 0.686 |
| 110 | 0.684 |
| 700x350 | 0.718 |
| | |
| Beamson and Briggs[2] | 0.85 |




Effective charge compensation is important for not only high energy resolution spectroscopy, but also for small area spectroscopy, angle-resolved XPS (ARXPS) and

imaging. If differential charging occurs across the irradiated area, changes in peak position due to charging can be misinterpreted as changes in composition in photoelectron images or spectra. Maintaining charge compensation as a sample is tilted can be difficult, since the x-ray flux and distribution change. In some configurations, the angle at which the low energy electrons are hitting the sample will also be affected. Table 3 lists the FWHM of the C 1s peak from PTFE as a function of angle. There is minimal broadening from differential charging. It is now possible to easily acquire spectra from insulating samples even at very shallow take-off angles.

Table 3: C 1s FWHM in PTFE

| Take-off Angle (degrees) | C 1s FWHM (eV) |
|---|---|
| 90 | 0.812 |
| 50 | 0.818 |
| 30 | 0.836 |
| 15 | 0.841 |

Promising results have also been reported using a charge compensation system consisting of a source of low energy Ar ions in combination with an electron gun. [4] The electron gun has a decreased electron energy spread as compared to conventional sources. The developers of this approach report that the energy spread of the electrons from the flood gun can create a negative surface charge, which repels electrons.[4] A low current of low energy positive ions is thus used simultaneously with a source of low energy electrons to improve charge compensation in this system. A FWHM of 0.76 eV from the O=C-O peak of PET has been reported using a 100 x 800 μm analysis area.

## Differential Charging Effects

The development of surface charge can have a number of effects on the data including

- shifts in binding energy ranging from tenths to ten's of eV
- distortions in photopeak shape
- changes in image intensity

The spectra and tables above show results which can be achieved when charge compensation methods work. It is worth discussing artifacts which are observed when charge compensation is not effective. This discussion will also highlight practical aspects that must be considered in the analysis of insulators.

*Horizontal Differential Charging*

Non-uniform x-ray flux over the analysis area can result in horizontal differential charging. With monochromatic sources, the surface area analyzed can be comparable to the area irradiated by the x-ray beam. Less charging will occur in areas receiving lower x-ray flux. Photoelectrons ejected from areas of lower x-ray flux will appear at a lower binding energy than those ejected from areas of higher x-ray flux. Figure 4 shows a large area Si 2p spectrum from an insulating silica glass, acquired using a monochromatic x-ray source and no charge-compensation. The peak is shifted in binding energy by approximately 100 eV and is broadened on the low binding energy side of the peak. This tailing on the low binding energy side of the peak results from horizontal differential charging.[5] The small area spectra shown in Figure 4 were acquired from areas with high, intermediate and low x-ray flux. The large area spectrum can be viewed as the sum of small area spectra which have been shifted differing amounts.

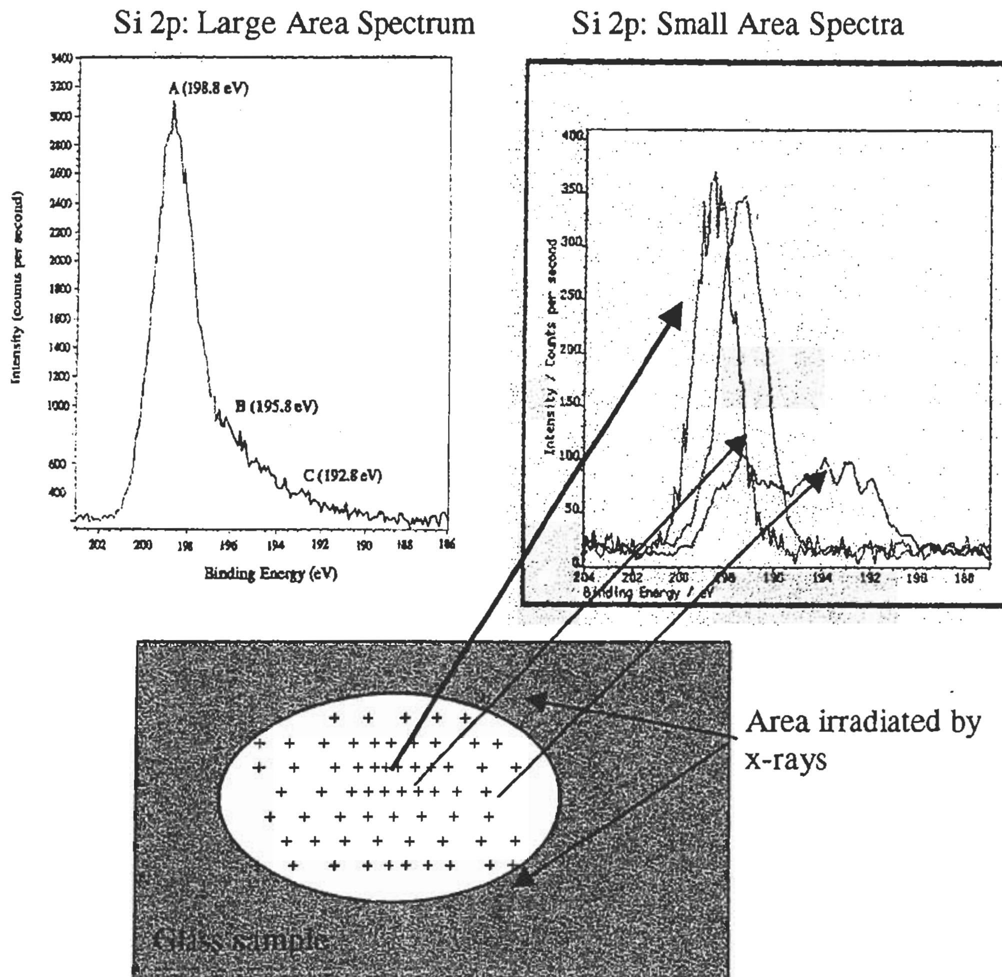
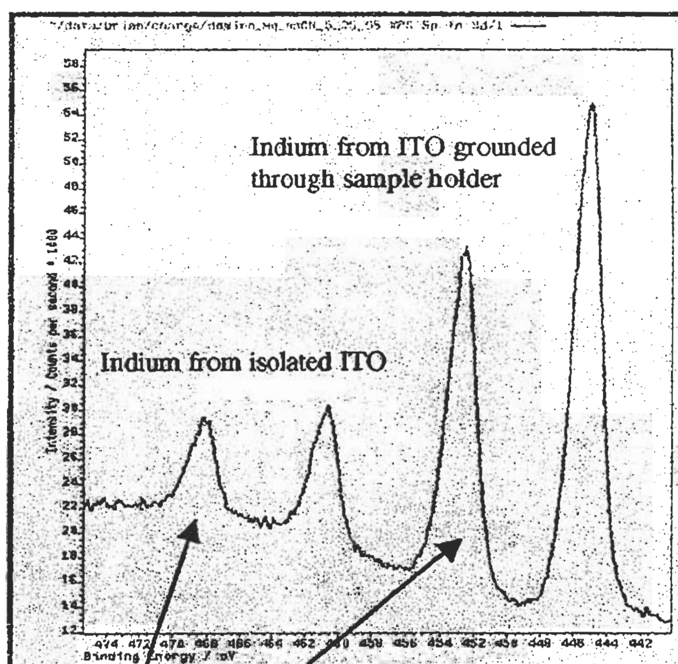



Figure 4: Horizontal differential charging is observed on bulk insulators in the absence of charge compensation. Variations in x-ray flux result in a non-uniform surface potential, causing photopeak broadening towards low binding energies. Small area spectra demonstrate the variation in binding energies observed.

Horizontal differential charging will also result if the charge compensation is not uniform over the analysis area, or if the sample holder is contributing to charge compensation. Areas of an insulating sample in contact with the sample holder may charge less than other regions on the sample. X-rays striking the sample holder can produce electrons, which contribute to charge compensation in the area immediately adjacent to the sample holder. This should be considered in the analysis of heterogeneous samples, which may contain both insulating and conducting components. The acquisition of small area spectra can help distinguish between chemical variations on a sample surface and horizontal differential charging effects. These effects will be much less noticeable with achromatic x-ray sources, which generally irradiate a much larger area than is analyzed.

*Vertical Charging and Substrate Effects*

Vertical charging refers to charging with depth into the sample, rather than across the sample surface. Although horizontal differential charging is the most significant mechanism in the analysis of bulk insulators, vertical differential charging and related substrate effects can be significant for layered samples or samples containing patchy overlayers. [6] There are numerous examples of vertical charging effects in the literature. Conducting substrates can act as a ground for the sample, and several groups have reported charging effects in the analysis of insulating overlayers on conducting substrates.[7,8] Results for samples containing overlayers can be strongly dependent upon sample mounting conditions. If care is not taken, it is possible to have a sample only partially grounded, resulting in unpredictable binding energy shifts.[9] Charging in heterogeneous samples may depend upon the conductivity of the substrate from point-to-point within the sample. Figure 5 shows In 3d spectra acquired from indium tin oxide (ITO) deposited on an insulating glass. The sample was mounted so that some of the ITO was isolated from the spectrometer, as shown. With no charge compensation, two different sets of In 3d spectra are observed.



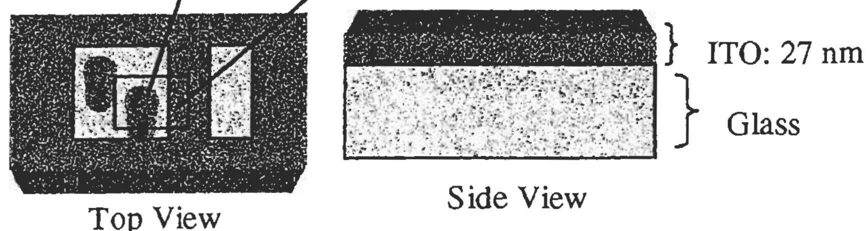




Figure 5: Substrate conductivity will affect charging of the overlayer.

The photoelectron emission from substrates can contribute to both charge compensation and sample damage. Beamson and Briggs have recently shown that PVA films degraded more rapidly when thin layers were deposited on substrates with high photoelectron and secondary electron yields.[10] The author has acquired photoelectron images from polymer overlayers which are charge-shifted different amounts, and correlated these changes with substrate conductivity variations.[11] If differential charging problems are suspected, it can be useful to repeat the analysis with the sample completely isolated from the spectrometer. This can be accomplished by mounting the sample on double-sided tape or teflon, or by floating the sample stage.

*Photopeak Shape*

Less severe effects than those shown in Figures 4 and 5 will frequently be observed in the presence of insufficient charge compensation. Figure 6 shows several C 1s spectra from PET, with dramatically varying photopeak shapes. It is important to notice that the peaks are shifted down in binding energy by approximately the same amount as the properly charge-compensated spectra (also shown in Figure 6). Binding

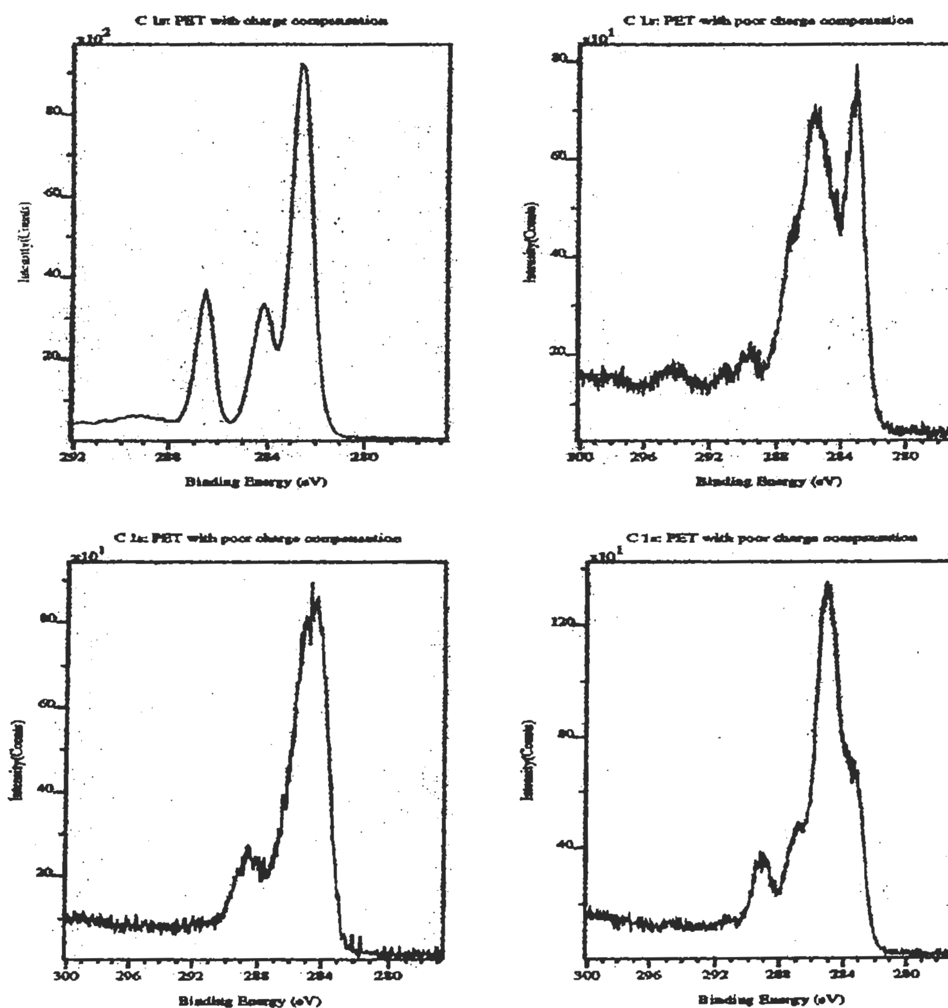


Figure 6: C 1s from PET with effective (top left) and poor charge compensation.

energy alone is not an adequate indicator of charge compensation. The most effective charge compensation systems overcompensate, shifting peaks to lower binding energy.

*Binding Energy Shifts*

In the presence of insufficient charge compensation, photopeaks may be shifted to higher binding energies. Alternatively, the most successful charge compensation methods result in photopeaks which are 2-6 eV lower in binding energy than expected. Binding energy referencing is required in either case. It is important to realize that multiple reference points may be required in heterogeneous samples, particularly if adventitious carbon is used as a reference.

## Conclusions

The analysis of insulating samples requires effective charge compensation and attention to sample mounting. Horizontal differential charging is important in bulk insulators. Vertical differential charging must be considered in the analysis of heterogeneous or layered samples. If differential charging effects are suspected, the analyst should vary experimental parameters and carefully evaluate any changes in the spectra. Parameters to consider varying include charge compensation conditions, x-ray flux, and the size and location of the area analyzed. It may be helpful to try isolating the sample from the sample stage (or isolating the sample stage) in order to obtain a uniform surface potential in heterogeneous or multilayer samples. Small area spectra or images can also provide insight into suspected charging phenomena.

## Acknowledgements

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