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XPS Guide: Charge neutralization and binding energy referencing for insulating samples

Running title: Guide to Charge Compensation in XPS

Running Authors: Baer et al.

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This guide deals with methods to control surface charging during XPS analysis of insulating samples and approaches to extracting useful binding energy information. The guide summarizes the causes of surface charging, how to recognize when it occurs, approaches to minimize charge buildup, and methods used to adjust or correct XPS photoelectron binding energies when charge control systems are used. There are multiple ways to control surface charge buildup during XPS measurements and examples of systems on advanced XPS instruments are described. There is no single, simple, and foolproof way to extract binding energies on insulating material, but advantages and limitations of several approaches are described. Because of the variety of approaches and limitations of each it is critical for researchers to accurately describe the procedures that have been applied in research reports and publications.

I. INTRODUCTION

XPS spectra collected from insulating materials or materials electrically isolated from the spectrometer differ in two ways from those collected on conducting materials connected to the spectrometer: i) surface charge buildup - there is a buildup of positive charge at and near a sample surface due to the emission of electrons. This charge buildup is not necessarily uniform and shifts the energy of photoelectrons emitted from the sample and frequently distorts peak shape; ii) vacuum level versus Fermi level referencing – even if there was no positive charge buildup, the Fermi level referencing that works for conductors and simplifies accurate photoelectron binding energy (BE) determination no longer applies. While the energies of the photoelectron peaks from conducting samples can be referenced to the Fermi level of the spectrometer and independent of the sample work function, for sample surfaces electrically isolated from the spectrometer the sample and spectrometer can be referenced with respect to their vacuum level (see vacuum level referencing ISO 18115-1 2013 definition 4.483). Charge accumulation and dipole layer formation near interfaces involving non-conducting or semiconducting phases near a surface can further complicate BE measurements. The impact of these differences is that in addition to chemically induced BE variations, measured energies of photoelectron peaks can be influenced by several factors including differences in the spectrometer and sample work functions, charge accumulation at interfaces, and surface charge accumulation.[1] The latter two behaviors depend on sample properties such as structure and quality, including surface cleanliness, phases present and preferred crystalline orientations all of which complicate the referencing problem.

As a consequence of these issues, XPS measurements on insulators require two actions: i) efforts to minimize impact of sample charging (buildup of surface potential) during data acquisition to enable photoelectron lines to appear nearly at the expected binding energy without sample damage or peak distortion and ii) applying a post-acquisition method to consistently adjust the peak position to an appropriate or useful value. Variations of BE data stored in various collections of XPS BE[2, 3] are impacted by the BE referencing approach used for insulating samples as well as issues related to sample quality and instrument calibration and stability.[3] Unfortunately, as discussed in section III, there is no simple fundamentally correct method to precisely adjust peak positions for insulating materials.

Charge buildup during XPS analysis is a well-studied phenomenon.[4, 5] In addition to the general problem identified above, characteristics and processes of surface charging important to understanding and addressing the issues during an XPS experiment are described below. Unless otherwise noted these derive from papers by Cazaux [4, 5]or summaries by Baer et. al.[6, 7]

- Specimens with conductivity less than $10^{-10}\Omega^{-1}\,m^{-1}$ or specimens isolated from the spectrometer ground will be expected to have surface and near surface charge buildup. Therefore, materials do not necessarily need to be highly conductive to minimize the appearance of surface charge. However, as described below, in non-uniform materials charge accumulation or trapping at interfaces in films and other multiphase structures is common and can shift or broaden spectra. Although these shifts complicate binding energy determination, such charging-related spectral distortions also carry useful information on the electric properties of specimens, as demonstrated by various studies.[8-11] Charge buildup is a time dependent three-dimensional phenomenon. Photoelectrons are generated throughout the X-ray penetration depth and charge can accumulate throughout the depth, often concentrating near interfaces. Variations in sample composition and X-ray flux spatial variations also lead to variations in surface and near surface charging.[12]

- Complex (and even relatively simple) materials can establish non-uniform (often called differential) charging in multiple ways. Causes include variations in photoelectron yields, film or sample thickness and compositions variations, and charge trapping at interfaces.
- Charge localization can occur (especially at defect sites and interfaces) in semiconductors, insulators and mixed phase materials leading to dipole fields and changes/deviations in photoelectron energies.
- Sufficient doping of semiconductors alters the position of the Fermi Level thereby shifting the position of the photoelectron BEs.[13] This is not a surface charging issue but another source of shifts in BE measurements even when specimens are conducting enough to enable Fermi Level alignment is possible. Theoretically, the Fermi level differences can be as large as the bandgap of the material. However, due to effects of band bending towards the sample's surface, the measured shifts tend to be significantly smaller in practice. As one example, shifts of 0.3 eV have been be observed in Si.[14]

- Processes that lead to charge buildup and migration can also drive changes in sample composition and structure (usually called damage).[4] Overviews of electron damage processes by Pantano et al.,[15] Baer et al.[16] and the content of a special issue of Surface Science Spectra[17] also provide some indication of the sensitivity of different materials and different molecular groups[18] to electron damage.
- Many 'real world' samples involve multiple materials with a range of physical and chemical properties. The measured binding energies of these materials are often a mix of intrinsic (chemistry and localized charge inherent in the sample) and extrinsic effects (effects associated with the XPS measurement including interactions with X-rays, secondary electrons or flood gun electrons on sample characteristics).[7] With creative application of XPS and charge compensation methods it is possible to obtain useful physical and chemical information about these materials and their interfaces.[19-24]

A model developed by Sambe and Ramaker[25] and described by Baer et al.[6] may be useful for understanding some of the phenomena associated with surface and interface charging, potential steps (e.g. upon the formation of interfacial dipoles) due to charge accumulation at interfaces and impacts of an electric field across the specimen. This model was developed in relation to oxide films on a conducting substrate (Al_2O_3 on Al in this example) and three different situations are shown in Fig. 1. (Note relevance of this model when examining the data reported in section II D.4 for Al_2O_3 on Al.)

i) Uniform potential - If the film and substrate are both conducting, the potential through the sample and analysis layer would be uniform (Fig. 1a).

ii) Step in potential - If the oxide is not fully conducting and charge is generated during oxide growth or during electron or x-ray exposure it is likely that some of this charge and image charges will collect near the interface and, along with associated image charges, a dipole layer will form creating a small potential step at the interface. (Fig. 1b). Although for thick or highly insulating oxides the potential through the oxide tends to vary, for thin oxides the potential within the oxide may be nearly uniform, whereas its step at the interface causes a shift in the BE of the oxide relative to the conducting substrate.

iii) Step in potential and an electric field - An electric field across the oxide would create a potential gradient (Fig. 1c) that will shift the measured binding energy and likely broaden the photoelectron peaks. Such a gradient in potential can be produced when the substrate is grounded and electrons from a flood gun are applied to charge compensate the surface. In this case the substrate is at ground potential and the outer surface potential is controlled by interaction with the flood gun. When two different potentials are present near the sample surface the spectra may be very complex, as shown for example in section II.B.2 for Pd in Fig. 3. For consistent referencing of photoelectron peaks, it is often useful to avoid having the sample at two potentials, which is one reason to deliberately isolate some samples from ground.

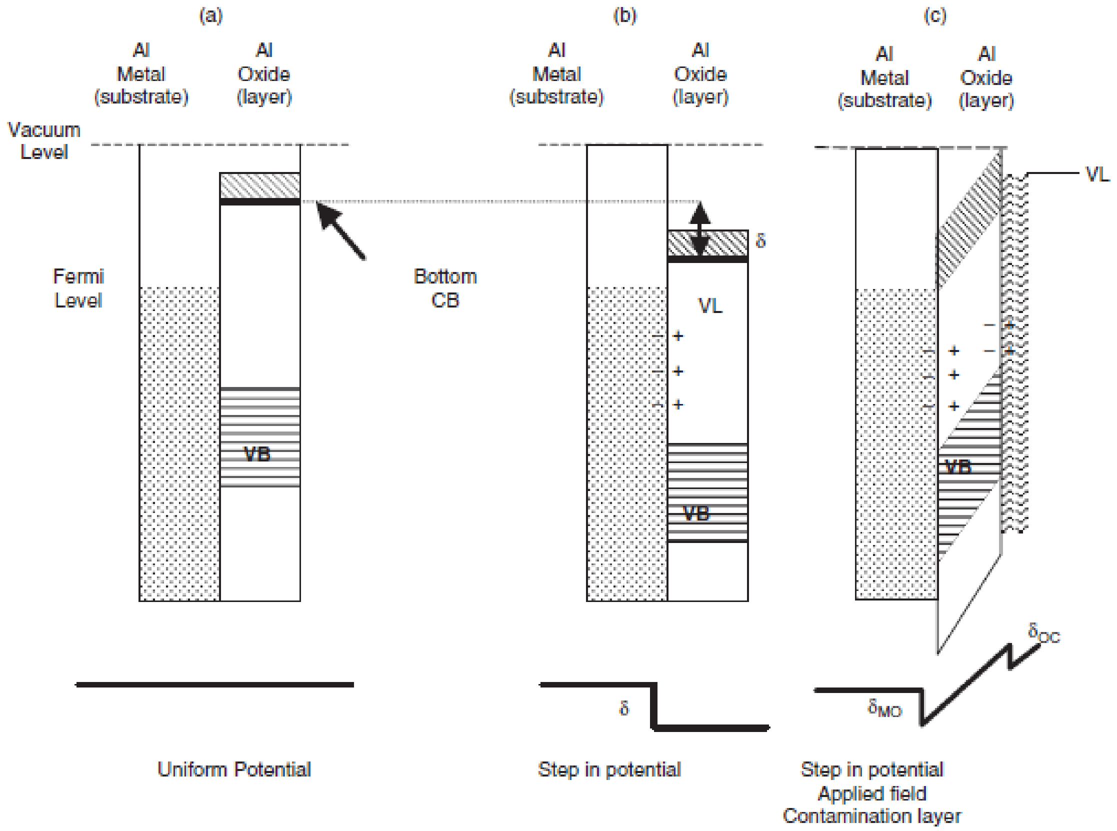


Fig. 1. Schematic drawing of energy level and potentials across an Al and AlOx sample based on concepts of Sambe and Ramaker (ref 25)for three situations: a) ideal uniform potential; b) with interfacial charge accumulation leading to a step in the potential; c) presence of both charge accumulation at the interface and an electric field across the film. From Baer et al. (ref 6)

Section II of this guide will describe approaches that have been implemented on modern instruments to successfully minimize or control charge buildup on samples during XPS and section III will describe some of the methods used to establish or correct the photoelectron binding energies. It is important to know that although there is an ASTM guide to charge control and charge referencing in XPS[26] and there is an ISO standard for reporting methods of charge control and charge referencing (with an appendix summarizing common methods)[27] it is appropriate to state clearly that there is

no universally accurate method to adjust or correct binding energies in the presence of surface charging. However, for experienced and careful XPS practitioner, it is usually possible to get the required information, as in many cases determination of the absolute binding energy is not necessary. The value and limitations of several methods commonly applied to adjust, or correct binding energies will be described.

Throughout this paper we refer to the accurately determined photoelectron peak energies as accurately determined BEs. Although these measured peak energies are often called BEs, for a variety of reasons, related to processes involved in creating photoelectrons, the peak energies we measure on the binding energy scale are different than the actual BEs associated with electron levels in the sample. The distinctions are discussed in part of a paper in Special Topic Collection on Reproducibility Challenges and Solutions, by Baer and Shard.[28]

II. MINIMIZING OR CONTROLLING SURFACE CHARGE

A. Recognizing charging and assessing the success of charge control

The emission of photoelectrons from insulating or electrically isolated samples inherently causes the buildup of positive charge. As the charge builds up (and usually reaches a steady state) photoelectrons will have lower kinetic energy, i.e.an apparent higher binding energy often presenting distorted peak shapes. Approaches to controlling or minimizing charge buildup include arranging or designing a sample to provide conducting pathways and the use of charge compensation facilities available on most XPS instruments.

Although the detailed methods used to control surface charge may vary with each analyst, analyzer system, and sometimes each sample, there are some common elements associated with recognizing the presence of charging and some frequent tests to verify that the charge control systems are working appropriately.

1. Recognizing differential charging

As indicated above, differential charging shifts the energy of the photoelectron peaks and can distort spectral shape. If samples are not adequately charge neutralized and photoelectron peaks are distorted, the information obtained can be highly misleading. See Fig. 2 of Edwards et al.[29] for peaks fits to adequately and inadequately neutralized C 1s spectra from a rough fabric surface. Therefore, it is necessary to identify the occurrence of differential charging within your high-resolution spectra if the intention is to rely on spectra for identifying and quantifying oxidation states / functional groups. There are a few quality checks that analysts employ for recognizing differential charging.

- Are the photoelectron peaks thought to be present for the sample appearing at nearly the expected (relative) energies and with appropriate peak shapes and widths?
    - If, for example, many peaks have an “extra” feature or features it may indicate differential charging and not the presence of an unexpected chemical state.
    - In extreme cases, no peak may be observed within the standard scan window for the core line under analysis.
- Are the peak energies and shapes relatively stable with small changes in analysis conditions, time and/or position on the sample?

    - Examining the leading edge of the main peak from multiple analysis points can be one way to identify peak broadening as a result of differential charging.
    - With the analyzer in snap-shot mode (where feasible), differential charging can cause the spectrum to shift across the BE scale, and the spectral envelope changes with time.
- Has the operation of the charge compensation system been verified by checking the resolution of a test sample, as described below?
    - Is the FWHM of the main peak(s) significantly larger than that obtained during set up or performance tests?

2. *Effectiveness of charge stabilization and operation of the charge control system*

Confirming the effectiveness of the charge neutralization system is recommended for insulating and semiconducting samples even when no obvious problems with the spectra are apparent. Most of these tests are directly related to the methods for recognizing differential charging noted above.

Although dependent somewhat on sample complexity, differential charging effects are often expressed in similar shifts and similar spectral distortions of the many elements related to a problematic phase of the sample. Therefore, slightly varying the flood gun conditions and observing spectral energy shifts and peak shape changes is often very useful for identifying such differential charging caused spectral distortions as distinguished from the desired information related to chemistry related peak shifts.

Since charge buildup is caused by the incident x-rays, changing the x-ray flux intensity or distribution, by altering the X-ray source current or the X-ray focus for systems with focused X-rays, may alter the extent of charging. Thus, taking comparison measurements at lower (or higher) x-ray flux and comparing the spectra, looking for differences in peak shape or position, offers an additional way to identify differential charging effects.

As differential charging often varies laterally across a sample, restricting the region of the sample being examined by decreasing the size of the volume from which electrons are accepted in the analyzer (mechanically or electronically decreasing an aperture size) may, for some systems and samples, help identify and even improve spectral quality.

It is important to test the operation of any charge neutralization system before applying it to samples of primary interest. Such testing of a charge neutralize system is often done by measuring a “test” sample that is run frequently and has well established properties. Although other insulating materials may be used, polyethylene terephthalate (PET) is an insulating polymer with well-established XPS spectrum (as shown in Fig. 2) that is often used to test and optimize the performance of charge neutralization systems. Vendors sometimes use PET as a test sample to demonstrate the operation of charge control systems and may identify a peak width as a parameter specified for instrument performance.

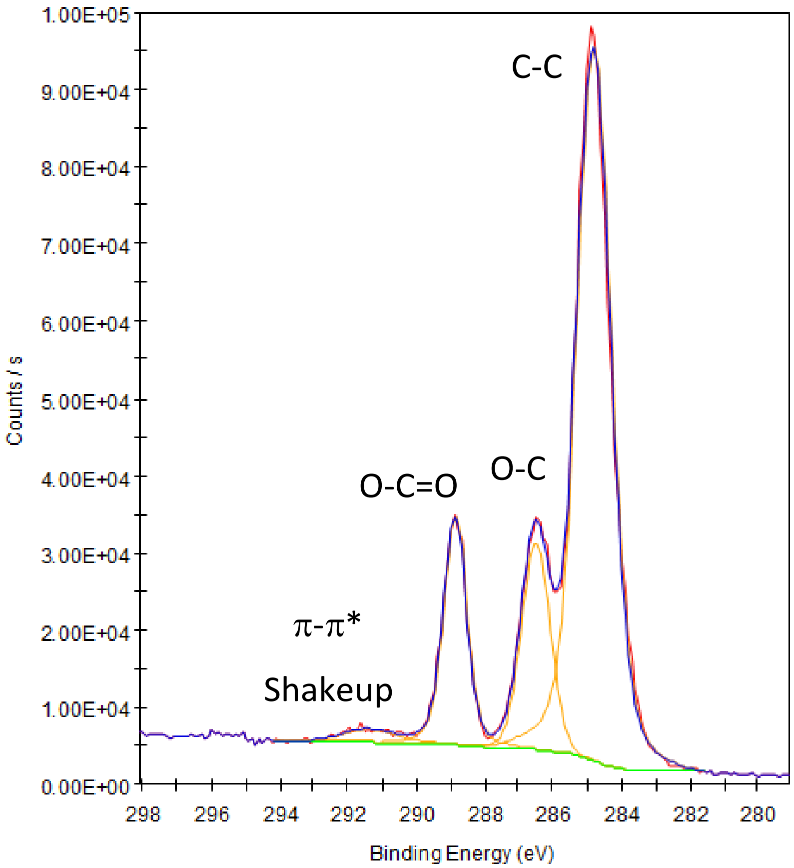


Fig. 2. C 1s spectrum PET. Such spectra are often used to test the performance of a charge neutralization system. The linewidth of the O-C=O peak is often used as a test to verity that the system is working appropriately. Data from a Thermo-Fisher system

For routine operation the parameters of the neutralization system can be adjusted until the FWHM of the O-C=O peak has an expected intensity and line width appropriate for the planned spectrometer operation mode. For systems using monochromatic Al Kα x-rays, the charge compensation parameters are frequently adjusted until the FWHM is 0.8 eV or better when data are collected in a high energy resolution mode.

Note that the history and freshness of the PET can be important. In a study by Beamson et al.[30] the relative C 1s peak amplitudes were found to vary some depending on the structure of the PET but these structure variations did not change the width of the O-C=O peak which is usually measured to verify charge neutralization. However, PET can be damaged by X-rays and contamination can complicate the measurement. One experienced operator noted that PET used for these tests can age or be contaminated during use and storage. After using a fresh section of PET, he would wrap the material in UHV quality Al foil and store in a glove box if possible. If repeated efforts found it difficult to achieve the desired/expected resolution with appropriate peak ratios, he would try a fresh PET sample before concluding that there were problems with the charge compensation system. Some analysts with an adequate PET supply use fresh material for each test.

B. Sample design and measurement configuration

Multiple methods can be used to create samples or establish methods for which the charging properties of samples can be well controlled and/or minimized. These include:

1. Enhanced electrical pathways

Multiple ways have been used to provide pathways to allow charge to find a pathway to ground. These include thinning samples to decrease resistance in the vertical direction and/or surrounding them with a conducting material, thus taking advantage of *surface* conductivity that is frequently higher than the bulk conductivity. In extreme cases one can also use a top conducting grid (Au for example), or a foil with a hole adjusted for the analysis spot, such as to shorten the surface conducting paths.

Sample illumination by white light is sometimes useful as well, thanks to photoconductivity mechanisms that enable improved charge evacuation from the surface. For broad bandgap materials, most effective will be the UV tail of the light source, yet frequently, even for very broad bandgaps, the likely presence of midgap trap states, and surface states allows visible light photoconductivity that helps suppression of the surface charging.

Heating – For some samples electrical conductivity increases sufficiently to minimize charging upon heating. This works for a limited number of samples, but effects of temperature on sample damage or alteration of surface composition need to be considered.[5]

2. Isolation from ground

Samples made up of materials with different degrees of conductivity may have parts of the sample at different potentials. Isolating such specimens from ground can minimize the leading sources of differential charging and is a recommended procedure for many samples. This approach allows the charge neutralization system to control sample surface potential.

Since seasoned XPS analysts recommend isolation of many types of samples from instrumental ground in order to minimize differential charging in a many circumances[31] and this recommendation may seem counter intuitive to less experienced operators, an example is provided in Fig. 3 to show how deliberate sample isolation from ground can benefit analysis. A Pb based paste for an advanced Pb acid battery was analyzed as mounted on a conducting sample holder with application of a low energy electron flood gun to compensate for any surface charge buildup. The Pd 4f XPS signals were unstable and not reproducible, even with charge neutralization, when the sample was grounded. Notably, the combination of charge compensation and isolation from ground suppressed the differential charging effects observed for the porous paste thereby removing the related spectral distortions. Having the sample at one potential also minimizes establishment of a potential gradient into the sample that can enhance sample damage during X-ray irradiation and flood gun exposure.

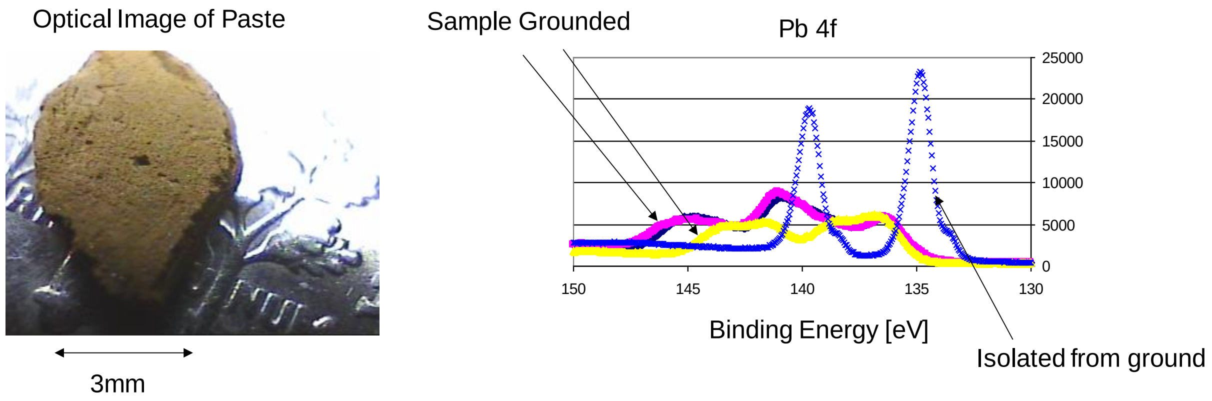


Fig. 3. a) Optical image of advanced battery electrolyte. b) Pb 4f XPS spectra collection from electrolyte with charge neutralization with the sample in grounded and isolated from ground configurations. For this relatively large XPS sample, the presence of both a ground potential and a potential controlled by the electron flood gun created differential charging and a highly distorted signal. With isolation of the sample from ground, the sample potential was controlled by the flood gun, differential charging was minimized and characteristic Pb photoelectron peaks were observed without significant distortion.

3. *Sample Biasing*

The application of a low-voltage bias (either constant or in an AC mode[32]) and observing the variations in binding energies and peak shape[33] of various photoelectron peaks can provide information about insulating and conducting parts of the sample in contact with the specimen holder.[34] Sample biasing strongly affects the magnitude of secondary electron emission (SEE), which is the dominant component in the buildup of surface charging. Thus, the bias can be varied such as to optimize the surface charge state.[10] This method can also be used to verify that peaks used for charge correction (e.g. Au, or C) shift with applied potential in the same manner as the peaks of interest in the specimen.[35] Such measurements can provide information about the need for better sample grounding or the need to isolate from ground.

4. Electron Flood Gun Variations

Varying the surface charge via control over the electron flood gun (eFG) parameters (or via sample bias variations under fixed eFG parameters) can provide a systematic means for differentiating between the ‘real’ chemical shifts and artifact differential charging related shifts.[10, 36, 37] On one hand, this approach enables novel extensions of XPS as an electrical probe, as mentioned above, but can also enhance chemical (and structural) analyses.

C. Example charge compensation systems

Although surface charge minimization efforts related to sample design or mounting are widely used, the buildup of positive surface charge has most often been addressed by providing a source of low energy electrons to neutralize or balance the positive charge buildup. In the 1990s significant advances in charge compensation were developed.[38] It was also recognized that stabilizing extra negative surface charge is frequently easier and more robust than what can often be achieved by sample design or mounting. Then, if the probed surface area is uniformly charged, it is easy to apply an offline correction of the energy scale. However, non-uniform surface charging often emerges, especially with the use of focused x-ray beams, for which the balance between outgoing (photo-ejected) electrons and the incoming electron flux from the neutralizer can vary strongly across the analysis area. Therefore, instruments using focused x-rays beams have found that the use of both low energy electrons and low energy ions can control surface charging and minimize differential charging.[29, 39, 40] The dual beam neutralization exploits the fact that under the supply of both extra electrons and extra positive ions at large amounts, charges can easily redistribute such as to rapidly compensate local fields that may emerge; similar in a way to the effect of a buffer in solution.

Methods that effectively minimize surface charging are usually an integral part of modern XPS instruments, with the design optimized for the specific spectrometer. Consequently, it is appropriate to have a description of the charge control systems for specific instruments or manufacturers along with examples of the use of the system. Descriptions of charge control approaches used by three manufacturers of XPS systems, Kratos Analytical, Physical Electronics (PHI) and Thermo-Fisher Scientific are provided below.

Although the examples presented represent data from the specific systems discussed, the issues they represent and consider are applicable in different ways to most measurements requiring charge compensation.

1. Kratos AXIS spectrometers

Kratos AXIS spectrometers, which do not use highly focused X-rays, use an electron only charge neutralization system which is made up of filament(s) and charge balance electrode(s) located at the end of the electrostatic lens column, directly above the sample (Fig. 4). Importantly, the neutralizer assembly sits within the magnetic field of a magnetic lens which forms part of the input optics for the lens/analyzer of the spectrometer.

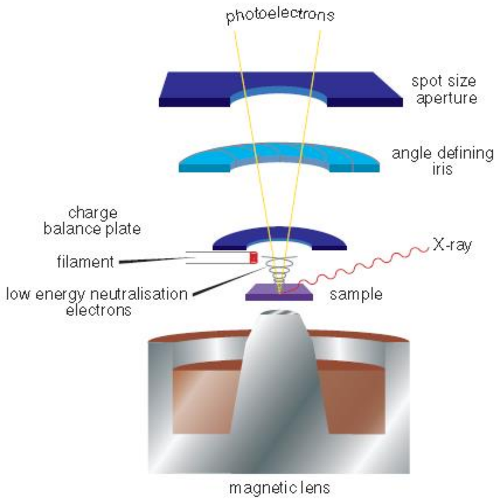


Fig. 4. Schematic diagram showing the charge neutralizer assembly, relative to the magnetic and electrostatic lenses of the AXIS spectrometer.

During use, a current is passed through the neutralizer filament(s), causing electrons to be thermionically emitted. A negative bias applied to the charge balance electrode(s) provides kinetic energy to these electrons. Electrons emitted from the filament and guided to the analysis position by the magnetic field are the primary source of electrons providing charge neutralization. A secondary source of charge neutralization electrons is provided by unfocused photoelectrons which may be incident on the charge balance electrode, causing secondary electrons to be emitted. These electrons are focused back towards the sample by the magnetic field and act in combination with the low energy electrons from the filament. As a charged particle moving through a magnetic field, the electron will feel a force perpendicular to the direction of motion, constraining it in a helix that terminates at the sample surface. The cyclic direction is essentially parallel to the specimen surface since the specimen analysis area is in the center of the electromagnet pole. Modelling shows that the charge neutralization electrons will follow this helical trajectory towards the sample, such that they impinge from all directions on the area of the specimen being analyzed. This is of specific importance for effective charge neutralization of rough samples or those with high levels of topography.

The AXIS charge neutralizer has three parameters that can be used to optimize charge neutralization, namely filament current (typically <0.46 A), filament bias voltage

(0 to 5 V) and charge balance voltage (0-5 V). Increasing the filament current will increase the number of electrons available for charge neutralization, as measured by an increase in landing current at the sample. A bias applied to the filament provides the initial energy for the electrons leaving the filament to overcome the space charge region. Above a threshold value, this parameter only slightly affects the number of electrons available for neutralization. The charge balance voltage applied to a plate adjacent to the filament and sets up a potential that is dynamically maintained between it and the sample surface by the neutralization electrons. Electrons moving back up towards the balance plate are being repelled to rejoin the cloud. The surface potential dynamically shifts in response to the charge balance voltage and sets the energy position for the best spectrum. This balance voltage is optimized to provide the narrowest peak with the highest intensity.

Values for the charge neutralizer settings are influenced by the age and condition of the filament assembly. Filament current should be increased in small increments only when it is considered necessary to improve performance and should be kept below the upper limit to prolong filament life. Once the upper limit is reached and no additional improvement can be obtained then it is likely the filament has reached end-of-life. At the time of writing, the values for filament current, filament bias voltage and charge balance voltage for the AXIS Nova instrument located in the CSIRO lab are 0.42 A, 3.8 V and 3 V, respectively.

During optimum operation of the Kratos AXIS charge neutralization system, photoelectron spectra are often shifted to lower binding energy, close to the difference between the balance and bias voltages on the neutralizer. The observed shift will result in a peak position of the adventitious hydrocarbon C 1s core level (BEmeas) between ca. 282.5 to 284 eV binding energy implying that there is a negative surface charge on an insulating sample. The binding energy scale may be corrected then according to a 'known' reference as discussed in section III.

2. Physical Electronics (Phi) Spectrometers

Current generation spectrometers from Physical Electronics use a focused X-ray source that benefits from a combination of electron and ions for charge compensation of the sample surface. For these Phi systems it is important to understand how the charge compensation works for the variety of X-ray beam conditions that may be used. As some PHI systems now use both Al kα and higher energy Cr kα X-rays it is also important to demonstrate the effectiveness of charge compensation for different energy of X-rays.

All current generation PHI XPS spectrometers are equipped with PHI's patented dual beam charge neutralization system[39] that utilizes both a cold cathode electron flood source (~1 eV) and a very low energy ion source (≤ 10 eV) to provide charge neutralization of all sample types. When highly focused x-rays were first introduced, new challenges with charge neutralization appeared. A careful experimental and modeling study identified that a significant range of surface potentials appeared with the buildup of positive charge where the x-rays were incident and presence of some effectively negative charge buildup in other areas related to the low energy flooding electrons with the highest energy.[40] This charge distribution made it difficult to deliver the needed compensating electrons to the area where the x-rays were incident. Based on a series of interesting studies, a charge control system was developed to address the problem. The system requirements involved decreasing the energy spread in the low energy electron flood gun and adding a low energy positively charged ion.[39] The resulting system is schematically shown in Fig. 5. The combination of an optimized low energy electron source with the low energy ion source has been demonstrated to minimize barriers to the delivery of low energy electrons to the analysis area.

As suggested by the schematic in Fig 5, the low energy ions cover a wide area of the sample while the flow energy flooding electron are somewhat directed toward the area where the x-rays are incident (1 or 2 V electron are not easily highly focused). Both ion and electron neutralizers are tuned by optimizing ion and electron beam focus and steering parameters that result in their convergence to the X-ray and analyzer focal point. X-ray beam induced secondary electron images (SXIs) are used to locate the center of the Faraday cup. The maximum current in the Faraday cup is used to align and tune both ion and electron guns. Typical cathodes used for the source of electrons are BaO or Ta. The electron neutralizer is typically running at 20 -21uA emission current with ~30V of extraction. and 1-1.5V of bias. The ion neutralizer is operating in a floating mode producing 3mA of filament emission current. The beam voltage is set to ~110V while applying a -103V float results in an ion energy of ~7 eV at the sample. Neutralization efficiency is verified using the PET resolution specification in the standard analysis position (X-rays at normal incident to the sample surface and photoelectrons at 45 degrees angle of emission to analyzer) adjusting focus and steering parameters to make sure that the O-C=O peak width is 0.8 eV or slightly better when using the monochromatic Al Kα X-ray source. . As discussed in II.D.3, some sensitive samples may be chemically damaged by ion and/or electron beam neutralization schemes. A feature of PHI's dual beam charge neutralization system is independent control over electron and ion gun settings allowing customized charge neutralization modes for electron damage-sensitive or challenging materials.

The following practices are characteristic of one analyst (MHE) but may be useful as a guide for others. To minimize the chances of sample damage he prefers to use the lowest voltages and current that work, but these may change with time depending on component aging. He uses an ion voltage setting of approximately 7 V. For a new or well operating electron flood gun he sets the current to 21 μA and the voltage at 1 to 1.5V. The electron flood gun is roughly aligned using a faraday cup to “center” the electron in the area of the incident x-rays. After this initial alignment a block of PET is mounted on the sample holder using double adhesive tape. The electron flood gun beam steering is then adjusted to optimize peak intensity and peak width, to make sure that the O-C=O peak width is 0.8 eV or slightly better.

With long experience on one Phi system he has found that after this set up the charge neutralization system works well for most samples. He would verify performance if X-ray beam conditions were altered significantly or the sample were to be oriented at a different angle. In addition, he has found that some adjustments (increased electron current or voltage) may be needed for particularly large insulating samples (> 1.5 inch in diameter) and that the cold cathode emission source for the low energy electron can age requiring further adjustments.

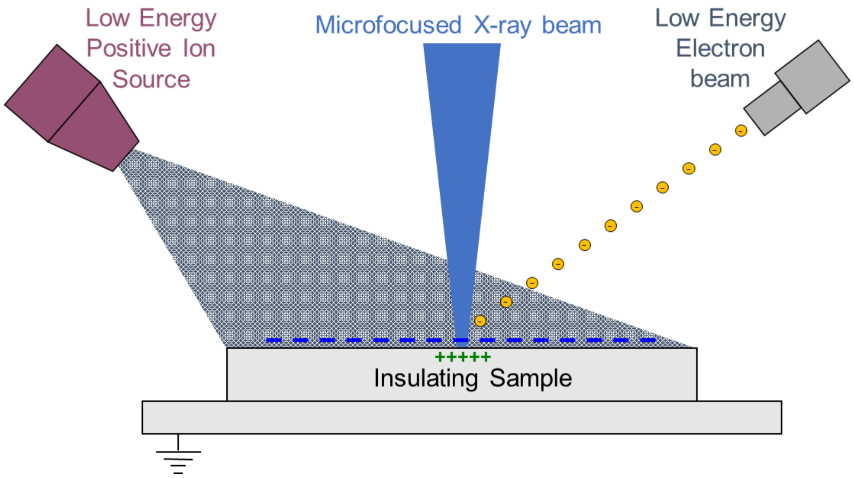


Fig. 5. PHI's dual beam charge neutralization method uses a low energy ion beam to eliminate electrostatic charges on the sample surface and a low energy electron beam to neutralize the charge created by the X-ray source.

3. Thermo Fisher Scientific Spectrometers

Many Thermo Fisher Scientific XPS systems involve micro-focused beams and for reasons already discussed all the XPS systems currently manufactured by Thermo Fisher Scientific (Thermo Scientific Nexsa, ESCALAB Xi$^+$ and K-Alpha) use a patented[41] combined low energy electron/argon ion approach to charge compensation schematically shown in Fig. 6. A general description of the operation of this charge compensation system is described by Edwards et al.[29] Charge compensating electrons and argon ions are created in a single source. Electrons generated by thermionic emission (Region 1 in Figure 6) are accelerated into a region of argon gas, where they interact with the gas to create argon ions (Region 2). The electrons and ions are then accelerated towards the exit of the flood source where both beams are focused onto the sample surface (Region 3). The low energy electrons compensate for the positive charge build-up due to photoemission, but the argon ions prevent the build-up of negative charge in the region around the X-ray spot. Common operating parameters are 0.1 V electrons with 100 µA emission current, 40 V extractor and 20 V gas cell voltages. Electrostatic deflector settings are used to focus electron and optimize the linewidths for PET as shown in Fig. 2. For some “smooth” polymer samples the emission current can be reduced to 20 μA and the extractor voltage to 30 V achieving good neutralization.

As described by Edwards et al. [29] in this type of combination source the flux and energy of the electron will influence the ion flux. By varying the electrical potential in regions 1 and 3 it is possible to vary the relative amounts of electrons and ions. There may be multiple sets of parameters set produce excellent data as shown by measurements on PET. As described in an example below (II.D.3), Edwards et. al.[29] developed a set of operating conditions, including reduction of the extractor voltage, that reduced the impact potential of electrons interacting with the ions to establish a condition that was effective at neutralization but minimized damage to highly sensitive samples.

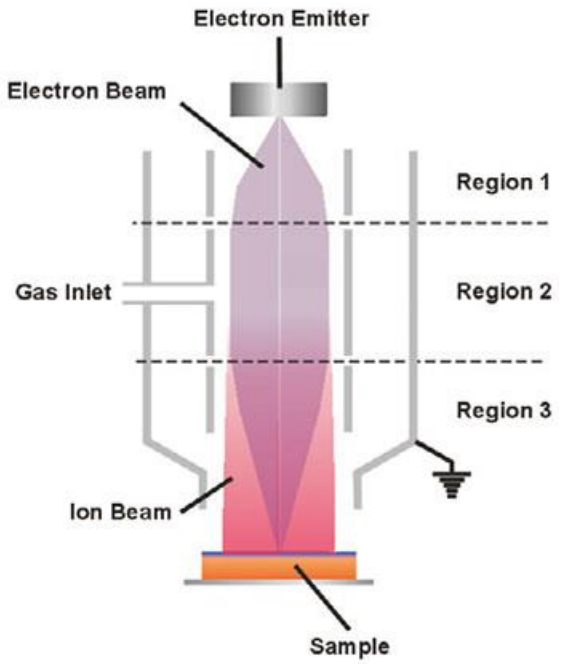


Fig. 6. Schematic diagram of Thermo Scientific XPS charge compensation source that introduces both low energy electron and ions to the sample. Electrons are emitted in

Region 1, electrons interact with and ionize Ar gas in Region 2. Both ions and electrons impinge on the sample traveling through Region 2.

D. Examples uses of charge compensation systems

1. Verifying the adequacy of charge compensation for multiple experimental conditions

The dual beam charge neutralization method can provide effective neutralization for most insulating samples on the Phi system. For the Phi systems, as for other vendors systems, there are multiple modes of instrument operation (small area, different x-ray scan rates, tilt angles, and in newer systems the use of monochromatic Al kα and higher energy monochromatic Cr Kα X-ray sources). Although this data is from a PHI system, the same types of consistency or validation checks are appropriate for any system as instrument parameters are varied.

As indicated in the description of charge neutralization system in PHI instruments (II.C.2), both ion and electron neutralizers are tuned by optimizing ion and electron beam focus and steering parameters that result in their convergence to the X-ray and analyzer focal point. As set up in this manner the neutralization is relatively robust working well for many sample types, both Al Kα and Cr Kα X-ray sources, and, as shown in, II.D.5, during depth profiles. Regardless, it is always useful to verify the charge compensation is working appropriately.

Many insulating samples or those isolated from ground have adequate charge compensation from modern charge control systems are set up and working for test specimens such as PET. However, some samples need extra attention and possible adjustments to charge compensation conditions. The nature of challenging samples may vary depending on the charge control system. As noted in section II.C.2, large flat samples can sometime require either charge neutralization adjustments or the addition of a mask. The efficiency of charge neutralization often decreases for thick non-conducting samples. As discussed in the next section (II.D.2), rough powder surfaces can complicate charge compensation and this may apply to other rough insulating surfaces as well. In earlier work it was noted that non-homogeneous systems, especially mixed conducting and non-conducting present a variety of challenges including differential charging.[6]

Data for alumina and carbon black shown in Figure 7 show that effective and reproducible charge neutralization can be achieved for all modes of acquisition on both insulating and mixed-conductive/non-conductive materials, different take-off-angles (TOAs), different sizes of micro-focused X-rays and different scan types (points, lines, areas). The samples used in these tests were all mounted using double sticky adhesive tape. As discussed above, the combination of isolation of insulating powder such as alumina from ground and charge compensation decreases the possible effects of differential charging. Using double sticky adhesive tape works equally well for conductive samples which simplifies mounting of powders on the sample holder and ensures efficient neutralization in case of possible differential charging.

All data was collected without adjusting the neutralization conditions from those described earlier. Normalized not BE corrected high-resolution spectra for insulating alumina ceramic sample obtained using different sizes of line scans (Figure 7a) and at three different TOAs (Figure7b). For carbon black sample, normalized uncorrected spectra are shown from three different areas on the sample obtained using 20-micron X-ray spot (Figure 7 c) and the same region of the sample using 100-micron and 10-micron

X-ray spots (Figure 7d). These unadjusted spectra without any BE correction demonstrate that good quality and reproducible spectra have been obtained. A method of adjusting the measured binding energy to appropriate values would still need to be applied.

As indicated in section II.A.2, PET is often used to verify charge neutralization performance. A comparison of the measurement of PET using monochromatic Al Kα and monochromatic Cr Kα X-rays are shown in Fig. 8. The same settings for ion and electron guns were used for both Al and Cr X-ray measurements. Good data is shown for each, but note that the resolution for the Cr is lower than for the Al. This is due to a wider natural width of the Cr source at 2.1 eV vs 0.83 eV for the Al source.

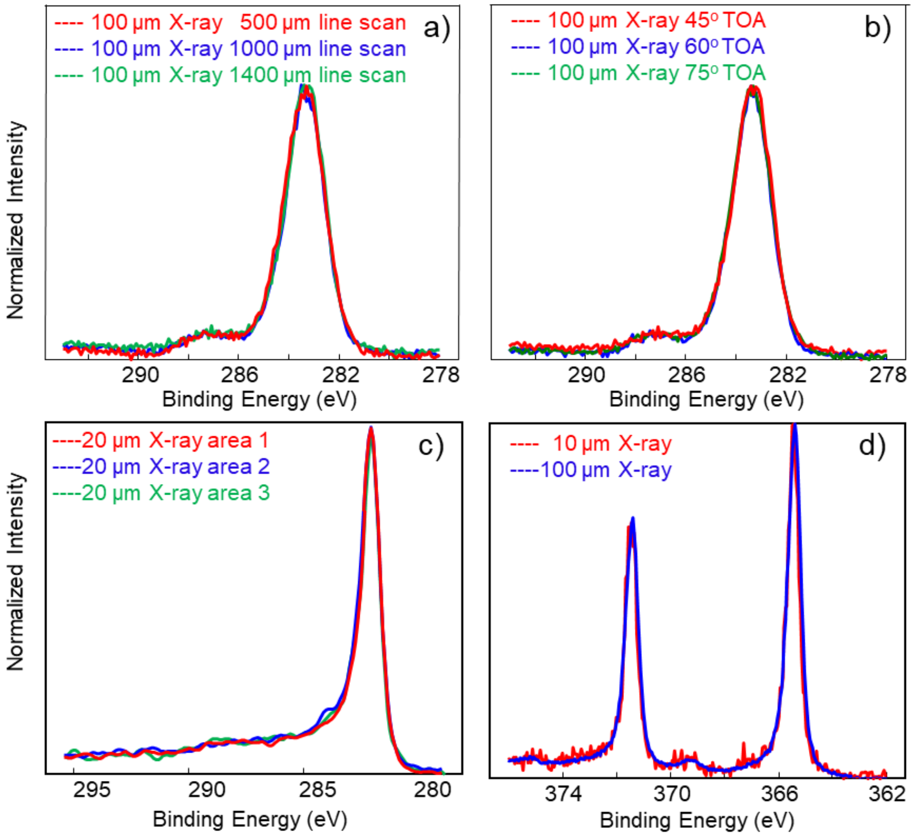


Fig. 7. Demonstration of neutralization stability for different modes of operation for a Phi system. All samples were mounted on double-sided non-conductive sticky tape. a) raw

data recorded under dual beam neutralization, showing the normalized high-resolution C 1s spectra from insulating alumina ceramic obtained using different line scans using 100 µm X-ray spot; b) non-charge corrected normalized high-resolution C 1s spectra from insulating alumina ceramic obtained using 3 different take-off-angles using 100 µm X-ray spot; c) non-charge corrected normalized high-resolution C 1s spectra from 3 areas on Ag-doped carbon black obtained using 20 µm X-ray spot and d) non-charge corrected normalized high-resolution Ag 3d spectra on carbon black obtained using 10 and 100 µm X-ray spots. Because charge compensation needs will vary with sample type and x-ray flux density, verifying adequacy of operation in different conditions can be important.

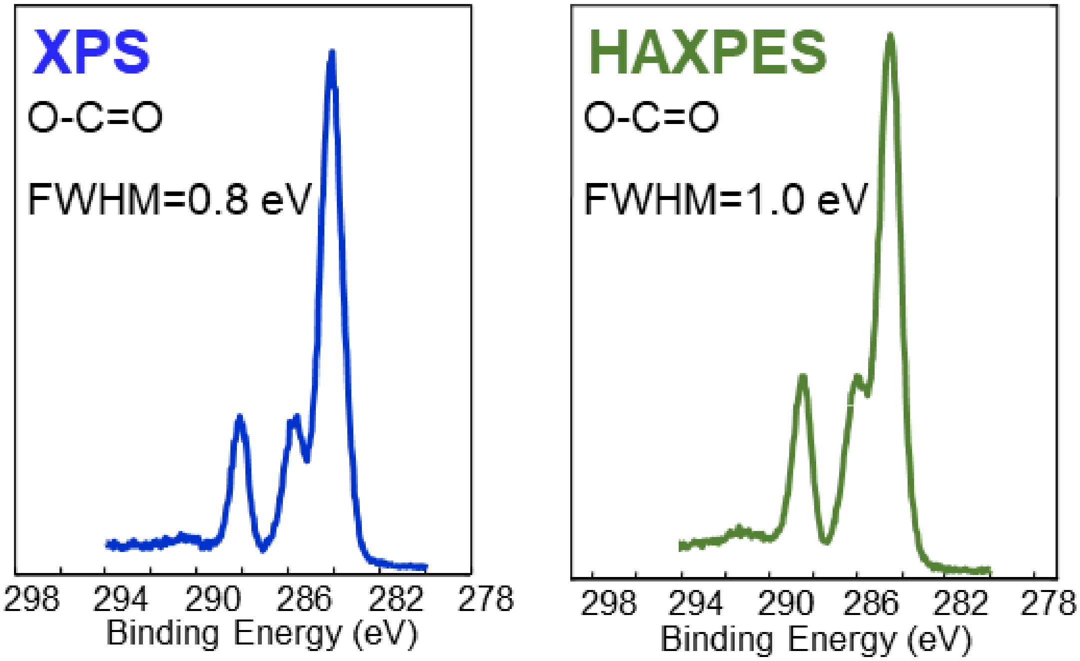


Fig. 8. High-resolution XPS (left) and HAXPES (right) C 1s spectra from PET obtained using Al Kα and Cr Kα X-ray sources on a PHI system. The consistent verification of the ability to observe the structure of test specimens such as PET provides an indication that the standard charge compensation settings work appropriately for either X-ray source. The difference in peak resolution are due to the difference X-ray line widths as noted in the text.

2. Preparation of powder samples and influence of surface topography

In this example the influence of surface topography on charge neutralization is demonstrated in a Kratos system, highlighting the importance of sample preparation for powders. There are a variety of approaches toward mounting powder specimens many of which are described in the guide to XPS analysis of polymers[31] or a guide to XPS analysis of nanoparticles.[42, 43] One option for presenting powder samples to the spectrometer is using custom made powder wells. Powder can be poured into the individual wells using a funnel crafted from filter paper. Depending on the size and mass of the particles and how they flow during loading, the powder may settle in to the well leaving a relatively uniform top surface without intervention, though this is not always the case.

For the data shown, spectra were collected from a metal organic framework (MOF), specifically UiO-67, that was loaded into a powder well without further intervention, leaving the top surface of the powder uneven for the initial scans. Once the initial analysis was completed, the samples were removed from the spectrometer and the powder was lightly compacted using a custom-made press to smooth out the top surface. The analysis of the MOF sample was then repeated under identical conditions (including the charge neutralizer).

As can be seen in Fig. 9, a significant improvement in spectral resolution can be observed comparing the initial spectra collected from two analysis points with the repeat analysis after compacting the sample. In the case of the rough, uneven sample surface presented during the initial analysis, it is difficult to neutralize the build-up of positive charge on the surface upon exposure to the X-ray source. This heterogeneity in the surface topography may result in shadowing of some regions on the sample that are at a different potential to other parts of the sample surface that are effectively neutralized. The spectra collected from the uneven sample can be smeared across the binding energy scale, typically on the falling higher BE edge side of the spectra, as a result of differential charging.

The improvement in spectral resolution observed once the top surface is more uniform is significant. Based on prior knowledge of the sample and what to expect, the data recorded from the smooth surface reflect the “true” spectral shape unaffected by differential charging, particularly evident in the case of the Zr 3d spectrum. A guide on how to identify such “charging problems” in XPS data has been provided in section II A (Recognizing charging and assessing the success of charge control). The fact that this is not a trivial problem is demonstrated by the number of examples in the published literature, where spectra distorted by differential charging are mistaken as spectra presenting multiple chemical states. In the case of powders presented here, ensuring the top surface is as smooth and uniform as possible is critical. For free standing films and substrates, minimizing sample lateral size while providing enough untouched area for analysis typically improves neutralization. Sharp and jagged edges of solid samples should be removed as they can impact data collection. There are other steps in this process, such as collecting multiple data points across multiple samples which provides confidence in the quality of your data.

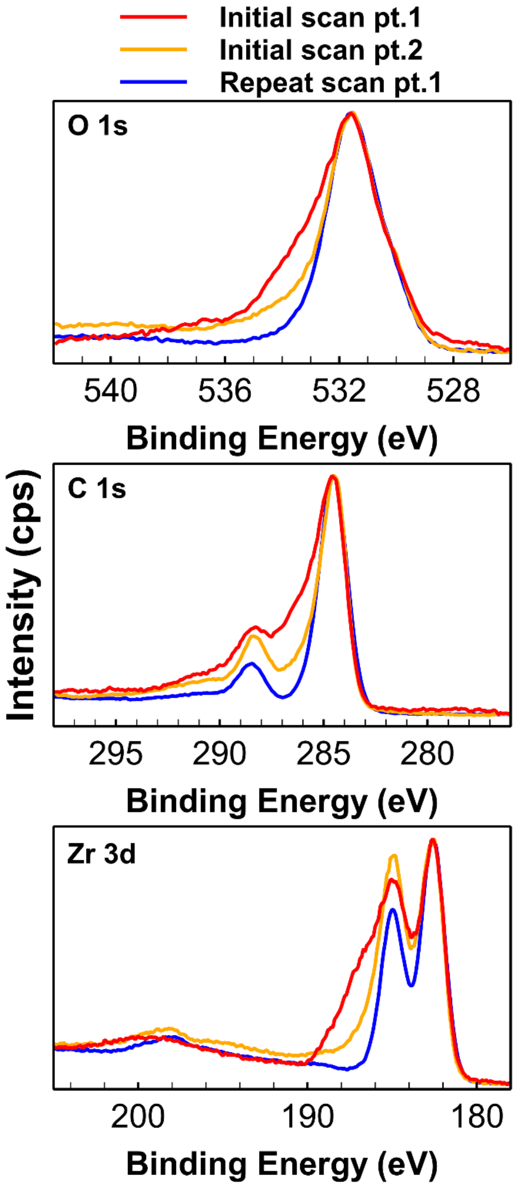


Fig. 9. Selected, representative high-resolution spectra from UiO-67 MOF collected under identical hardware parameters. Initial scans at pt. 1 (red line) and 2 (orange line) are collected from a powder sample that is unevenly packed into a sample well, presenting a relatively rough top surface to the spectrometer. Repeat scan pt. 1 (blue line) is data collected from same sample after lightly compressing powder to give a more uniform top surface. In addition to identifying the impact of surface topology on sample charging and charge compensation, the example highlights the value of considering possible causes of “odd” peak shapes.

3. Minimizing damage to highly sensitivity samples

Charge compensation methods on modern instruments work extremely well for a wide variety of insulating samples with few undesirable side effects such as sample damage. However, there are some important highly sensitive materials/samples for which damage is a great concern and often observed. In some cases, damage has been attributed to the X-ray exposure, but in other cases the use of flooding electrons and/or ions appears to cause sample reduction. These include higher oxidation states of Cr such as CrO_3 which is of environmental importance and V_2O_5 a material relevant to advanced batteries. In recent work described below for the Thermo-Fisher charge neutralization system it was found that some relatively minor changes to the operation of the charge compensation system could decrease damage to several materials.

Edwards et al.[29] examined the impact of two different operating conditions using the Thermo Fisher charge composition system on damage of highly sensitive systems. Condition A is characteristic of a common neutralization set up described in II.C.3 and condition B involved lowering the extraction voltage to 30 V likely forming a lower, but effective flux of Ar ions. Both settings were observed to produce high quality spectra from PET. However, compensation setting B produced much less damage to Cr(VI) on a flake of CrO_3 (Fig. 10). Setting B also worked well for a variety of other highly sensitive materials.

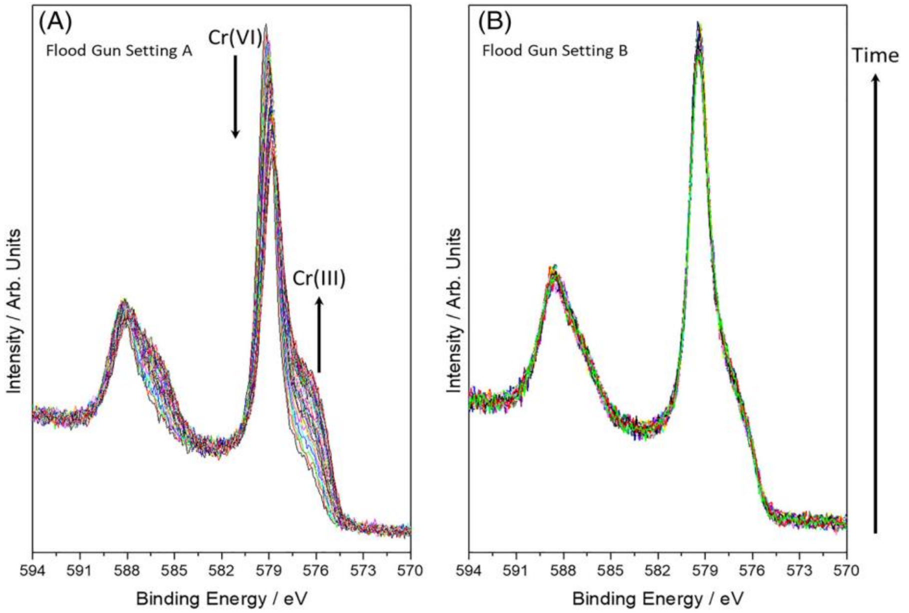


Fig. 10. Overlaid Cr 2p core - level spectra for CrO_3, using two different flood gun settings A and B, the latter clearly showing less reduction of Cr (VI) to Cr(III). See text for details.

An important message from this example is that even for highly advanced compensation system it is useful to check to see if standard operating conditions in combination with the needed time for data collection produce sample damage. It is possible to optimize either the charge compensation or data collection to minimize any such effect if observed.

4. Al foil with native oxide - effects of grounding, isolation from ground, impacts of charge neutralization and limitations of substrate referencing

This example looks at different ways of collecting data from an aluminum foil with a native 4 - 5 nm thin alumina passivation layer. This example highlights important aspects of sample neutralization and BE referencing such as substrate referencing and isolation from ground that are universal, i.e. not unique to the Kratos AXIS spectrometers on which this data was collected.[6] For the measurements described here, identical samples were mounted, one in electrical contact with the sample holder (spectrometer) using conductive tape and a second sample electrically isolated from the sample holder. High resolution XP spectra were acquired for the core levels using monochromatic Al Kα excitation. Acquisition was performed with and without AXIS charge neutralization for the two samples.

Alumina is a wide band gap insulator (≈7 eV)[44] which for a bulk sample would require the use of the charge neutralizer during XPS analysis to prevent charging of the sample during photoemission. However, when alumina is present as a thin passivation layer it may be analyzed without charge neutralization. Fig. 11(A) shows the high-resolution Al 2p region from the sample mounted in electrical contact with the spectrometer and data acquired without use of the electron flood gun. As shown in Table I, the FWHM of the Al 2p3/2 component is measured to be 0.43eV and is BE at 72.8eV. The energy separation (ΔE) between the Al 2p3/2 (metal) - Al 2p3/2 (oxide) is 2.69 eV. If data acquisition is repeated with the charge neutralizer on, a very different spectrum is observed, shown in Fig. 11(B). Both components are shifted to lower binding energy implying there is a negative charge at the surface. The FWHM of the Al 2p3/2 (metal) is slightly broader at 0.46 eV but more significantly the separation between the oxide and metal components is 1.64 eV, significantly smaller than that measured from the same sample without charge neutralization. The differential charging between the surface oxide and bulk metallic aluminum significantly distorts the spectrum and compromises the chemical shift information that can be determined. The potential of the charge neutralizer in combination with the thin insulating film causes a greater shift to lower binding energy for the oxide than the metallic aluminum.

The approach that is recommended for samples where differential charging is problematic is to float the sample such that it is not in electrical contact with the sample holder and use the AXIS charge neutralizer. Results for this configuration are shown in Fig. 11(C), where the sample has been mounted floating and therefore both the oxide and metal are electrically isolated from the spectrometer. The charge neutralizer fixes the surface potential for both oxide and metallic components. For this study, the ΔE separation between the Al $_{2p3/2}$ (metal) - Al $_{2p3/2}$ (oxide) is 2.87 eV and FWHM of the metallic Al $_{2p3/2}$ component = 0.44eV. It is noted that the reported literature values for ΔE separation between the aluminum metallic and oxide photoemission peaks vary between ca. 1.7 eV to 3.3 eV with the oxide film thickness,[6, 45] the film structure as well as approach to mounting and acquiring the XPS data and electron beam irradiation[6] all having an impact on the measured separation. For a thin passivation oxide layer such as the one measured here, a survey of the literature suggests ΔE separation of 2.7±0.2 eV is

Table I. Properties of Al spectral data from Fig. 11

	(A) Conducting CN off	(B) Conducting CN on	(C) Floating CN on
FWHM of Al2$p_{3/2}$ ox [eV]	1.52	1.98	1.46
FWHM of Al2$p_{3/2}$ met [eV]	0.43	0.46	0.44
BE of Al2$p_{3/2}$ ox [eV]	75.45	73.03	70.71
BE of Al2$p_{3/2}$ met [eV]	72.76	71.39	67.84
Δ (BE Al ox – BE Al met) [eV]	2.69	1.64	2.87

expected.[46, 47]

The samples discussed here involve multiple interfaces generally parallel to the surface and may influence the BEs observed in significant or subtle ways. For example, electrons emitted from the metal layer travel through the oxide before entering the analyzer and would be influenced by any surface or interface charges. The presence of oxide layers at the back of the sample as well as between the metal foil and spectrometer ground will influence the potential of the metal layer and impact the energy of electrons observed. This example highlights challenges of substrate referencing (section III.C). Careful analysis of insulating samples requires thought, experimental care and a consistent approach.

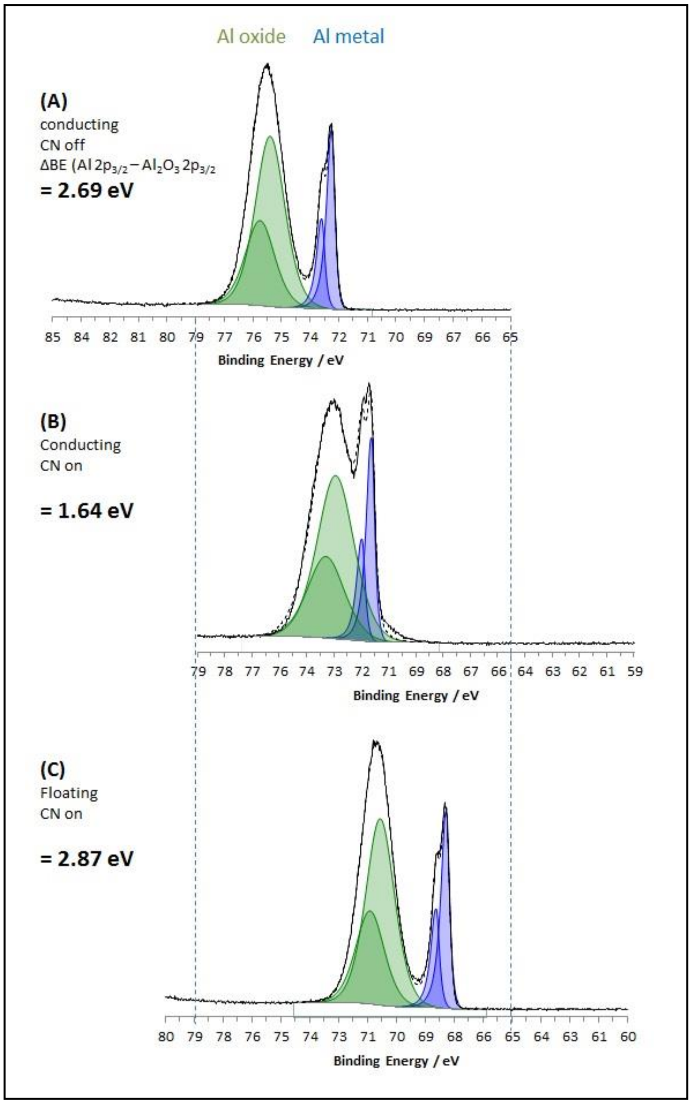


Fig. 11. Al 2p spectra acquired (A) sample mounted in electrical contact with the sample holder, neutralizer off. (B) sample mounted in electrical contact with the sample holder, neutralizer on and (C) sample mounted floating, electrically isolated from the sample holder, neutralizer on. This example highlights the importance of isolating a specimen from ground and points out challenges associated with referencing elements in a thin film to components in a conducting substrate.

5. *Charge compensation during sputter depth profiles*

Robust neutralization is critical during the depth profiling, particularly of mixed inorganic and organic composited and layered structures. When depth profiling differential charging can be introduced by the normal XPS process, but also by the ion sputter beam. In addition to charging issues samples are often altered by reduction or alteration by the sputtering process (differential sputtering varying sputter rates, ion beam-induced chemistry). Usually XPS measurements are collected between increments of sputtering, but data can be collected on a continuous basis while sputtering in some situation.

The two examples shown involve the use of ions made up of large clusters of Ar molecules,[48-50] on Phi (Fig. 12) and Thermo-Fisher (Fig. 13) systems. Sputtering using these clusters is often highly effective in achieving good depth profile data minimizing damage to organic materials. In the first example, monotonic Ar ion sputtering is used to achieve needed sputter rates for the inorganic ITO substrate.[50]

The spectra and depth profile of solar cell with an organic layer consisting of Poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) and inorganic indium tin oxide (ITO) layer are shown in Figure 12. The sample was mounted on double-sided adhesive tape to ensure efficient electrical isolation from ground and thereby avoiding potential differential charging for a mixed-layered system. An alternating depth profile was obtained using two different ion guns. The data from the organic top layer were obtained using an 1800 atom Ar cluster ion beam which minimized ion beam related damage to the organic, following by monatomic Ar^+

sputtering through the ITO layer. A 100 μ X-ray spot was used for acquisition of the spectral data, and "standard" charge neutralization conditions, tuned as discussed above, were applied. The consistency of peak shape and lack of peak shifting during the profile indicated that sample charging did not vary during the depth profile. Non charge-corrected spectra are shown to demonstrate that both components of the organic and inorganic structure are well charge-neutralized.

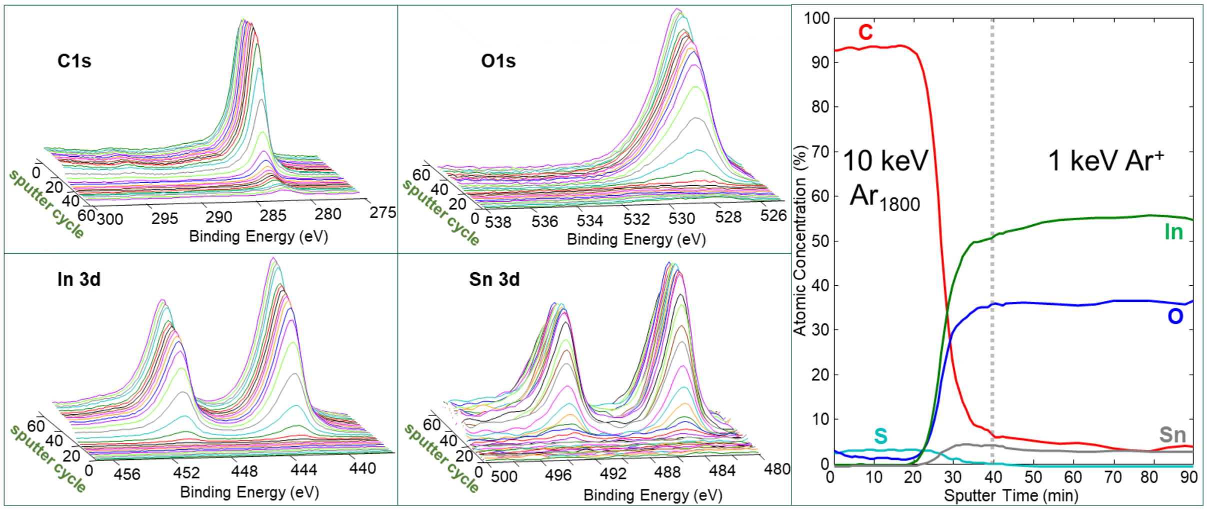
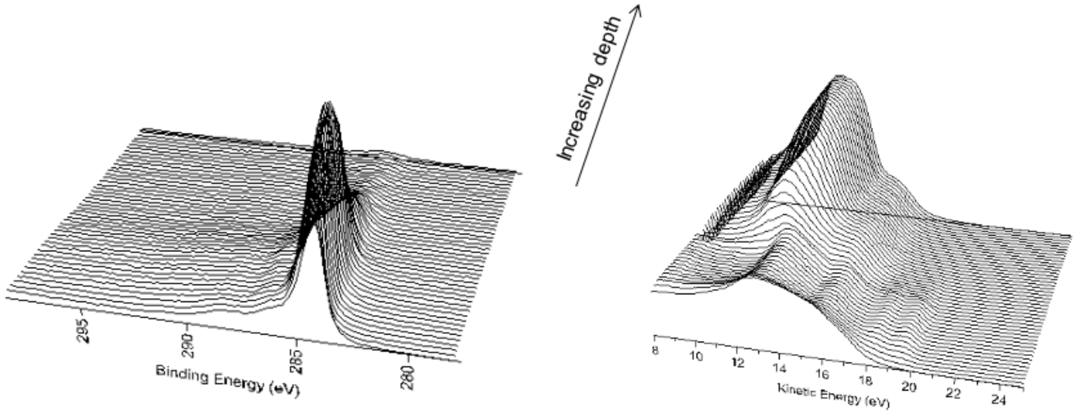


Fig. 12. Multilayered solar cell with 250 nm P3HT:PCBM organic layer and 10 nm ITO layer on glass. 10 keV Ar_{1800}^+ followed by 1 keV Ar^+ (partial depth profile is shown). Non-charge corrected high-resolution C 1s, O 1s, In 3d, and Sn 3d spectra as a function of the sputter cycle. Since sample properties may vary during a depth profile, knowing that charge compensation is working well for the whole profile is useful.

Another feature of modern surface analysis systems is the inclusion of multiple surface analysis techniques, each providing complementary information to XPS. In this example, depth profile on a Thermo-Fisher system, a 10nm C_{60} film deposited on an ≈2 cm diameter insulating CaF_2 substrate and mounted on the sample holder using double sided adhesive tape was analyzed by collecting both XPS and ultraviolet photoelectron Spectroscopy (UPS) data during argon cluster depth profiling (4keV Ar_{2000}^+ clusters from Thermo Scientific MAGCIS source).[49] This allowed collection of elemental/chemical composition of the film using XPS while simultaneously acquiring high quality data relating to the UPS measurements of valence band structure of the C_{60}.

Since the C_{60} film was deposited onto an insulating substrate it was necessary to use the combined electron/argon ion charge compensation source described above. The data was collected sequentially with an increment of sputtering followed by a period of data collection. The charge neutralization condition was such that there was no need to use different compensation modes for XPS and UPS. Even though the probe sizes and sampling depths of XPS and UPS are quite different, the standard XPS charge compensation mode could be successfully used for UPS during the depth profile.



C1s spectra from XPS/UPS cluster profiling

He(I)UPS spectra from XPS/UPS cluster profiling

Fig. 13. Combined XPS/UPS 4keV Ar_{2000}^{+} depth profile of 10nm C_{60} on CaF_2. Both data types were collected using the same charge neutralization parameters.

III. BINDING ENERGY CORRECTION APPROACHES – STRENGTHS AND LIMITATIONS OF COMMON METHODS

Most modern charge compensation systems enable XPS spectra to be collected with the peaks appearing close to the appropriate or expected BEs. However, detailed analysis often requires more precise knowledge of the measured BEs of the photoelectron peaks in the spectra. A variety of methods have been used to determine the amount of binding energy shift that needs to be corrected on insulating samples. These generally assume that differential charging is no longer present on the sample, or at least significantly minimized, and a simple BE correction (Δ_{corr}) can be applied to all the measured BEs from the specimen. As discussed in the introduction, because charging is a three-dimensional time-dependent process influenced by many sample properties, the assumption of a simple BE correction is generally only an approximation.

Several common approaches to determining Δ_{corr} will be described. Each of them has potential applications but also limitations. There is no single simple method to determine absolute BEs from insulating samples. In a study testing two methods of charge referencing for Al-Si-N composite thin films, Pelisson-Schecker et al.[51] make the important observation that one of the methods they tested (gold particles) could be used to reliably "study chemical shifts of sample-relevant species, but that absolute binding energies could not be determined." Although it can sometimes be difficult to extract precise BEs from measurements on insulating materials for the many reasons discussed in the present paper, many different approaches have been successfully used to obtain the needed information.

A. BE correction based on the C 1s peak of adventitious carbon (AdC) – fundamental limitations

By far the most common method for correcting the BE scale for possible charging effects is the approach introduced by Siegbahn and co-workers in the early days of x-ray photoelectron spectroscopy.[52] This method relies on the use of the C 1s spectra of adventitious carbon (AdC) present on essentially all surfaces exposed to the ambient air. This common AdC occurrence together with its simplicity accounts for the great popularity of this technique. As described in ISO and ASTM guides[26, 27] it is assumed that the C-C/C-H component of the measured C 1s spectrum of AdC would have a binding energy in the range of 284.6 to 285.0 eV and that the Δ_{corr} can be determined from the measured peak and applied as a constant shift to all other peaks in the spectrum.

Although the use of AdC for referencing remains important and useful for a variety of purposes, referencing spectra using AdC has inherent fundamental limitations for use as an absolute BEs for both conducting substrates and insulating materials. The identified limitations do not mean that the AdC peak and BE are of no use when dealing with charging on insulators. When the uncertainties described below are recognized and appropriately taken into consideration, the measured BE and shape of C 1s photo peaks will remain a useful indicator of the presence or absence significant surface charging and the adequacy of charge compensation on many types of insulating samples. As described in the polymer guide, C 1s BE referencing (sometimes including AdC) remains useful and valuable tool in many circumstances, but is frequently only part of the consistency check for charge correction (see internal referencing discussion in section III.D).[31]

Limitations regarding the accuracy of use of C 1s method for BE referencing have been pointed out in several papers over the years (for historical perspective see Greczynski and Hultman[1]) – however, such concerns have been overwhelmed by the continuously increasing wave of XPS papers (unfortunately not followed by the corresponding increase in the number of XPS experts) which have used the method because of its simplicity and the apparent lack of easily-accessible and effort-free alternatives. The criticism of this technique includes (a) the unclear chemical nature of AdC, (b) the lack of a well-defined single energy value associated with the C 1s peak of AdC, (c) differences in the methodology of the BE scale correction, (d) use of poor quality spectra as a result of adequate charge neutralizer settings and/or poor sample mounting leading to differential charging, (e) use of spectra with insufficient intensity to accurately identify the main peak, and (f) the lack of understanding when other correction methods could make a correction employing AdC unnecessary.[1]

Recent systematic studies covering a wide range of conducting material systems have confirmed issues raised by others[53] showing in some detail that the chemical nature of an AdC layer varies with the substrate type, the environment it has been exposed to, and the exposure time.[54, 55] Moreover, the BE of the C-C/C-H peak of AdC accumulating on metallic samples (thus free from charge buildup effects) was shown to vary by more than 2 eV.[34] As the magnitude of typical chemical shifts is in the same range, correcting the BE scale to the C 1s peak set at 284.5 eV, or any other arbitrary chosen value, can result in unphysical results and/or incorrect peak assignments. For example, setting the C

1s peak at 284.5 eV, i.e., at the recommended value, for a range of transition metal nitride thin film samples results in a non-zero density of states above the Fermi level.[33]

Perhaps the most important lesson to learn from these studies is that, contrary to common notion, the measured BE of the C 1s peak, as demonstrated of these conducting substrates, is not an inherent property of the AdC layer alone. The substrate influence is decisive – for the wide range of conducting substrates studies the BE of the C 1s peak E_B^F correlated with the sample work function ϕ_{SA}, in such a way that the sum $E_B^F + \phi_{SA}$ = 289.58±0.14 eV,[55] suggesting that invariant binding energy of the AdC C 1s peak with respect to the vacuum level (VL). Such VL alignment may arise under lack of electrical interaction/coupling and no Fermi Level alignment with the substrate (and spectrometer). Effectively, the AdC is not necessarily an integral part of the analyzed sample.

As stated earlier, the AdC C 1s peak has a variety of important uses, but it is not reliable as an absolute BE reference and its use should be evaluated with appropriate care using approaches described in section III.

B. A gold standard?

The presence of a thin metal layer deposited on a sample or metal particles directly or indirectly deposited on a sample has been used to provide a signal with known BE for a charge reference. The metal may be connected to the spectrometer ground by clip, providing both an electrical pathway and BE reference. Au is the most common metal used for this purpose and it may be connected to ground by a conducting clip or isolated on an insulator.[35] Although in some cases the use of Au as a BE reference produced consistent results, it does not necessarily provide an accurate BE reference.[51] It has been found that Au referencing has a significant variety of problems that include island formation, variation of the Au 4f BE with cluster size, substrate interactions, and surface coverage effects. [27, 56, 57] Au referencing can still be useful for some applications but it is not a solution for absolute BE determination[51] and used less frequently now than in the past.

C. Substrate Referencing

For studies involving films on conducting substrates, for which the film is thin enough such that peaks from both the film and the substrate can be measured, it is often assumed that the substrate can be used as an accurate reference for peaks in the film. Often this approach is applied without application of a charge compensation method. Three data collection modes can be imagined: i) substrate grounded, no charge compensation; ii) substrate grounded and charge compensation; iii) substrate isolated from ground with charge compensation applied. Based on the example in section II.D.4, along with the work reported by Sambe and Ramaker[25] and Baer et al. [6, 7] each of these configurations can produce different results. Processes such as charge accumulation at interfaces, film thickness effects, and possibly interfacial interactions limit the accuracy of this approach. The approach may provide useful information and consistent measurements for a set of similar samples. Many in the community recommend that for many types of thin film samples the data would be consistent using mode iii (using charge compensation and the sample isolated from ground). For some samples mode i) can work. Mode ii) usually places a potential gradient across the film and is not recommended for using the substrate as a BE reference.

D. Internal Referencing

Many samples come with some degree of information about the sample composition and chemistry. Such information frequently provides insight that can be used in combination with some of the methods above to establish a self-consistent set of BEs for components in the sample. In the polymer guide,[31] as one example, it is noted that the hydrocarbon components in a polymer backbone often provide “known” peaks that can be used for charge referencing. The guide also notes that other common polymer peaks are also quite useful as listed in table VI.[31] These include hydroxyl groups in cellulose, CF_2 in PTFE and more. In the above examples, charge correcting using the stated C 1s refence values is reliable as the specific functional group chosen are part of the same phase as the rest of the sample under analysis, i.e. the part of the sample chosen as a reference is at the same potential as the rest of the sample.

Catalysts commonly involve an oxide or other substrate made up of well-known materials that may provide a good source for internal referencing. XPS data from a TiO_2 based Pt catalyst that also contains K is shown in Fig. 14. In the figure the spectra for the material in two conditions are shown as referenced to C 1s. As noted in the figure, the structure and shape of the TiO_2 peaks are unchanged and not likely to have been altered in the processing between the two samples while the nature of the C on the catalyst has a significant probability of change during processing. Using carbon as a reference produces roughly equal shifts of the K and Ti peaks before and after processing (≈0.75 eV). With the observation that the major TiO_2 has the same peak structure before and after processing and is unlikely to have a significant change in position, the approach that appears to produce consistent result for this sample is BE referencing is to the Ti $2p_{3/2}$

from TiO_2 peak for determining Δ_{corr} . In this example C 1s is not the best choice for a reference for charge correction as the AdC likely acts as another phase relative to the bulk TiO_2.

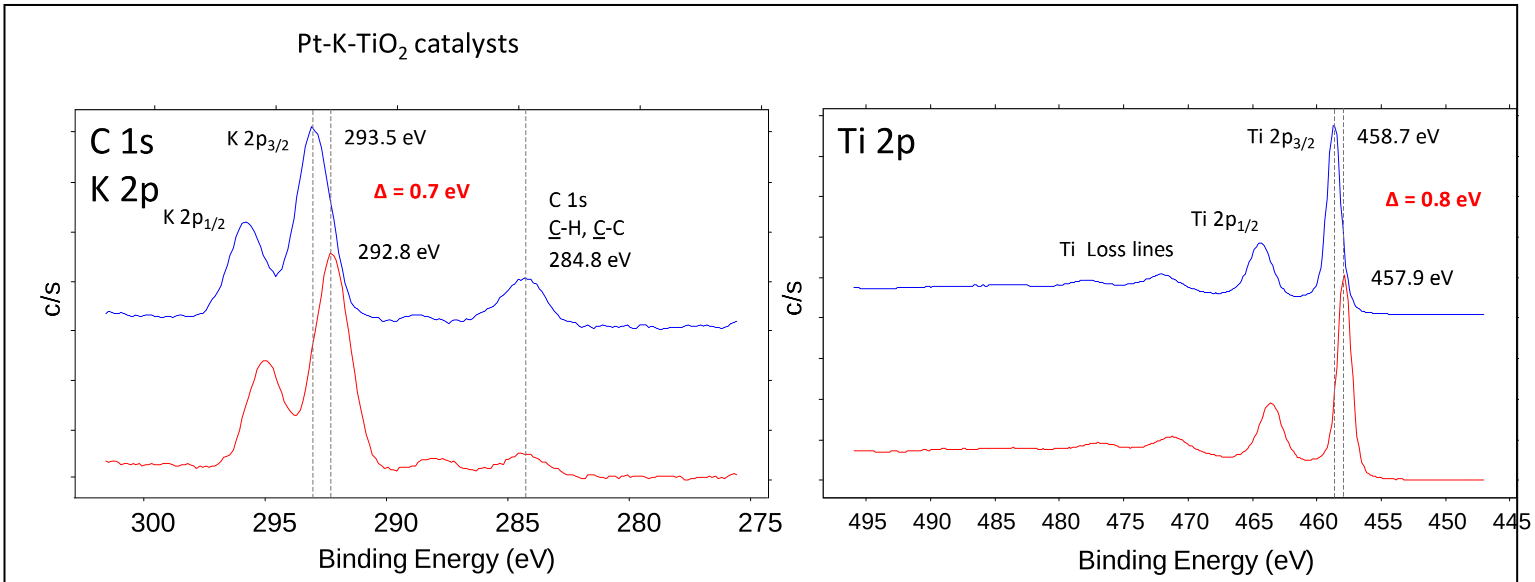


Fig. 14. XPS high resolution of the Ti 2p, C 1s and K 2p photoelectron peaks from a Pt-K-TiO_2 catalyst. When the photoelectron peaks are referenced to C 1s at 284.8 both the Ti and K 2p photoelectron peaks have ≈ 0.75 eV shift before and after catalyst processing. As it is unlike that the Ti 2p peaks have shifted, it appears that the carbon referencing is unreliable and that using known energies for TiO_2 as the basis for determining Δ_{corr} would be most consistent.

E. Using multiple ways to check for data consistency

Often it is useful to consider or apply multiple approaches to determine a useful Δ_{corr} when in the effort to determine the BEs of charge compensated insulating samples. Although this process may be approached in multiple ways, there are several questions that may guide the process:

- Although C 1s is not a reliable absolute BE reference it is frequently useful as a “tentative” reference to determine the adequacy of charge compensation as a preliminary set of BE determinations. It is useful to ask if this preliminary reference produces results consistent with what might be the known chemical composition of the sample?

  - There may be multiple ways to learn if C 1s signals are misleading. For example, when there are chemical changes in a sample due to processing of some type, one chemical species on the sample may be oxidized while another is reduced, and the separation of the peaks will change. If all elements except C have the same relative positions (peak separation) it is likely that there are changes to the C 1s photopeak and nothing else has been altered. Are there signs of differential charging in the spectral envelope? If so, it would be necessary to repeat the experiment with different neutralizer settings or sample mounting approach to obtain a good quality spectrum, if feasible, before relying on the C 1s spectrum for reliable charge referencing. An example of the possible impact of distorted C 1s peak shapes due to inadequate charge compensation is shown in Fig 2 of reference [29]

- Is there a component of the sample that is or might be stable enough or well enough known to be considered to have a *known BE for use as an internal reference*?
  - When considering a photoelectron peak as a possible internal reference, look at the whole peak shape, including loss lines and other features for consistency in peak structure. If considering a one of a kind sample the spectrum might be compared to a standard. When needing to compare several specimens, constancy of peak shape and structure might allow useful comparison.
  - If more than one compound or photoelectron peak might be considered as a known, do they produce consistent Δ_{corr} values?
  - Assuming the species identified above to be a useful reference, do other elements have sensible BEs indicating reasonable chemical states and composition?

    - It may be useful to remember that both chemical environment and electrostatic effects arising from molecular dipoles can influence core level BE measurements.[58] Thus the assumed position of the BEs of known species may be somewhat influenced by factors such as surface coverage, interfacial charge, and the configuration of neighboring molecules.
- For chemical species tentatively identified, are the peak intensities for all elements consistent with the compound compositions expected? For example, if CF_2 is identified in the C 1s spectrum, is the appropriate amount of F present?

IV. IMPORTANCE OF REPORTING METHODS USED

Because of the variety of methods that can be used for charge control and assumptions that can be used in determination of binding energy corrections in XPS it is critical for analysts to report procedures applied in their analysis to enable other to assess and understand the reported data and results. ISO standard 19318 *Surface chemical analysis — X-ray photoelectron spectroscopy — Reporting of methods used for charge control and charge correction* addresses this issue. The introduction of the standard notes that “There is, at present, no universally applicable method or set of methods for charge control or for charge correction. This International Standard specifies the information that shall be provided to document the method of charge control during data acquisition and/or the method of charge correction during data analysis.”[59]

V. Summary

The use of XPS for the analysis of fully or partially insulating samples is of increased importance in many areas of science and technology. This guide summarizes the issues and challenges associated with the analysis of such specimens, suggests ways to identify when surface charging is an issue, provides examples of approaches to controlling surface charge and summarizes some of the methods that can be used to determine appropriate BEs for such materials.

It is important to note that there are many sources of BE shifts in insulating and semiconducting materials and there is no simple way to obtain the “ideal” fundamentally correct BE for each peak in a spectrum in many circumstances. Regardless, with appropriate care it is usually possible to collect and analyze XPS data on such materials to obtain the desired information as the determination of the absolute binding energies is not always necessary. It is important for analysts to report the procedures that they have applied to deal with sample charging and the approach used to determine BEs. ISO Standard 19318 provides information about what should be reported.

Differential charging within or along the surface of specimens is a common problem. In many circumstances it has been found useful to isolate specimens from ground so the charge compensation system in a spectrometer controls the sample potential. Although the build-up of charge during XPS analysis is often viewed as a problem, it also can be used to extract important information about sample properties.

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Appendix - Terminology related to surface charging and charge referencing

There are many terms associated with surface charging, charge neutralization and binding energy referencing in XPS. Several of the most relevant consensus definitions developed by ASTM International Committee E 42 on surface analysis and International Organization for Standardization (ISO) Technical Committee 201 (TC201) on Surface Chemical Analysis are included below. The full set of this terminology (ISO 18115 part 1) is available at no cost from several websites.[60, 61] The importance of consistent terminology for XPS reproducibility has been discussed by Shard and Baer.[28] It is also important to remember that definitions may need to change or evolve as understanding advances. A new version of ISO 18115 is being developed and your suggestions for improvements, clarification, or additional terms is most welcome. Suggestions can be made to the chairman or secretaries of ISO TC201 or the terminology subcommittee ISO TC201 SC1.

The terms below may provide some background or clarification of issues identified or discussed in this paper. In addition to defining the terms, there are often notes with the definitions that provide additional context and application notes. Many of these notes are included in this annex as well. The numbers contained within brackets stated within or after definitions or notes refer to definitions of other terms in ISO document 18115-1.

Many of the concepts and issues identified in this paper are called out in the notes. For example, *adventitious carbon referencing* is defined, but note 2 for that definition includes the statement, “This method does not determine the true *charging potential* (4.103) since the true binding energy of the adsorbed hydrocarbons is not known.” The three-dimensional nature of surface charging and the importance of interfaces are called out in the definition of *charging potential* which contains two notes. Note 1, different charging potentials can occur on different areas or at different depths in a sample, arising from sample inhomogeneities or non-uniform intensity of the incident *flux* (4.221) of radiation. Note 2, the surface and bulk potentials can differ, for example as a result of band bending, *interface* (4.253) dipoles and charge centers.

Definitions and Notes from ISO 18115-1[61] relevant to sample charging, charge neutralization, and charge referencing

sample charging (definition 4.392): change in the electrical potential in the sample or on the sample *surface* (4.458) caused by particle or photon bombardment *charging potential* (definition 4.103): electrical potential of the surface region of an insulating sample, caused by irradiation

> Note 1 to entry: Different charging potentials can occur on different areas or at different depths in a sample, arising from sample inhomogeneities or non-uniform intensity of the incident *flux* (4.221) of radiation.
>
> Note 2 to entry: The surface and bulk potentials can differ, for example as a result of band bending, *interface* (4.253) dipoles and charge centers.

charge modification (definition 4.97): alteration of the amount or the distribution of charge at a sample *surface* (4.458)

Fermi level referencing (definition 4.212): establishing the *binding energy* (4.82) scale for a particular sample by assigning the *kinetic energy* (4.278) corresponding to the *Fermi level* (4.211), as determined by analysis of the sample's *XPS* (3.23) or *UPS* (3.22) spectrum, as the point of zero binding energy

> Note 1 to entry: See *vacuum level referencing* (4.484).

vacuum level referencing (definition 4.484): method of establishing the *kinetic energy* (4.278) scale in which the zero point corresponds to an electron at rest at the *vacuum level* (4.483)

> Note 1 to entry: See *Fermi level referencing* (4.212).

vacuum level (definition 4.483) electric potential of the vacuum at a point in space

> Note 1 to entry: See *Fermi level* (4.211).
>
> Note 2 to entry: In electron spectroscopy, the point in space is taken at a sufficiently large distance outside the sample such that electric fields caused by different *work functions* (4.487) of different parts of the *surface* (4.458) are zero or extremely small.

charge neutralization (definition 4.98) [DEPRECATED: charge compensation and charge stabilization]: maintenance at a fixed potential, usually near neutrality, of the *surface* (4.458) of a non-conducting or poorly conducting sample material under bombardment by primary particles or photons

> Note 1 to entry: Charge neutralization can be accomplished by bombarding the surface with electrons or, more rarely, ions or photons.

electron flooding (definition 4.188) irradiation of a sample with low-energy electrons in order to change or stabilize the *charging potential* (4.103)

charge referencing (definition 4.99): method by which the *charging potential* (4.103) of a sample is determined in order to correct the measured energies so that those energies correspond to a sample with no surface charge

> Note 1 to entry: Charge referencing is often conducted using *adventitious carbon referencing* (4.4), using *internal carbon referencing* (4.257) or by *gold decoration* (4.234).

Note 2 to entry: Different charging potentials can occur on different areas or at different depths in a sample, arising, for example, from sample inhomogeneities or non-uniform intensity of the incident *flux* (4.221) of radiation.

adventitious carbon referencing (definition 4.4): determining the *charging potential* (4.103) of a particular sample from a comparison of the experimentally determined C 1s *binding energy* (4.82), arising from adsorbed hydrocarbons on the sample, with a standard binding energy value

Note 1 to entry: See *Fermi level referencing* (4.212) and *internal carbon referencing* (4.257).

Note 2 to entry: A nominal value of 285,0 eV is often used for the binding energy of the relevant C 1s peak, although some analysts prefer specific values in the range 284,6 eV to 285,2 eV, depending on the nature of the substrate. This method does not determine the true *charging potential* (4.103) since the true binding energy of the adsorbed hydrocarbons is not known.

Note 3 to entry: Different *sample charging* (4.392) potentials can occur on different areas on the *surface* (4.458), or at different depths, arising, for example, from sample inhomogeneities or non-uniform intensity of the incident radiation *flux* (4.221).

internal carbon referencing (4.257): method by which the *charging potential* (4.103) of a particular sample is determined from a comparison of the experimentally determined C 1s *binding energy* (4.82) arising from a specific carbon group within the sample with a standard binding energy value for that carbon group

Note 1 to entry: See *adventitious carbon referencing* (4.4) and *Fermi level referencing* (4.212).

Note 2 to entry: A hydrocarbon group within the sample is often used for this purpose.

gold decoration (definition 4.234): method whereby a very small quantity of gold, deposited as unconnected islands on an insulator, is used for *charge referencing* (4.99)

Note 1 to entry: See *adventitious carbon referencing* (4.4) and *internal carbon referencing* (4.257).

Note 2 to entry: The gold can be deposited by evaporation or by immersion of the *surface* (4.458) in a solution that produces a colloidal gold deposit.

Note 3 to entry: The *binding energy* (4.82) for the Au 4f7/2 peak is often taken as 84,0 eV, although measured values of this binding energy for gold deposited on a conducting substrate vary with the average gold island diameter.

The definitions for *peak energy*, *chemical shift*, *binding energy*, and *Auger parameter* are not primarily associated with charge neutralization or energy referencing but are none-the-less relevant. An analyst is usually interested in *chemically* related *shifts* of photoelectron *peak energies* that are associated with changes in the *binding energy* of electrons in the sample and not those induced by sample charging. As indicated by note 4, the Auger parameter can sometimes be useful to obtain chemical information in the face of binding energy uncertainties.

peak energy (definition 4.327): energy value corresponding to the intensity maximum in a direct spectrum (4.173) or to the intensity minimum for a differential spectrum (4.171).

chemical shift (definition 4,105): change in *peak energy* (4.327) arising from a change in the chemical environment of the atom

binding energy (definition 4.82): energy that shall be expended in removing an electron from a given electronic level to the Fermi level (4.211) of a solid or to the vacuum level (4.483) of a free atom or molecule.

Auger parameters (definition 4.41) *kinetic energy* (4.278) of a narrow *Auger electron* (4.37) peak in a spectrum minus the kinetic energy of the most intense photoelectron peak from the same element

> Note 1 to entry: See initial-state *Auger parameter* (4.42) and *modified Auger parameter* (4.43).
>
> Note 2 to entry: The value of the Auger parameter depends on the energy of the X-rays, which therefore needs to be specified.
>
> Note 3 to entry: The Auger parameter is sometimes called the *final state* (4.215) Auger parameter.
>
> Note 4 to entry: The Auger parameter is useful for separating chemical states for samples in which charging causes uncertainty in the *binding energy* (4.82) measurement or in which the binding energy shift is inadequate to identify the chemical state.
>
> Note 5 to entry: The Auger parameter is useful for evaluating the *relaxation energy* (4.380) of the ionized matrix atom associated with the generation of a core *hole* (4.237) for those *Auger transitions* (4.46) between core levels which have similar *chemical shifts* (4.105).

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