ORCA – Online Research @ Cardiff

Citation for final published version:

Baer, Donald R., Artyushkova, Kateryna, Cohen, Hagai, Easton, Christopher D., Engelhard, Mark, Gengenbach, Thomas R., Greczynski, Grzegorz, Mack, Paul, Morgan, David J. and Roberts, Adam 2020. XPS guide: Charge neutralization and binding energy referencing for insulating samples. Journal of Vacuum Science and Technology A 38 (3) , 031204. 10.1116/6.0000057

Publishers page: http://dx.doi.org/10.1116/6.0000057

JVST A
Journal of Vacuum Science & Technology A

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

Cite as: J. Vac. Sci. Technol. A **38**, 031204 (2020); https://doi.org/10.1116/6.0000057
Submitted: 30 January 2020 . Accepted: 06 April 2020 . Published Online: 24 April 2020

Donald R. Baer, Kateryna Artyushkova, Hagai Cohen, Christopher D. Easton, Mark Engelhard, Thomas R. Gengenbach, Grzegorz Greczynski, Paul Mack, David J. Morgan, and Adam Roberts

COLLECTIONS

Paper published as part of the special topic on Special Topic Collection: Reproducibility Challenges and Solutions
Note: This paper is part of the Special Topic Collection on Reproducibility Challenges and Solutions.

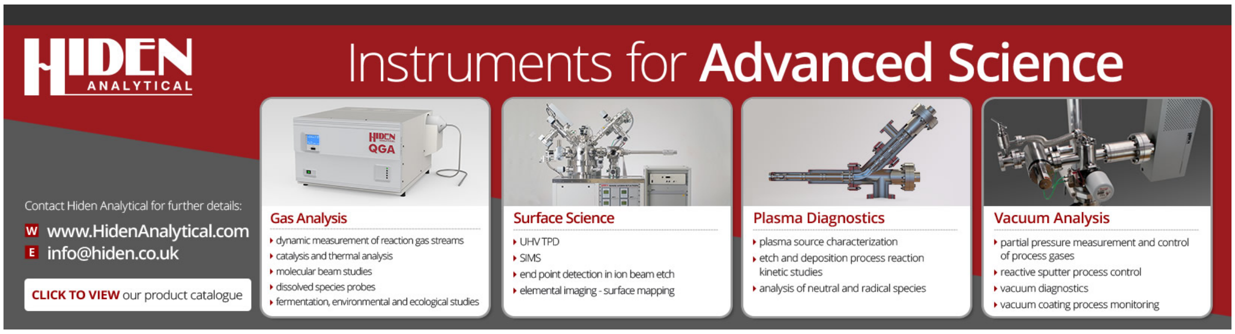
View Online
Export Citation
CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Practical guides for x-ray photoelectron spectroscopy: Analysis of polymers
Journal of Vacuum Science & Technology A **38**, 023207 (2020); https://doi.org/10.1116/1.5140587

Uncertainties in photoemission peak fitting accounting for the covariance with background parameters
Journal of Vacuum Science & Technology A **38**, 033211 (2020); https://doi.org/10.1116/1.5143132

Misconceptions in interpretation of nitrogen chemistry from x-ray photoelectron spectra
Journal of Vacuum Science & Technology A **38**, 031002 (2020); https://doi.org/10.1116/1.5135923



HIDEN ANALYTICAL
Instruments for Advanced Science
Contact Hiden Analytical for further details:
W www.HidenAnalytical.com
E info@hiden.co.uk
CLICK TO VIEW our product catalogue

Gas Analysis
- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

Surface Science
- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

Plasma Diagnostics
- plasma source characterization
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species

Vacuum Analysis
- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

J. Vac. Sci. Technol. A **38**, 031204 (2020); https://doi.org/10.1116/6.0000057 **38**, 031204

© 2020 Author(s).

JVST A
Journal of Vacuum Science & Technology A

TUTORIAL

avs.scitation.org/journal/jva

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

Cite as: J. Vac. Sci. Technol. A **38**, 031204 (2020); doi: 10.1116/6.0000057
Submitted: 30 January 2020 · Accepted: 6 April 2020 ·
Published Online: 24 April 2020

Donald R. Baer,[1,a)] Kateryna Artyushkova,[2] Hagai Cohen,[3] Christopher D. Easton,[4] Mark Engelhard,[1] Thomas R. Gengenbach,[4] Grzegorz Greczynski,[5] Paul Mack,[6] David J. Morgan,[7] and Adam Roberts[8]

AFFILIATIONS

[1] Pacific Northwest National Laboratory, Richland, Washington 99352
[2] Physical Electronics, 18725 Lake Drive East, Chanhassen, Minnesota 55317
[3] Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel
[4] CSIRO Manufacturing, Clayton, Victoria 3168, Australia
[5] Department of Physics (IFM), Linkoping University, SE-581 83 Linkoping, Sweden
[6] Thermo Fisher Scientific, East Grinstead, West Sussex RH19 1XZ, United Kingdom
[7] School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom
[8] Kratos Analytical Ltd, Manchester M17 1GP, United Kingdom

Note: This paper is part of the Special Topic Collection on Reproducibility Challenges and Solutions.
[a)] **Electronic mail:** don.baer@pnnl.gov

ABSTRACT

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: (1) *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; (2) *vacuum level (VL) 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 and the Appendix of this paper).

Charge accumulation and dipole layer formation near interfaces involving nonconducting 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: (1) 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 (2) applying a *postacquisition 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 Sec. 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 $10^{-10}\,\Omega^{-1}\,\mathrm{m}^{-1}$ 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 nonuniform 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.[12] 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.
  - ○ Complex (and even relatively simple) materials can establish nonuniform (often called differential) charging in multiple ways. Causes include variations in photoelectron yields, film or sample thickness and composition 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 toward 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 neutralization 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 the relevance of this model when examining the data reported in Sec. II D 4 for Al_2O_3 on Al.)

(1) Uniform potential—If the film and substrate are both conducting, the potential through the sample and analysis layer would be uniform [Fig. 1(a)].
(2) 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. 1(b)]. 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.
(3) Step in potential and an electric field—An electric field across the oxide would create a potential gradient [Fig. 1(c)] 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 Sec. II B 2 for Pb 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.

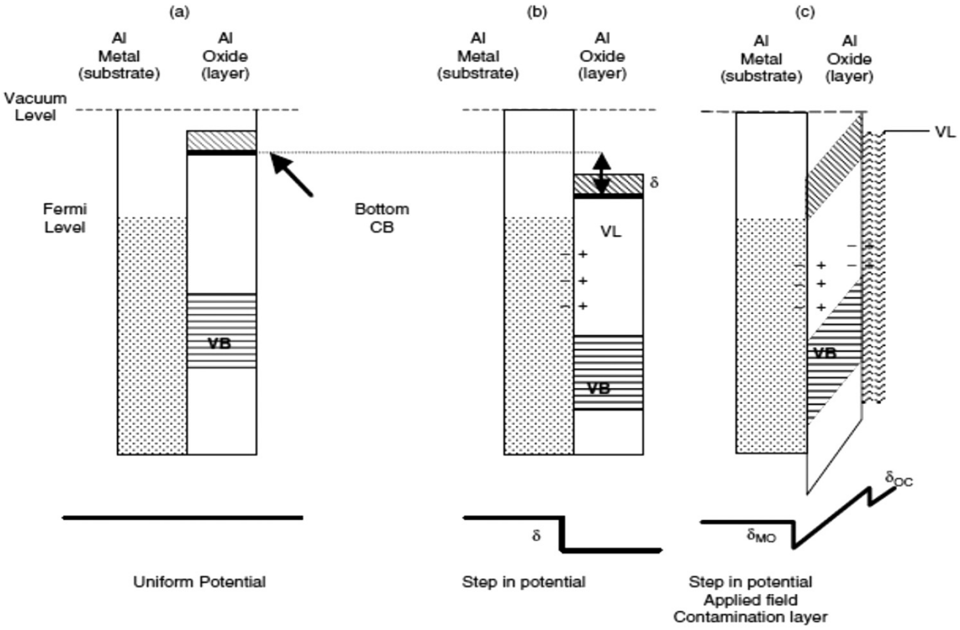


FIG. 1. Schematic drawing of energy levels and potentials across an Al and AlO_x sample based on concepts of Sambe and Ramaker (Ref. 25) for three situations: (a) ideal uniform potential; (b) with interfacial charge accumulation leading to a step in the potential; (c) presence of both charge accumulation at the interface and an electric field across the film. Used with permission from Baer *et al.*, Surf. Interface Anal. **33**, 781 (2002). Copyright 2002, John Wiley & Sons, Ltd.

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 Sec. 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 an 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 the 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 neutralization 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 peak 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 main peaks from multiple analysis points can be one way to identify peak broadening as a result of differential charging.
  - ○ With the analyzer in snapshot mode (where feasible), differential charging can cause the spectrum to shift across the BE scale and the spectral envelope to change with time.
- Has the operation of the charge neutralization 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 setup or performance tests?

2. Effectiveness of charge neutralization 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, e.g., by altering the x-ray source current, 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 and/or position, offer an additional way to identify differential charging effects. It may be similarly useful to modify the x-ray beam shape and size, which is easy to do in systems with focused x rays.

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 neutralization 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.

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 linewidth appropriate for the planned spectrometer operation mode. For systems using monochromatic Al Kα x rays, charge neutralization parameters are frequently adjusted until the FWHM is 0.8 eV or better when data are collected in a high energy resolution mode.

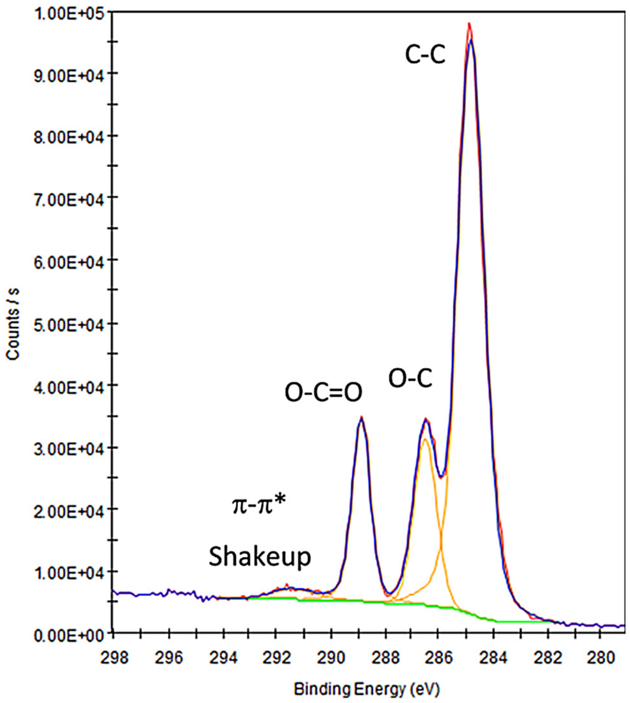


FIG. 2. C 1s spectrum PET. Such spectra are often used to test the performance of a charge neutralization system. The linewidth of the O—C═O peak is often used as a test to verity that the system is working appropriately. Data from a Thermo Fisher system.

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, depending on the structure of the PET, but these structure variations did not change the width of the O—C═O peak that is usually measured to verify homogeneous 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 glovebox 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 neutralization 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 the following:

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, the UV tail of the light source would be the most effective, 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 Pb 4f XPS signals were unstable and not reproducible, even with charge neutralization, when the sample was grounded. However, the combination of charge neutralization and isolation from the 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 also enhance sample damage during x-ray irradiation and flood gun exposure.

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, 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 way 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 parameters of an electron flood gun (eFG) (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] This approach enables novel extensions of XPS as an electrical probe, as mentioned above, and can also be applied enhance chemical (and structural) analyses.

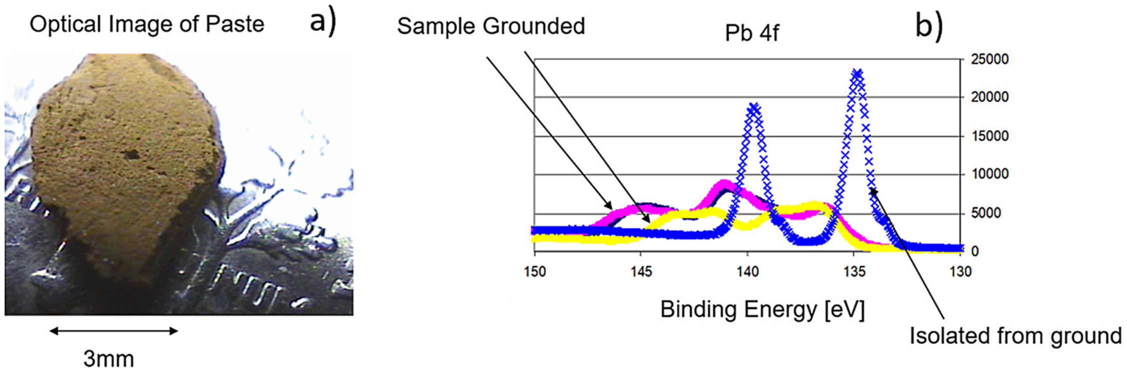


FIG. 3. (a) Optical image of advanced battery electrolyte. (b) Pb 4f XPS spectra collected from electrolyte with charge neutralization with the sample in grounded (two datasets as marked) and isolated from ground configurations. For this relatively large XPS sample, the presence of both a ground potential and a potential controlled by the electron flood gun created differential charging and a highly distorted signal. With the sample isolated 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.

C. Example charge neutralization 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 neutralization 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, nonuniform surface charging often emerges, especially with the use of focused x-ray beams, for which the balance between outgoing (photoejected) electrons and the incoming electron flux from the neutralizer can vary strongly across the analysis area. Therefore, instruments using focused x-ray 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 neutralization systems for specific instruments or manufacturers along with examples of the use of the system. Descriptions of charge neutralization 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 neutralization.

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 that forms part of the input optics for the lens/analyzer of the spectrometer.

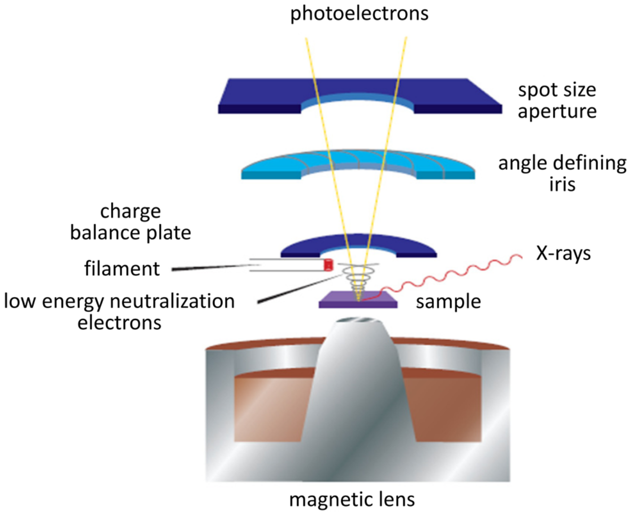


FIG. 4. Schematic diagram showing the charge neutralizer assembly, relative to the magnetic and electrostatic lenses of the Kratos AXIS spectrometer.

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 that may be incident on the charge balance electrode, causing secondary electrons to be emitted. These electrons are focused back toward 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. Modeling shows that the charge neutralization electrons will follow this helical trajectory toward 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 (0–5 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 is 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 toward 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 that 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 the measured peak position of the adventitious hydrocarbon C 1s core level between ∼282.5 and 284 eV 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 Sec. III.

2. Physical Electronics (PHI) spectrometers

The current generation of spectrometers from Physical Electronics use a focused x-ray source that benefits from a combination of electrons and ions for charge neutralization of the sample surface. For these PHI systems, it is important to understand how the charge neutralization 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 neutralization 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 the 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.

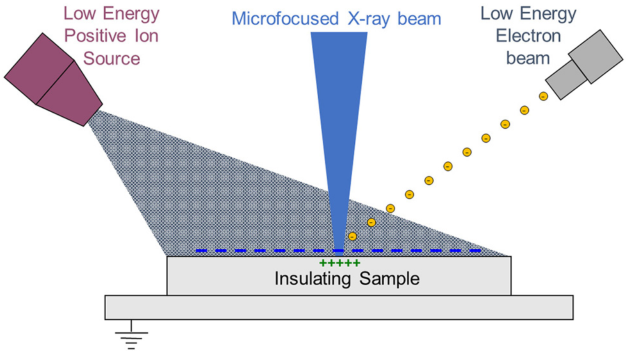


FIG. 5. Schematic drawing of PHI's dual beam charge neutralization method that uses a low-energy electron beam to neutralize the charge created by the x-ray source simultaneously with a low-energy ion beam to eliminate electrostatic charges on the sample surface.

As suggested by the schematic in Fig. 5, the low-energy ions cover a wide area of the sample while the low-energy flooding electrons 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 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 20–21 μA emission current with ∼30 V of extraction and 1–1.5 V of bias. The ion neutralizer is operating in a floating mode producing 3 mA of filament emission current. The beam voltage is set to ∼110 V while applying a −103 V float, which 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 incidence to the sample surface and photoelectrons at 45° 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 Sec. II D 3, some sensitive samples may be chemically damaged by ion and/or electron beam neutralization schemes. PHI's dual beam charge neutralization system enables independent control over electron and ion gun settings, thus allowing customized charge neutralization modes for electron damage-sensitive or challenging materials.

The following practices are characteristic of one analyst (M.E.) 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 are effective, 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 1–1.5 V. 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-sided 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 setup 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 in. in diameter) and that the cold cathode emission source for the low-energy electrons can age requiring further adjustments.

3. Thermo Fisher Scientific spectrometers

Many Thermo Fisher Scientific XPS systems involve microfocused 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 neutralization schematically shown in Fig. 6. A general description of the operation of this charge neutralization system is given 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 Fig. 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 toward 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 buildup due to photoemission, but the argon ions prevent the buildup 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 the electrons 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.

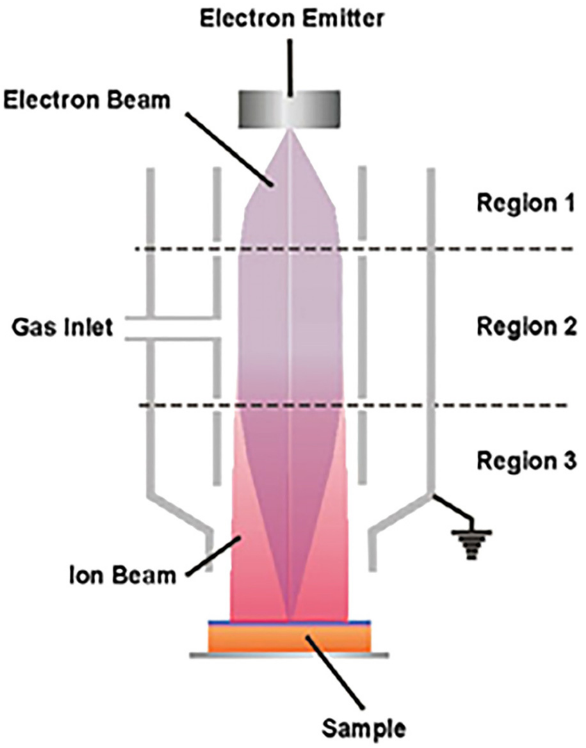


FIG. 6. Schematic diagram of Thermo Scientific XPS charge neutralization system that introduces both low-energy electrons and ions to the sample. Electrons are emitted in region 1; electrons interact with and ionize Ar gas in region 2. Both ions and electrons impinge on the sample traveling through region 3. From Edwards *et al.*, Surf. Interface Anal. **51**, 925 (2019). Copyright 2019, John Wiley & Sons, Ltd.

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 that produce excellent data, as shown by measurements on PET. As described in an example below (Sec. 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.

D. Example uses of charge neutralization systems

1. Verifying the adequacy of charge neutralization 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 vendor systems, there are multiple modes of instrument operation (small area, different x-ray scan rates, tilt angles, and in newer systems that use monochromatic Al kα and higher energy monochromatic Cr Kα x-ray sources). Although these data are 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 (Sec. 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. With this setup, neutralization is relatively robust, working well for many sample types, with both Al Kα and Cr Kα x-ray sources, and during depth profiles as shown in Sec. II D 5. Regardless, it is always recommended to verify that the charge neutralization is working appropriately.

Many insulating samples or those isolated from ground have adequate charge neutralization from modern charge control systems that were previously optimized using test specimens such as PET. However, some samples need extra attention and possible adjustments to charge neutralization conditions. The nature of challenging samples may vary depending on the charge control system. As noted in Sec. 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 nonconducting samples. As discussed in Sec. II D 2, rough powder surfaces can complicate charge neutralization, and this may apply to other rough insulating surfaces as well. In an earlier work, it was noted that nonhomogeneous systems, especially mixed-conducting and nonconducting, present a variety of challenges including differential charging.[6]

Data for alumina and carbon black shown in Fig. 7 show that effective and reproducible charge neutralization can be achieved for all modes of acquisition on both insulating and mixed-conductive/nonconductive materials, different takeoff angles (TOAs), different sizes of microfocused x rays, and different scan types (points, lines, areas). The samples used in these tests were all mounted using double-sided adhesive tape. As discussed above, the combination of isolation of insulating powder such as alumina from ground and charge neutralization decreases the possible effects of differential charging. Using double-sided (nonconducting) 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 were collected without adjusting the neutralization conditions from those described earlier. Amplitude normalized but not energy corrected, high-resolution spectra for insulating alumina ceramic sample were obtained using different sizes of line scans [Fig. 7(a)] and at three different TOAs [Fig. 7(b)]. For a carbon black sample, amplitude normalized energy uncorrected spectra are shown from three different areas on the sample obtained using 20-μm x-ray spot [Fig. 7(c)] and the same region of the sample using 100- and 10-μm x-ray spots [Fig. 7(d)]. These unadjusted spectra without any energy 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 Sec. 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 quality data are 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 vs 0.83 eV for the Al source.

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, which was loaded into a powder well without further intervention, leaving the top

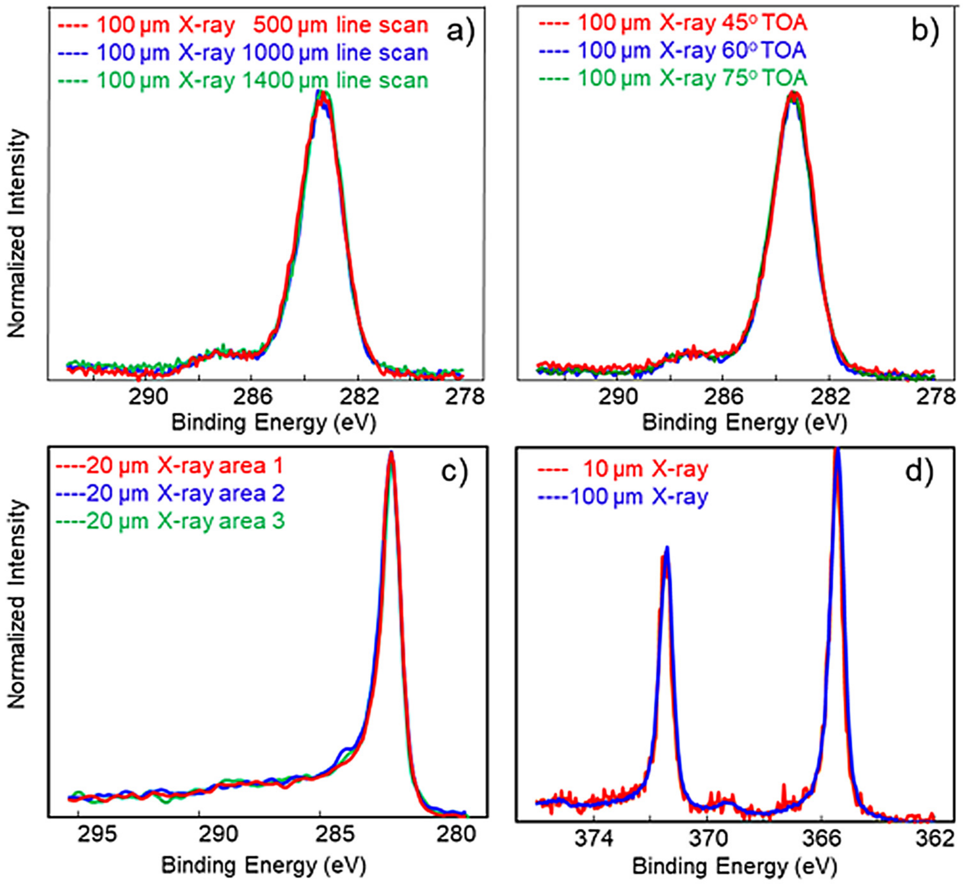


FIG. 7. Demonstration of neutralization stability for different modes of operation for a PHI system. All samples were mounted on double-sided nonconductive sticky tape. (a) Raw data recorded under dual beam neutralization, showing the normalized high-resolution C 1s spectra from insulating alumina ceramic obtained using different line scans with a 100 μm x-ray beam size; (b) non-charge-corrected normalized high-resolution C 1s spectra from insulating alumina ceramic obtained at three different takeoff angles using a 100 μm x-ray beam; (c) non-charge-corrected normalized high-resolution C 1s spectra from three areas on Ag-doped carbon black obtained using a 20 μm x-ray beam; and (d) non-charge-corrected normalized high-resolution Ag 3d spectra on carbon black obtained using 10 and 100 μm x-ray beam sizes. Because charge neutralization needs will vary with sample type and x-ray flux, verifying adequacy of operation in different conditions can be important.

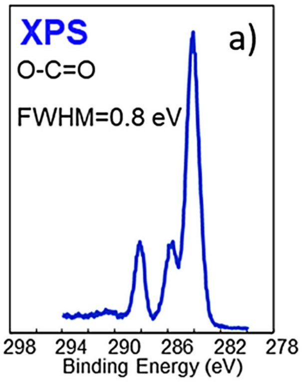


FIG. 8. (a) High-resolution XPS and (b) HAXPES C 1s spectra from PET obtained using Al Kα and Cr Kα x-ray sources on a PHI system. The consistent verification of the ability to observe the structure of test specimens such as PET provides an indication that the standard charge neutralization settings work appropriately for either x-ray source. There is a difference in peak resolution due to the difference in x-ray linewidths as noted in the text. For the Al Kα source, data were collected with a 13 eV pass energy and for Cr Kα source a 26 eV pass energy was used. For each, data were collected with a step size of 0.05 eV.

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 buildup 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 Sec. 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

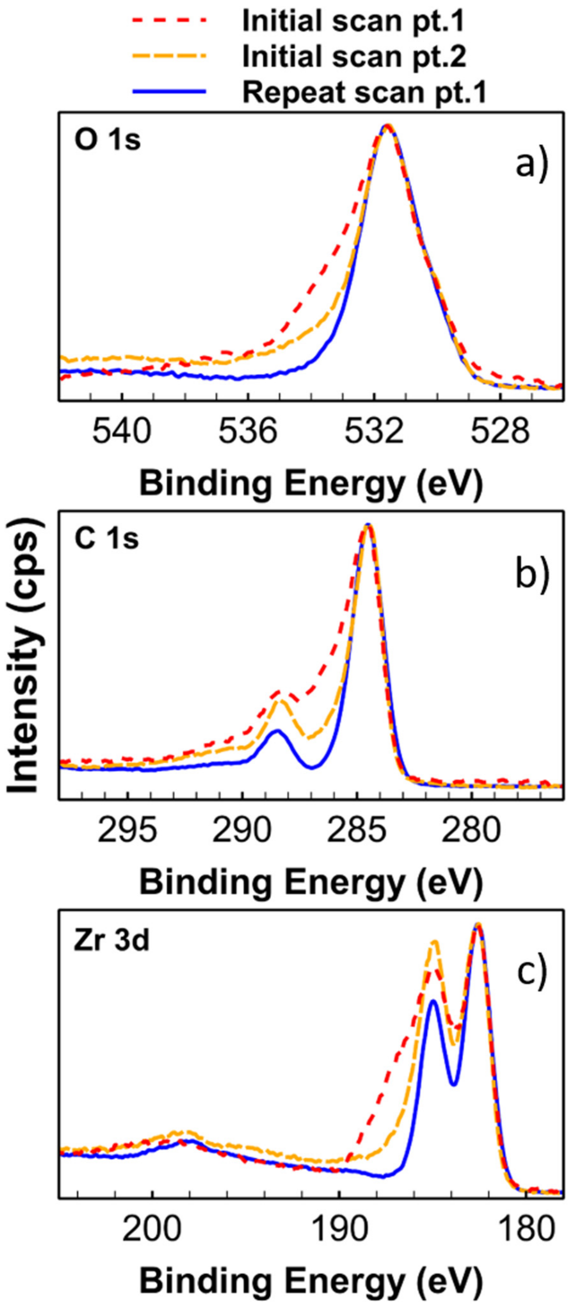


FIG. 9. Representative high-resolution (a) O1s, (b) C 1s, and (c) Zr 3d spectra from UiO-67 MOF collected under identical hardware parameters. The intensity in all panels is normalized at the major peak. Initial scans at pt. 1 (dotted line) and 2 (dashed line) are collected from a powder sample that was unevenly packed into a sample well, presenting a relatively rough top surface to the spectrometer. Repeat scan pt. 1 (solid 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 neutralization, the example highlights the value of considering possible causes of “odd” peak shapes.

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 provide confidence in the quality of your data.

3. Minimizing damage to highly sensitivity samples

Charge neutralization 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 neutralization system could decrease damage to several materials.

Edwards *et al.*[29] examined the impact of two different operating conditions using the Thermo Fisher charge neutralization system on damage of highly sensitive systems. Condition A is characteristic of a common neutralization setup described in Sec. 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, neutralization 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.

An important message from this example is that even for a highly advanced neutralization system, it is useful to check if standard operating conditions in combination with the needed time for data collection produce sample damage. It is possible to optimize either the charge neutralization 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 these data were 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 bandgap 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. Figure 11(a) shows the high-resolution Al 2p region from the sample mounted in electrical contact with the spectrometer and data acquired

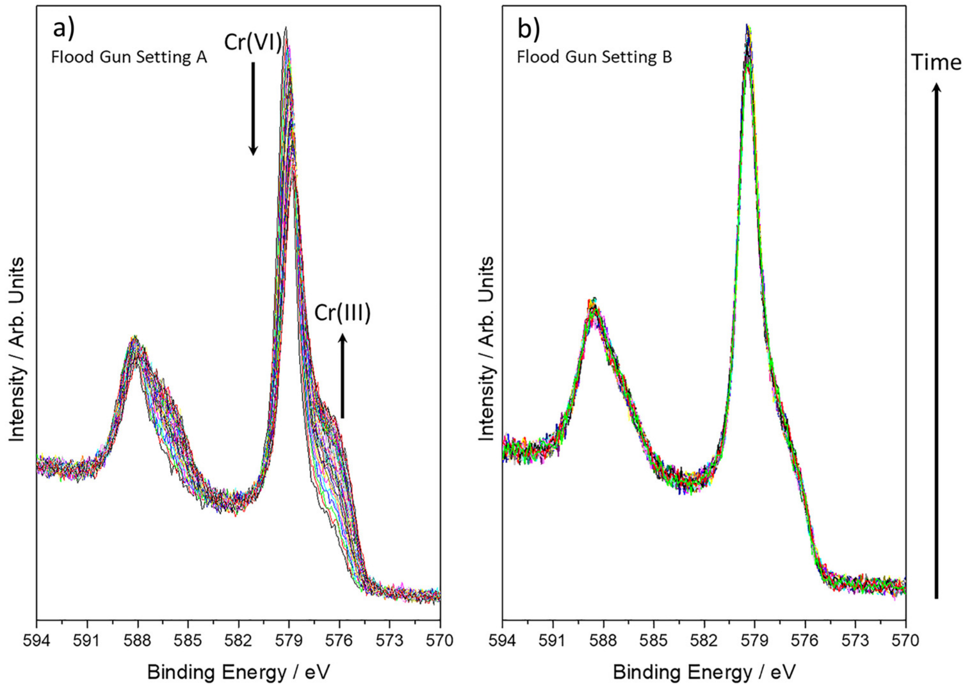


FIG. 10. Overlaid Cr 2p core-level spectra for CrO_3 showing differences in damage rates for a highly sensitive material depending on neutralizer settings: (a) using the normal flood gun setting A and (b) using flood gun parameters, B, optimized to neutralize but minimize damage for highly sensitive materials. Clearly, setting B had less reduction of Cr(VI) to Cr(III). See text for details. From Edwards *et al.*, Surf. Interface Anal. **51**, 925 (2019).Copyright 2019, John Wiley & Sons, ltd.

without use of the electron flood gun. As shown in Table I, the FWHM of the Al $2p_{3/2}$ component is measured to be 0.43 eV and its BE at 72.8 eV. The energy separation (ΔE) between the Al $2p_{3/2}$ (metal)–Al $2p_{3/2}$ (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 $2p_{3/2}$ (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.

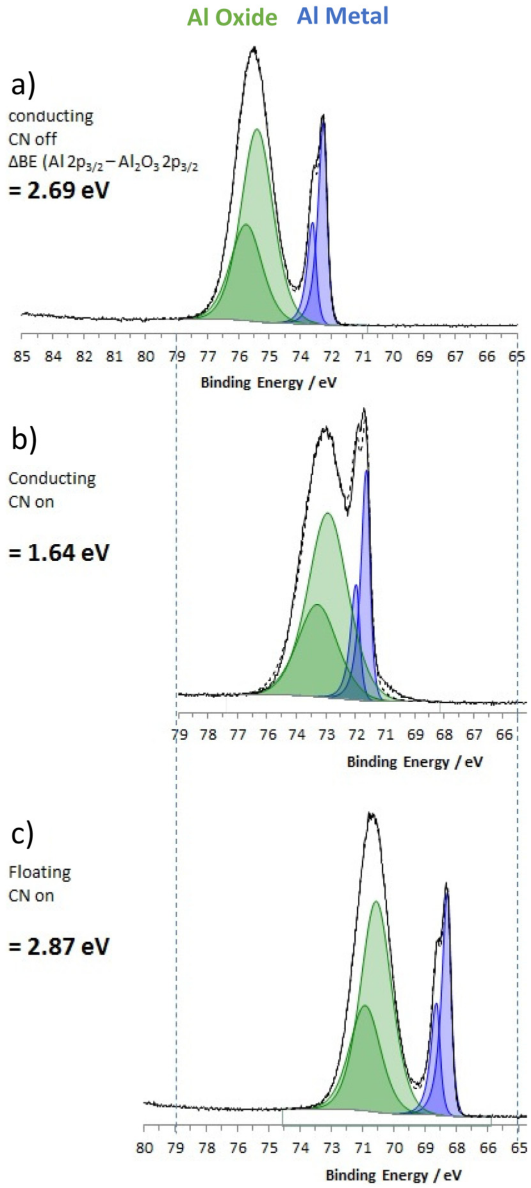


FIG. 11. Al 2p spectra acquired using different combinations of grounding and neutralizer operation: (a) the sample mounted in electrical contact with the sample holder, neutralizer off; (b) the sample mounted in electrical contact with the sample holder, neutralizer on; and (c) the sample mounted floating, electrically isolated from the sample holder, neutralizer on. This example highlights advantages of isolating a specimen from ground and points out challenges associated with referencing elements of a thin film to components of an underlying conducting substrate.

TABLE I. Properties of Al spectral data from Fig. 11. CN=charge neutralizer, ox=Al oxide, met=Al metal.

	(a) Conducting CN off	(b) Conducting CN on	(c) Floating CN on
FWHM of Al $2p_{3/2}$ ox (eV)	1.52	1.98	1.46
FWHM of Al $2p_{3/2}$ met (eV)	0.43	0.46	0.44
BE of Al $2p_{3/2}$ ox (eV)	75.45	73.03	70.71
BE of Al $2p_{3/2}$ met (eV)	72.76	71.39	67.84
Δ (BE Al ox—BE Al met) (eV)	2.69	1.64	2.87

The recommended approach 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 configuration, the ΔE separation between the Al $2p_{3/2}$ (metal)–Al $2p_{3/2}$ (oxide) is 2.87 eV and FWHM of the metallic Al $2p_{3/2}$ component = 0.44 eV. It is noted that the reported literature values for ΔE separation between the aluminum metallic and oxide photoemission peaks vary between ~1.7 eV and 3.3 eV with the oxide film thickness,[6,45] the film structure, as well as the 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.[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 (Sec. III C). Careful analysis of insulating samples requires thought, experimental care, and a consistent approach.

5. Charge neutralization during sputter depth profiles

Robust neutralization is critical during the depth profiling, particularly of mixed inorganic and organic composited and layered structures. During a depth profile differential charging can be introduced by the normal XPS process and 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 at minimized damage to organic materials. In the first example, monatomic Ar ion sputtering is used to achieve needed sputter rates for the inorganic ITO substrate.[50]

The spectra and depth profile of a 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 Fig. 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. A 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, followed by monatomic Ar^+ sputtering through the ITO layer. A 100 μm 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-stabilized.

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 10 nm 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 (4 keV Ar^+_{2000} clusters from Thermo Scientific MAGCIS source).[49] This allowed collection of elemental/chemical composition of the film using XPS while also 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 neutralization source described above. The data were 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 neutralization modes for XPS and UPS. Even though the probe sizes and sampling depths of XPS and UPS are quite different, the standard XPS charge neutralization mode could be successfully used for UPS during the depth profile.

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

Most modern charge neutralization systems enable XPS spectra to be collected with the peaks appearing close to the

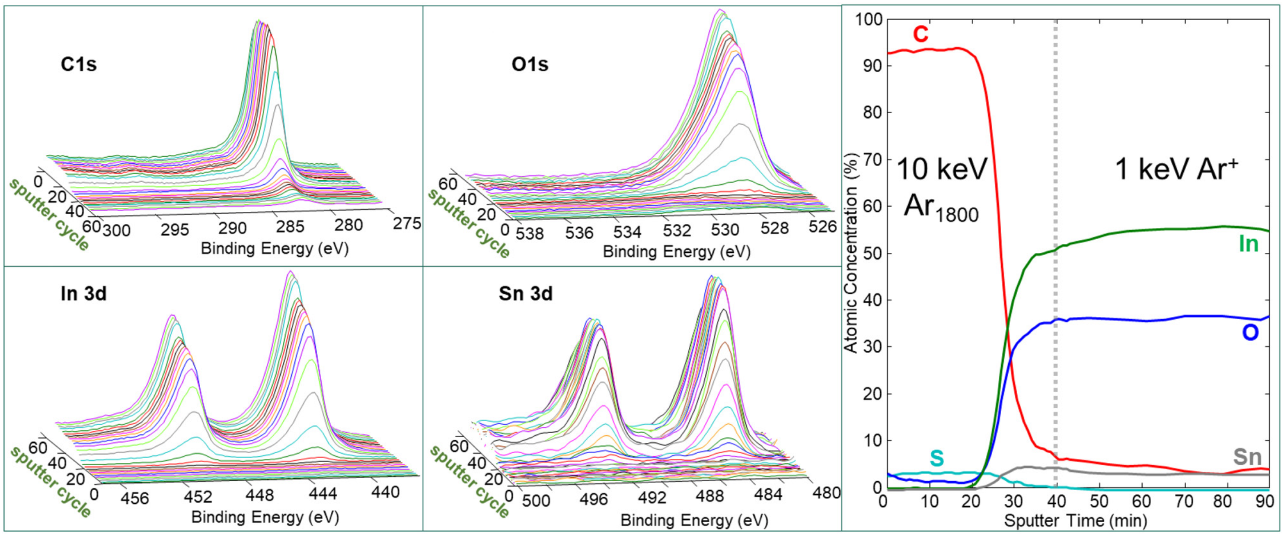
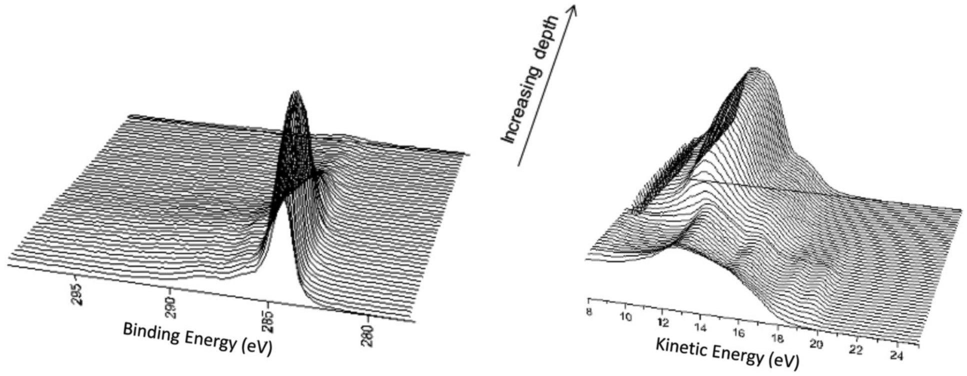


FIG. 12. Compilations of C 1s, O 1s, In 3d, and Sn 3d spectra collected during a depth profile of a multilayered solar cell with a 250 nm P3HT:PCBM organic layer and a 10 nm ITO layer on glass. 10 keV Ar^+_{1800} clusters were used to sputter through the organic later followed by 1 keV Ar^+ for the ITO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



C1s spectra from XPS/UPS cluster profiling

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

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

appropriate or expected values for the measured 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 energy shift that needs to be applied to correct the BE scale for 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] made 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—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 284.6–285.0 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 BE 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 photopeaks will remain a useful indicator of the presence or absence of significant surface charging and the adequacy of charge neutralization on many types of insulating samples. As described in the polymer guide, C 1s BE referencing (sometimes including AdC) remains a useful and valuable tool in many circumstances but is frequently only part of the consistency check for charge correction (see internal referencing discussion in Sec. III D).[31]

Limitations regarding the accuracy of the use of C 1s for BE referencing have been pointed out in several papers over the years (for an historical perspective, see Greczynski and Hultman[1])—however, such concerns have been overwhelmed by the continuously increasing number of XPS papers (unfortunately not accompanied 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) the use of poor quality spectra as a result of inadequate charge neutralizer settings and/or poor sample mounting leading to differential charging, (e) the 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 nonzero 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 on 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 studied 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 $E_B^F + \phi_{SA} = 289.58 \pm 0.14\,\text{eV}$,[55] suggesting that the binding energy of AdC C 1s peak is invariant with respect to the VL. Such VL alignment may arise under the 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 also using other approaches described in this section.

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 significant 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 the application of a charge neutralization method. Three data collection modes can be imagined: (i) substrate grounded, no charge neutralization; (ii) substrate grounded and charge neutralization; (iii) substrate isolated from ground with charge neutralization applied. Based on the example in Sec. 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 experienced XPS operators recommend that for many types of thin film samples, the data would be consistent using mode (iii) (using charge neutralization 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 quite useful as listed in Table VI.[31] These include hydroxyl groups in cellulose, CF_2 in polytetrafluoroethylene (PTFE), and more. In the above examples, charge correcting using the stated C 1s reference 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 a consistent result for this sample is BE referencing to the Ti $2p_{3/2}$ peak of the TiO_2, to be used 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.

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 neutralization 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.

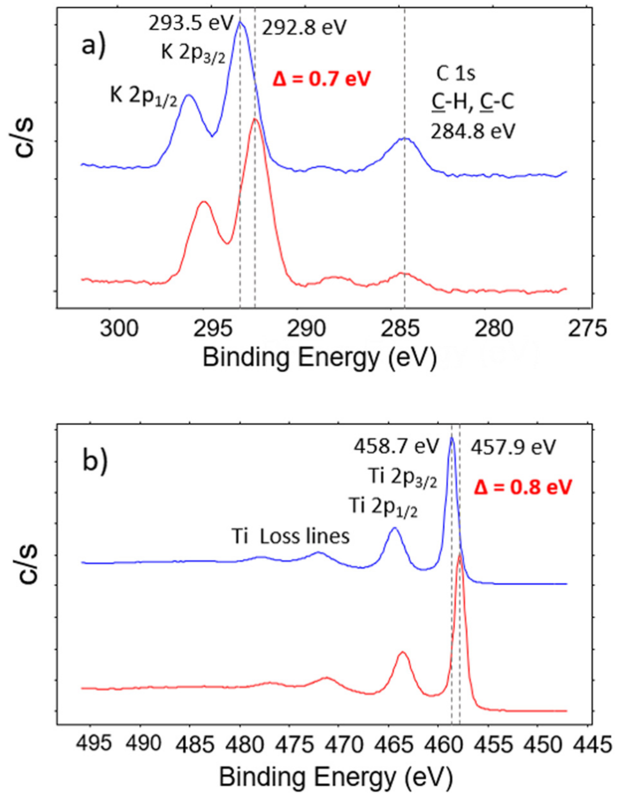


FIG. 14. XPS high-resolution photoelectron peaks from a Pt-K-TiO_2 catalyst: (a) C 1s and K 2p and (b) Ti 2p. When the photoelectron peaks are referenced to C 1s at 284.8, both the Ti and K 2p photoelectron peaks have ≈0.75 eV shift before and after catalyst processing. As it is unlikely that the Ti 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.

  - 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 neutralization is shown in Fig. 2 of Ref. 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 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 others 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 neutralization system in a spectrometer controls the sample potential. Although the buildup of charge during XPS analysis is often viewed as a problem, it also can be used to extract important information about sample properties.

ACKNOWLEDGMENTS

The input from many members of ASTM Committee E 42 on Surface Analysis and ISO TC 201 Committee on Surface Chemical Analysis is appreciated. G.G. acknowledges financial support from the Swedish Research Council VR (Grant No. 2018-03957) and Carl Tryggers Stiftelse Contract (No. CTS 17:166). D.R.B. and M.E. acknowledge that portions of the work were conducted in the EMSL, the Environmental and Molecular Sciences Laboratory, a US Department of Energy User Facility supported by the DOE Office of Biological and Environmental Research.

APPENDIX: TERMINOLOGY RELATED TO SURFACE CHARGING AND ENERGY REFERENCING

Key terms associated with surface charging, charge neutralization, and energy referencing in XPS are briefly described for those who may be unfamiliar with them. It should be noted that this discussion is focused on XPS relevant context only. Parts of the definitions below are adaptions of terminology developed by the International Organization for Standardization Technical Committee 201 on Surface Chemical Analysis contained in ISO 18115 part 1 but the descriptions below are provided for information and are not formally accepted or approved definitions.

1. Terminology related to surface charging

Sample charging: In the context of XPS measurements, this term refers to the buildup of net charge in a sample due to its exposure to the x-ray beam and, possibly, to other incident particles, e.g., like flood gun electrons or ion beams. Inherently, the ionizing x-ray radiation tends to induce net *positive* charge. Sample charging can also evolve via other effects, including desorption or adsorption of molecules, temperature changes, and more.

Charging potential: The change in surface potential due to the development of sample charging. The charging potential is directly expressed as a change in the measured binding energy of XPS-detected signals.

Differential charging: A situation commonly encountered, for reasons discussed in this guide, where the spatial distribution of charge is nonuniform and, therefore, different charging potentials affect the spectrum simultaneously. The application of a charge neutralization system does not necessarily eliminate all causes of differential charging and, sometimes, can even magnify them.

2. Terminology related to control of surface charging

Charge neutralization: In response to the charging effect, neutralization of the surface is usually attempted, such as to achieve zero net charge. This process is termed "charge neutralization." Practically, however, perfect neutralization is very difficult to stabilize and, even worse, very difficult to directly measure and hence be identified. Therefore, *partial* control over the magnitude of charging is a much more common situation.

Charge compensation: The use of various means to reduce the amount of net charge at the surface and to achieve partial control on its magnitude. Most common is the application of low-energy electrons (via an electron flood gun), with or without low-energy ions of a noble gas, in order to stabilize very low net surface charge.

Charge neutralization system: Components in an XPS spectrometer intended to minimize or control the buildup of charge during an XPS measurement. As described in Sec. II C, these systems usually involve an electron flood gun of some type and may also involve low-energy ions.

Electron flood gun (eFG): Frequently, neutralization is attempted by supplying a flood of low-energy electrons from an eFG. Essentially, these electron sources are designed to supply a broad, large diameter, beam spot, such as to verify a uniform flux of electrons across the (much smaller) analysis area.

3. Terms related to energy scale referencing

Vacuum level: In its electrical context, the vacuum level is defined as the energy of a free stationary electron that is outside of any material (it is in a perfect vacuum).[60]

Local vacuum level: This term is an extension of the formal concept of vacuum level. It applies to cases where electrostatic fields dictate different vacuum levels at different spatial locations.[61] In particular, the local vacuum level at the sample surface is frequently different from the one at the detector. Importantly, abrupt changes in the local vacuum level are frequently realized across interfaces within samples, in particular, between compounds of different work function (see below) values; a feature of broad use in devices consisting of electronic materials.

Work function: In its present context, the work function of a given material is the minimal work needed to be done on an electron within that material in order to bring it to the local vacuum level. Alternatively, derived from the latter definition, the work function is equal to the energy difference between the Fermi level and the vacuum level next to the surface of that material.

Fermi level referencing: Setting the energy scale such that its origin coincides with the Fermi level of the sample. Fermi level referencing is the common convention for binding energies, because under contact with the spectrometer, the sample's Fermi level equalizes with that of the instrument and, hence, with a very reliable and robust reference: the instrument's electrical ground. Note that the measured photoelectron energies are normally independent of the sample work function, but instead, depend on the detector's work function, which is in principle a known instrumental parameter.[62]

Vacuum level referencing: Setting the energy scale such that the local vacuum level at the sample surface equalizes with the one at an instrumental component (often the eFG). As discussed by many, including Lewis and Kelly,[62] for insulating and electrically isolated samples, there is no Fermi level alignment and measured photoelectron energies are determined relative to a vacuum level at the spectrometer. This lack of Fermi level alignment can also occur in cases where the sample substrate is metallic, with a good back contact, but an insulating medium on top of the substrate prevents establishing thermodynamic equilibrium between the sample's surface (where XPS signals are probed from) and the substrate. To maintain the convention of referencing peak energies to the Fermi level in XPS, a correction is needed for the energy scale.[62] A procedure for extracting the instrumental parameter is described in Ref. 63.

Note that, by historic convention, the electron energies in Auger electron spectroscopy (AES) are referenced to the vacuum level of the spectrometer, because *kinetic energies* in this process are independent of the excitation source and, therefore, gain broader validity than Fermi-level-based scales for Auger electrons. Comparison of Auger peaks collected during an XPS measurement and observed on the BE scale (hence, Fermi level referencing) with those collected using a dedicated AES instrument requires conversion from the BE scale to a kinetic energy scale and appropriate accounting for the spectrometer work function.[64,65]

Charge correction (Δ_{corr})*:* This term refers to the correction in *energy* required due to *charging*-induced energy shifts. Frequently, when differential charging is encountered, a single Δ_{corr} is insufficient to correct all observed photoelectron peak energies. Note that this energy scale adjustment is often, somewhat ambiguously, referred to as *charge referencing*, which is misleading, because referencing in XPS applies to energies, not charge. Practically, charge correction is often attempted using a known *internal reference*, or an external one like *adventitious carbon* or *gold decoration*, all subject to limitations described in this guide.

AdC referencing: Determining the charge correction (Δ_{corr}) for a sample by comparing the experimentally measured C 1s binding energy of hydrocarbons adsorbed on the sample surface, with a standard binding energy value associated with these molecules. As discussed in Sec. III A, the standard value is not necessarily known *a priori*, due to system specific variations in the hydrocarbon C 1s binding energy. Yet, values are limited to remain within a range of a few electron volts at the most, usually less than ±1 eV, such that a rough energy scale calibration can be verified, which is particularly helpful in extreme cases of charging.

Internal referencing: Determining the charge correction (Δ_{corr}) for a specific sample by comparing the experimentally determined binding energy of an element (or elements) in a known chemical state in that sample, to a standard binding energy value for that signal. Using the C 1s of a specific group within the sample may be such an example, but, in general, internal references are sample specific. There are several reasons and circumstances for which internal referencing has limited accuracy, often including multiphase and other complex samples. As with other energy referencing methods, it needs to be used with appropriate care and an evaluation of data consistency (Sec. III E).

Gold decoration: Use of a very small quantity of gold with an assumed binding energy of 84.0 eV, deposited as unconnected islands on an insulator, for establishing the charge correction (Δ_{corr}). Limitations of this method are discussed in Sec. III B.

Peak position: The peak position of a given spectral line refers to the energy at which the signal intensity is maximal. This term, which is common to spectroscopy, in general, and normally used for expressing the related measured core-level binding energy, should be considered carefully when differential charging is encountered, and line shape distortions are encountered.[22,29]

Correct use of terminology is important for reliable and reproducible reporting of XPS measurements.[28] The full set of this terminology (ISO 18115 part 1) is available at no cost from several websites.[65,66] This terminology has been developed by many people over four decades and is now undergoing a systematic review. Several terms are being updated based on new or revised concepts and identification of inconsistencies that have evolved over time. Suggestions for improvements, clarification, or additional terms are most welcome and can be made to the chairman or secretaries of ISO TC201 or the terminology subcommittee ISO TC201 SC1.

REFERENCES

[1] G. Greczynski and L. Hultman, Prog. Mater. Sci. **107**, 100591 (2020).
[2] NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20 (National Institute of Standards and Technology, Gaithersburg MD, 20899), see https://srdata.nist.gov/xps/Default.aspx.
[3] B. V. Crist, J. Electron Spectrosc. **231**, 76 (2019).
[4] J. Cazaux, J. Electron Spectrosc. **105**, 155 (1999).
[5] J. Cazaux, J. Electron Spectrosc. **113**, 15 (2000).
[6] D. R. Baer, M. H. Engelhard, D. J. Gaspar, A. S. Lea, and C. F. Windisch, Jr., Surf. Interface Anal. **33**, 781 (2002).
[7] D. R. Baer, C. F. Windisch, Jr., M. H. Engelhard, and K. R. Zavadil, J. Surf. Anal. **9**, 396 (2002).
[8] W. M. Lau, Appl. Phys. Lett. **54**, 338 (1989).
[9] I. Doron-Mor, A. Hatzor, A. Vaskevich, T. van der Boom-Moav, A. Shanzer, I. Rubinstein, and H. Cohen, Nature **406**, 382 (2000).
[10] K. Shabtai, I. Rubinstein, S. R. Cohen, and H. Cohen, J. Am. Chem. Soc. **122**, 4959 (2000).
[11] H. Cohen, Appl. Phys. Lett. **85**, 1271 (2004).
[12] S. Dey *et al.*, J. Chem. Phys. **151**, 174704 (2019).
[13] H. Sezen and S. Suzer, J. Chem. Phys. **135**, 141102 (2011).
[14] M. Krzywiecki, L. Grządziel, L. Ottaviano, P. Parisse, S. Santucci, and J. Szuber, Mater. Sci. Poland **26**, 287 (2008).
[15] C. G. Pantano, A. S. D'Souza, and A. M. Then, in *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*, edited by A. Czanderna, C. J. Powell, and T. E. Madey (Springer-Verlag, New York, 1998), Vol. 5.
[16] D. R. Baer, D. J. Gaspar, M. H. Engelhard, and A. S. Lea, in *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, edited by D. Briggs and J. T. Grant (IM Publications and Surface Spectra, Chichester, 2003).
[17] D. R. Baer, M. H. Engelhard, and A. S. Lea, Surf. Sci. Spectra **10**, 47 (2003).
[18] E. Frydman, H. Cohen, R. Maoz, and J. Sagiv, Langmuir **13**, 5089 (1997).
[19] H. Sezen and S. Suzer, Thin Solid Films **534**, 1 (2013).
[20] S. Suzer, Anal. Chem. **75**, 7026 (2003).
[21] D. Ehre and H. Cohen, Appl. Phys. Lett. **103**, 052901 (2013).
[22] A. Givon, H. Piao, J. McMahon, G. Zorn, and H. Cohen, Appl. Phys. Lett. **107**, 173101 (2015).
[23] N. Filip-Granit, M. E. van der Boom, R. Yerushalmi, A. Scherz, and H. Cohen, Nano Lett. **6**, 2848 (2006).
[24] Y. Feldman, A. Zak, R. Tenne, and H. Cohen, J. Vac. Sci. Technol. A **21**, 1752 (2003).
[25] H. Sambe and D. E. Ramaker, J. Vac. Sci. Technol. A **10**, 2991 (1992).
[26] ASTM E1523-15, *Standard Guide to Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy* (ASTM International, West Conshohocken, PA, 2015).
[27] *ISO 19318:2004 "Surface Chemical Analysis—Reporting of Methods Used for Charge Control and Charge Correction"* (International Organization for Standardization, Geneva, 2004).

[28] D. R. Baer and A. G. Shard, “Role of consistent terminology in XPS,” J. Vac. Sci. Technol. A **38**, 031203 (2020).
[29] L. Edwards, P. Mack, and D. J. Morgan, Surf. Interface Anal. **51**, 925 (2019).
[30] G. Beamson, D. T. Clark, N. W. Hayes, D. S. L. Law, V. Siracusa, and A. Recca, Polymer **37**, 379 (1996).
[31] C. D. Easton, C. Kinnear, S. L. McArthur, and T. R. Gengenbach, J. Vac. Sci. Technol. A **38**, 023207 (2020).
[32] U. K. Demirok, G. Ertas, and S. Suzer, J. Phys. Chem. B **108**, 5179 (2004).
[33] T. Dickinson, A. F. Povey, and P. M. A. Sherwood, J. Electron Spectrosc. **2**, 441 (1973).
[34] B. J. Tielsch and J. E. Fulghum, Surf. Interface Anal. **25**, 904 (1997).
[35] M. J. Edgell, D. R. Baer, and J. E. Castle, Appl. Surf. Sci. **26**, 129 (1986).
[36] V. Artel, Q. Guo, H. Cohen, R. Gasper, A. Ramasubramaniam, F. Xia, and D. Naveh, NPJ 2D Mater. Appl. **1**, 6 (2017).
[37] A. Rozenblat, Y. Rosenwaks, L. Segev, and H. Cohen, Appl. Phys. Lett. **94**, 053116 (2009).
[38] J. B. Metson, Surf. Interface Anal. **27**, 1069 (1999).
[39] P. E. Larson and M. A. Kelly, U.S. patent 5,990,476A (November 23, 1999), JP patent P3616714B2 (February 2, 2005), and EP patent 0848247B1 (July 3, 2002).
[40] P. E. Larson and M. A. Kelly, J. Vac. Sci. Technol. A **16**, 3483 (1998).
[41] B. R. Barnard, M. H. Humpherson, and A. R. Bayly, U.S. patent 7,067,821B2 (June 27, 2006), and GB2411763B (February 18, 2009).
[42] D. R. Baer, J. Vac. Sci. Technol. A **38**, 031201 (2020).
[43] D. R. Baer, D. J. H. Cant, D. G. Castner, G. Ceccone, M. H. Engelhard, and A. S. Karakoti, “Preparation of nanoparticles for surface analysis,” in *Characterization of Nanoparticles: Measurement Procedures for Nanoparticles*, edited by W. E. S. Unger, A. G. Shard, and V.-D. Hodoroaba (Elsevier, Oxford, 2019), Chap. 4.2.
[44] E. O. Filatova and A. S. Konashuk, J. Phys. Chem. C **119**, 20755 (2015).
[45] Y. Wu, E. Garfunkel, and T. E. Madey, Surf. Sci. **365**, 337 (1996).
[46] M. R. Alexander, G. E. Thompson, and G. Beamson, Surf. Interface Anal. **29**, 468 (2000).
[47] F. Bart, M. J. Guitteta, M. Henriot, N. Thromata, M. Gautier, and J. P. Duraud, J. Electron Spectrosc. **69**, 245 (1994).
[48] A. G. Shard *et al.*, Anal. Chem. **84**, 7865 (2012).
[49] P. Mack and A. Wright, “Depth profiling of an organic FET with XPS and argon cluster ions,” Thermo-Fisher Application Note, see https://assets.thermofisher.com/TFS-Assets/CAD/Application-Notes/AN52476_E_1113M_H.pdf.
[50] About gas cluster ion beams (PHI, 2014), see https://www.ulvac-phi.com/en/surface-analysis/topics/gcib/.
[51] A. Pelisson-Schecker, H. J. Hug, and A. Patscheider, Surf. Interface Anal. **44**, 29 (2012).
[52] K. Siegbahn, C. Nordling, and A. Fahlman, *ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksell, Uppsala, 1967).
[53] P. Swift, Surf. Interface Anal. **4**, 47 (1982).
[54] G. Greczynski and L. Hultman, ChemPhysChem **18**, 1507 (2017).
[55] G. Greczynski and L. Hultman, Appl. Surf. Sci. **451**, 99 (2018).
[56] S. Kohiki and K. Oki, J. Electron Spectrosc. **36**, 105 (1985).
[57] S. Kohiki, Appl. Surf. Sci. **17**, 497 (1984).
[58] T. C. Taucher, I. Hehn, O. T. Hofmann, M. Zharnikov, and E. Zojer, J. Phys. Chem. C **120**, 3428 (2016).
[59] D. R. Baer, Surf. Interface Anal. **37**, 524 (2005).
[60] J. Bardeen, Phys. Rev. **71**, 717 (1947).
[61] D. Cahen and A. Kahn, Adv. Mater. **15**, 274 (2003).
[62] R. T. Lewis and M. A. Kelly, J. Electron Spectrosc. **20**, 105 (1980).
[63] H. Cohen, C. Nogues, I. Zon, and I. Lubomirsky, J. Appl. Phys. **97**, 113701 (2005).
[64] J. F. Watt and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, 2nd ed. (Wiley, Chichester, 2019).
[65] *ISO 18115: Surface Chemical Analysis—Vocabulary—Part 1: General Terms and Terms Used in Spectroscopy* (ISO, Geneva, 2013).
[66] Websites hosting ISO 18115 terminology: American Vacuum Society (AVS): http://www.avs.org/Technical-Library/Technical-Resources; UK National Physical Laboratory: https://www.npl.co.uk/surface-technology/standardisation-traceability; Environmental Molecular Sciences Laboratory: https://www.emsl.pnnl.gov/emslweb/vocabulary-definitions; Surface Analysis Society of Japan (SASJ): http://www.sasj.jp/iso/ISO18115.html; National Institute of Advanced Industrial Science and Technology: http://www.aist.go.jp/aist_e/dept/iso.html; PTB Germany: https://www.ptb.de/cms/en/ptb/fachabteilungen/abt5/fb-51/dkd-guidelines-and-standards.html; BAM Germany: https:/www.bam.de/Navigation/EN/About-us/Organisation/Organisation-Chart/President/Department-6/Division-61/division61.html; ASEVA Spain: http://aseva.es/iso18115/.