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## Surface Science Insight Note: Charge Compensation and Charge Correction in X-ray Photoelectron Spectroscopy

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### Abstract

Practical strategies to deal with sample charging effects on X-ray photoelectron spectroscopy spectra are presented. These strategies combine charge compensation (or lack of) via a flow of electrons and an electrical connection (or lack of) of samples to the ground. Practical examples involving samples with a range of different electrical properties, sample structure/composition and sensitivity to X-rays, illustrate the correlation between sample properties, measurement strategies and the resulting XPS data. The most appropriate measurement strategy for a particular sample is also recommended. We highlight the crucial importance of appropriate XPS data acquisition to obtain a correct data interpretation.

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## Introduction

X-ray Photoelectron Spectroscopy (XPS) data is visualized by plotting photoemission intensity versus energy. Conventionally, spectra plot electron counts-per-second (CPS) against binding energy ( $E_{BE}$ ) in electron Volts (eV), where  $E_{BE}$  is expressed as positive values [1].  $E_{BE}$  is the minimum quantum of energy required to create an ion. As the  $E_{BE}$  of a core-level or valence band depends on the chemical environment of the atom, it constitutes the key parameter that XPS utilizes to extract chemical information from a sample. However, XPS instruments measure the kinetic energy ( $E_{KE}$ ) of emitted electrons rather than the  $E_{BE}$ . Therefore, for XPS analysis  $E_{KE}$  must be converted to  $E_{BE}$ .

In principle, given a known photon energy ( $E_{Ph}$ ) and a known  $E_{BE}$ , the conversion to  $E_{KE}$  should be straightforward (Eq. 1). However, XPS measurements are influenced by instrumental effects. An electron emitted from an atom is exposed to electrical fields due to a potential difference between the sample and the point in the instrument at which the electron is detected. A conducting sample electrically connected to the instrument (grounded) still creates a potential difference that retards electrons emitted from the sample. The loss of  $E_{KE}$  due to overcoming this *work-function potential* is assumed to be a constant for a given instrument and must be included when converting  $E_{KE}$  to  $E_{BE}$  via the term  $E_{WF}$  (Eq.1). However, assuming a constant  $E_{WF}$  is an idealization. In practice, factors influencing the precise measurement of kinetic energy for an electron include the stability of the electronic components of an instrument, the thermal stability of monochromator geometry and the width of both entrance and exit apertures to the energy analyzer. When multiple detector instruments are used, the precision with which software combines data streams measured concurrently but offset in energy to form a single spectrum is also a source of uncertainty in the kinetic energy assigned to an electron. Nonetheless, for well-maintained instruments, Eq. 1 is sufficient for data collected from conducting samples to convert between kinetic energy and binding energy.

$$E_{KE} = E_{Ph} - E_{BE} - E_{WF} \quad (1)$$

Another factor influencing the  $E_{KE}$  of photoemitted electrons is sample charging. Since the photoelectron emission leaves behind positively charged atoms, this generated positive charge over measurement time has a strong influence on XPS spectra. Samples that inhibit the flow of electrons within the solid state, i.e. insulating or wide band gap materials, tend to charge positively over X-ray exposure time, effectively retarding the negatively charged emitted electrons, i.e. lowering their  $E_{KE}$  (or equivalently, increasing their  $E_{BE}$ ) by an energy amount  $-E_{SQ}(t)$ , where SQ indicates sample charge (Eq. 2).

$$E_{KE}(t) = E_{Ph} - E_{BE} - E_{WF} - E_{SQ}(t) \quad (2)$$

In practice, sample charging is alleviated by a charge compensation (CC) mechanism, which should compensate for the charge developed on the sample and eliminate the time dependence. CC is usually achieved by supplying charged particles to the sample that effectively deliver a flux of low-energy electrons to the sample [2]. Ideally, charge compensation is effective when the flux of electrons emitted by the sample is equal to the flux of electrons supplied to the sample by CC mechanisms. On the other hand, if CC supplies an excess of electrons, the sample would be negatively charged, which would lead to a repulsive potential, or equivalently a  $+E_{SQ}(t)$  in Eq.2, accelerating the emitted electrons, i.e. having a higher  $E_{KE}$  (or lower  $E_{BE}$ ). In this case, the excess negative sample charge can be dealt with by an adequate connection to the ground, provided that the sample is conducting.

In general, dealing with sample charging is not a trivial task. Experience in the analysis of samples has led to identify three groups of variables that influence sample charging. Namely, (1) sample electrical properties derived from chemical composition, (2) heterogeneity on the constitution of the sample and direction of the heterogeneity of the sample, i.e. across the exposed area to X-rays (basal plane of the sample) or along cross-sections, i.e. layered materials, in which case, the thickness of each layer and the overall sample are highly relevant, and (3) sensitivity of the sample to X-rays [3][4]. Often, there is a correlation between these variables affecting each other during XPS measurements. An example of XPS spectra variations due to heterogeneity is what is known as *differential charging*, consisting of multiple photoemission signals corresponding to the same photoemission source and due to a non-uniform potential across the analyzed sample area (basal planes) [5][6].

Here, we present four different approaches to deal with sample charging that combine CC via a low energy flow of electrons with a second electron flow from sample to ground via grounded/non-grounded (floating) electrical connections (Table 1). Namely, a sample may be (1) connected to ground (*Grounded only*), (2) disconnected from ground (*Floating only*), (3) disconnected from ground plus charge compensated by low energy electrons (*Floating + CC*) or (4) grounded plus charge compensated by low energy electrons (*Grounded + CC*). A usual experimental setup of a grounded sample consists of mounting the sample over an electrically conducting tape that is stuck to the metallic sample holder. A floating sample setup is achieved by simply introducing a paper on top of the conducting tape followed by the so electrically insulated sample. Then, we demonstrate four measurement cases that illustrate the charging effects of four different samples during standard XPS measurements and the crucial and contrasting influence of a couple of different selected measuring approaches (Table 1). The correlation between the above-described variables that influence sample charging and the measuring approach is described. Finally, we suggest the most recommended approach to measure a sample of specific properties.

Table 1. Summary of methods to deal with sample charging when performing XPS.

Approach	The flow of electrons to the ground	Application of an electron flow (CC)	Label
1	Yes	No	Grounded only
2	No	No	Floating
3	No	Yes	Floating + CC
4	Yes	Yes	Grounded + CC

## Results and Discussion

### Case I. An insulating sample: Polytetrafluoroethylene

Polytetrafluoroethylene (PTFE) is an insulating material that degrades over time under measurement by XPS [7]. Nevertheless, PTFE and the degraded PTFE (remaining insulating) do not allow a flow of electrons through the sample, and the generated charge built up requires CC. A PTFE sample was measured using *Floating* and *Floating + CC* conditions (Figure 1). First, there was an offset to lower  $E_{BE}$  of the *Floating only* spectrum (Figure 1). This is due to the positive charging of the sample,  $-E_{SQ}(t)$  (Eq.2), which effectively retarded the photoemitted electrons lowering their  $E_{KE}$ , or equivalently, increasing their  $E_{BE}$ . This shift was corrected by calibrating using the F KLL signal of the *Floating + CC* spectrum (Figure 1a). However, this did not align all the photoemission signals (F 1s, C 1s and F 2s), e.g. F 2s (inset Figure 1b), which described time-dependent sample charging effects affecting the XPS spectra. The shift of the photoemission signal was enhanced with time affecting more the signal at lower  $E_{BE}$  such as F 2s (as the spectrum was measured from high to low  $E_{BE}$ ). Therefore, *CC* is recommended for insulating samples such as PTFE. Since PTFE is an insulating sample, floating and grounded conditions should be equivalent resulting in a null flow of electrons. However, the *Floating* settings ensure uniform insulation across all of the sample.

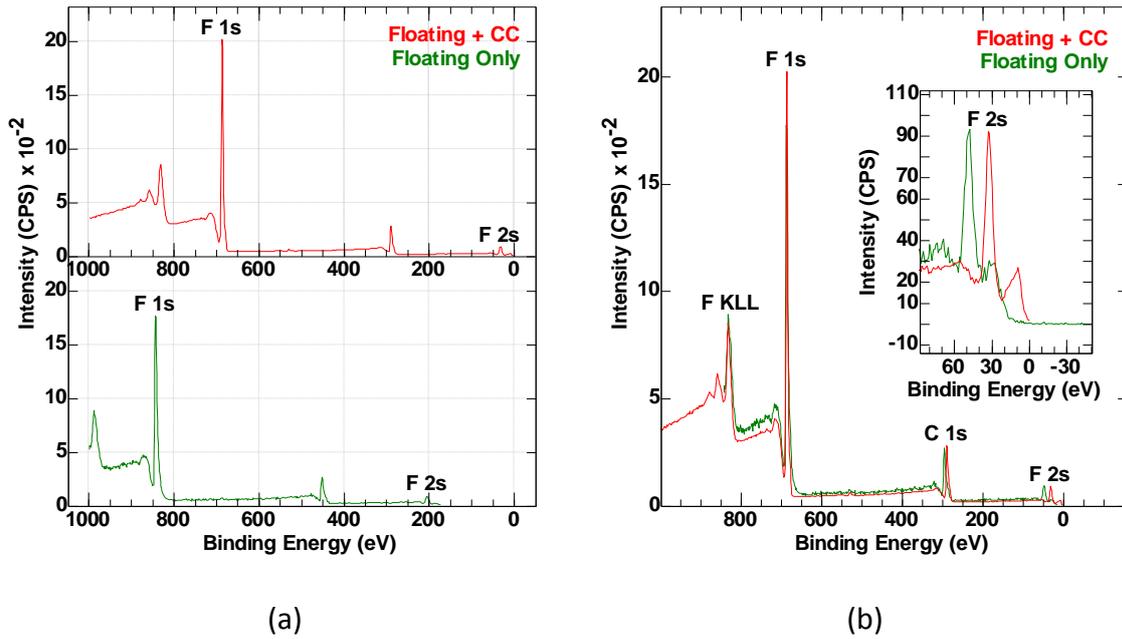


Figure 1. An insulating PTFE sample measured using *Floating + CC* and *Floating only* conditions (Table 1). (a) XPS survey spectra before calibration and (b) after calibration using the maximum of the F KLL spectral signal. The inset in (b) shows the misalignment of the F 2s spectra due to time-dependent changes in potential experienced by electrons emitted from the PTFE sample when no charge compensation is performed.

## Case II. An electrically heterogeneous sample: Aluminium Foil + aluminum oxide

Here we study the case of Al foil surface covered by aluminium oxide at the bottom and the top. The sample was measured using *Grounded* (Figure 2a) and *Floating + CC* conditions (Figure 2b). The first approach seeks to allow for an electron flow compensating for any charge built up. However, grounding the sample is not effective due to the presence of the insulating layers of aluminium oxide. Interestingly, due to the heterogeneous nature of the sample, this resulted in the stability of the Al 2p XPS signal of the metal but not of the metal oxide, which shifted over measurement time to higher  $E_{BE}$  (lower  $E_{KE}$  resulting from a positive charging of the sample). In contrast, when the sample was measured using *Floating + CC* conditions, the time-dependent charging of the aluminium oxide leading to the  $E_{BE}$  shift was eliminated (Figure 2b). In this case, the developed positive charging of the floating sample was effectively charge compensated by a negative flow of electrons. However, an “overcompensation” led to an overall negative, but uniform through aluminium and aluminium oxide layers, the potential of the sample causing a shift to lower  $E_{BE}$  (i.e. higher  $E_{KE}$  or repulsion of electrons from a negatively charged sample). In this sample under grounded conditions, the insulating layer of aluminium oxide, similar to the PTFE sample, is affected by a time-dependent shift to higher  $E_{BE}$ . Under *Floating + CC* conditions, and unlike the uniformly insulating PTFE, the presence of the Al metal in this sample must play a role in

charge distribution during CC favoring an overall negative charge through both the Al and Al oxide layers. The *Floating + CC* conditions are recommended.

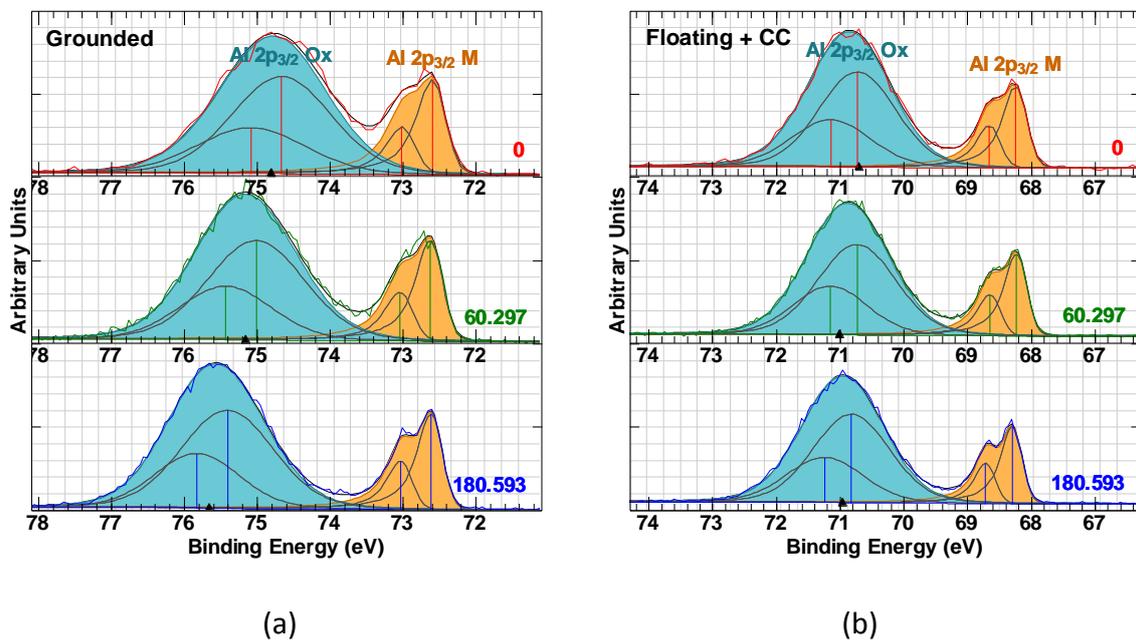


Figure 2. A sample of Al metal with layers of aluminum oxide at the bottom and the top. Al 2p spectra measured at increasing times (top to bottom panels) using (2a) Grounded and (2b) Floating + CC settings (Table 1). In (a), the Al 2p binding energy for the metal is the expected binding energy, whereas the corresponding signal for the aluminum oxide systematically changes with time. In (b) no shifts in binding energy were observed over time but the spectra of Al and aluminium oxide shifted consistently to lower binding energy. Spectra were fitted using CasaXPS [8].

Importantly, if this measurement had been done only once when using the *Grounded* conditions, we would not have seen the selective shifting over time of the Al 2p signal of the aluminum oxide which unequivocally would have led to the wrong interpretation. This highlights the importance of considering initial multiple measurements of a sample. On the other hand, this example highlights the different effects of *Floating + CC* conditions on samples of uniform (PTFE) vs. heterogeneous (Al + Al oxide) electrical properties.

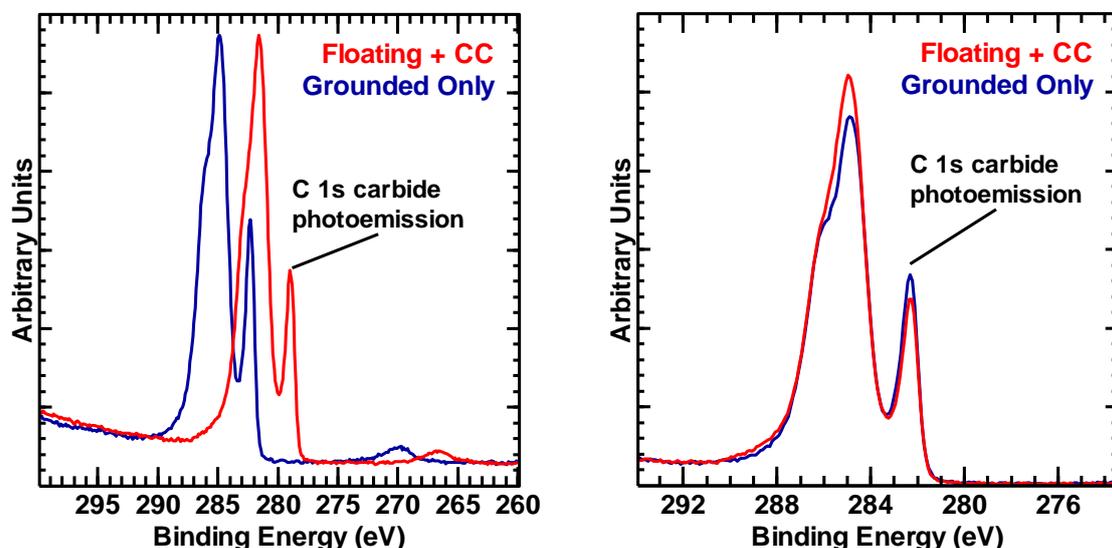
### Case III. Vanadium Carbide (metallic) + an ultrathin layer of vanadium oxide (insulating).

The next example shows two vanadium carbide film samples. Except for a degree of heterogeneity in the distribution of surface chemical groups, these samples had identical chemistry and, thus, were expected to have identical XPS signals. These samples are expected to consist of a metallic film with an ultrathin coverage of vanadium oxides.

These samples were measured using the *Grounded* only and the *Floating + CC* approaches, respectively (Table 1). Survey and narrow spectra including F 1s, V 2s, O 1s, V 2p, Cl 2p, Al 2s, V 3s and valence band were acquired. These spectra offer a wide energy range over which the effectiveness of these two measuring approaches can be assessed. By comparison of the C1s spectra (Figure 3a), the obvious difference is a shift to lower  $E_{BE}$  of the *Floating + CC* spectrum concerning the *Grounded* spectrum. The *Grounded* spectrum seems to be effectively charge compensated as the C 1s signal is around expected values. The *Floating + CC* spectrum had shifted to a lower  $E_{BE}$  due to the same reason as the Al/Al oxide sample described in the previous example, i.e. an overcompensation of charge leading to an overall negative sample potential. If there are no spectra distortions in either spectra other than a  $E_{BE}$  shift, a simple calibration should make for a full alignment of the two spectra.

The most widely used approach for calibration of XPS data is the use of the C 1s signal of adventitious carbon  $sp^3$  and correct for a value of 284.9 eV [9]. However, in this case, the C1s  $sp^3$  signal was part of a complex envelope involving several C bonds, whereas a well-defined vanadium carbide signal at the lowest  $E_{BE}$  is a better choice for calibration. Alternatively, the Cl  $2p_{3/2}$  signal, also well-defined, was a good choice for calibration. Using the latter of the *Grounded* spectrum, the two C 1s spectra were indeed well aligned (Figure 3b). A similar alignment of all other narrow spectra was achieved. Thus, this proved that these measurement approaches for this particular sample are equivalent. The samples can be measured by either approach but the less invasive (*Grounded*) approach will be preferred. This is shown in the next example.

Unlike the Al/Al oxide sample, the vanadium carbide sample measured using *Grounded* conditions did not show a time-dependent  $E_{BE}$  the shift of the vanadium oxide layer. This was due to the ultrathin nature of it, affecting little the electrical properties of the overall sample. Therefore, the thickness of the insulating layer on a sample is an important variable during XPS measurements.



(a)

(b)

Figure 3. The vanadium carbide sample measured using the *Grounded only* and the *Floating + CC* approach (Table 1). C1s spectra (a) as-acquired and (b) calibrated using as reference the  $E_{BE}$  of the Cl 2p<sub>3/2</sub> spectral signal of the *Grounded* spectrum.

#### Case IV. An X-ray sensitive semiconducting sample: Molybdenum trioxide

Molybdenum trioxide (MoO<sub>3</sub>) is a material sensitive to X-rays. If no special sample preparation measures are taken, the material properties evolve under X-rays resulting in distorted XPS spectra [10]. This process is accelerated by sample heating [3]. However, besides X-ray-induced spectral changes, XPS spectra distortions are also introduced by charge compensation processes. A MoO<sub>3</sub> powder sample was measured using the *Grounded + CC* approach at room temperature (Figure 4). The first Mo 3d spectrum shifted to a lower  $E_{BE}$  than the expected value under no measurement artifacts (Mo 3d<sub>5/2</sub> 232.6 eV). Over the following measurements, the Mo 3d spectra shifted progressively to higher  $E_{BE}$  until stabilization around 232.6 eV. The corresponding O 1s spectrum behaved consistently (Figure 4b). Such phenomenon was observed when measuring in both a *ThermoFischer Nexsa G2* and a *Kratos Axis Nova* instrument which implies that the results here presented are reproducible and independent of the different charge compensation approaches of such different instruments [2].

These  $E_{BE}$  shifts are explained as follows. MoO<sub>3</sub> is a semiconductor. Therefore, similar to the PTFE sample, grounding the sample had no effect and the sample was effectively floating. When low energy electrons are applied for charge compensation, a negative charge is built up shifting the spectra to lower  $E_{BE}$ . Over repeated measurements, and due to X-ray irradiation, the electrical properties of the sample evolved towards a more conducting behavior progressively allowing the flow of electrons from sample to ground leading to sample charge neutralization and, consequently, a shift of the XPS spectra to a higher  $E_{BE}$  until signal stabilization around the expected value of 232.6 eV.

Since the X-ray-induced sample changes cannot be avoided, a recommended measurement approach is to use *Floating + CC* conditions. This will eliminate the progressive shift to lower  $E_{BE}$ . Charge compensation would then compensate for positive charges generated over photoemission leading to negative charging built up and shift to lower  $E_{BE}$ . This shift would be corrected by usual calibration procedures, which, nevertheless, would not solve, spectral changes potentially induced by sample degradation.

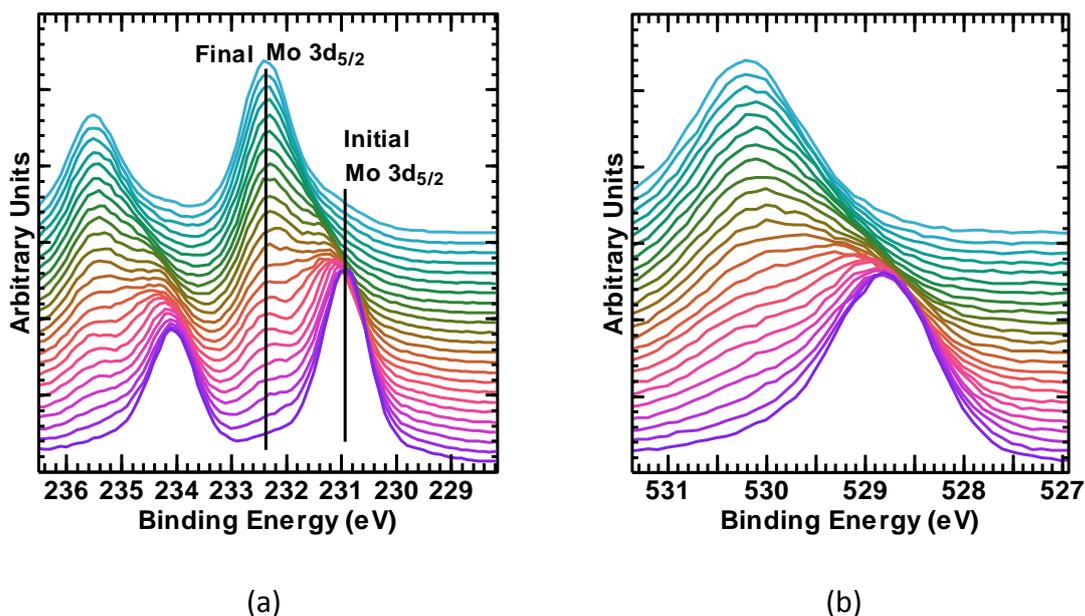


Figure 4.  $\text{MoO}_3$  powder sample measured repeatedly using the Grounded + CC approach (Table 1). (a) Mo  $3d_{5/2}$  and (b) O  $1s$  spectra. The apparent binding energy shift of both spectral regions is consistent.

## Conclusions

We have presented sample charging effects and the importance of selecting the most convenient measuring approach according to sample properties and their behavior under X-rays over time. Key recommendations can be summarised as follows:

- (1) Pre-tests are of key importance for first-time measured samples. This is often regarded as unimportant. The cautious XPS scientist would devote time to working out the best method for XPS data acquisition, that contains information about the sample chemistry rather than artifacts that would unnecessarily complicate analysis and frequently lead to the wrong interpretation.
- (2) Repeated measurements are the source of key information that otherwise, would not be noticed. We have illustrated that several sample charging or sample degradation effects under X-rays cannot be observed with a single measurement. Repeated measurements are a must.
- (3) Whereas prior information about the sample, especially electrical properties and sample architecture and thickness, constitute suitable guidance to select the most convenient measuring approach (Table 1), we suggest trying at least two measuring approaches. They will be a source of the required contrast to understand the sample behavior and evolution over time during XPS measurements.

(4) Acquisition and evaluation of the survey as well as a range of narrow spectra is recommended. This will gather key information on sample behavior over XPS acquisition time while informing about inconsistencies of spectra over the overall binding energy scale correlated to measurement artifacts.

This methodology of sample evaluation under X-rays and different measuring approaches over repeated experiments should then lead to the selection of the most appropriate measuring approach.

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### Author contributions

Beatriz Mendoza-Sanchez: Investigation (lead); Methodology (equal); Validation (equal), Writing – review and editing (lead). Vincent Fernandez: Investigation (lead); Methodology (equal); Validation (equal). Pascal Bargiela: Investigation (lead); Writing – review and editing (equal). Neal Fairley: Conceptualization (lead); Methodology (lead); Formal Analysis (lead); Data curation (lead); Visualization (lead); Writing – original draft (lead). Jonas Baltrusaitis: Methodology (supporting); Writing – review and editing (equal).

### Competing interests

The authors declare no competing interests.

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