NOTES AND INSIGHTS

Surface science insight note: Charge compensation and charge correction in X-ray photoelectron spectroscopy

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Strategies to deal with sample charging effects on X-ray photoelectron spectroscopy (XPS) 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.

KEYWORDS
Al_2O_3/Al, MoO_3, PTFE, sample charging, vanadium carbide, XPS

1 | INTRODUCTION

X-ray photoelectron spectroscopy (XPS) data are visualized by plotting energy versus photoemission intensity. Conventionally, spectra are displayed as binding energy (E_{BE}), expressed as positive values, versus electron counts-per-second (CPS).[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 (Equation 1). However, XPS measurements are affected by sample properties and instrumental effects, often highly correlated. 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 alters the kinetic energy of electrons emitted from the sample.[2] 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} (Equation 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, Equation (1) is sufficient for data collected from conducting samples to convert between kinetic energy and binding energy.

$$E_{KE} = E_{Ph} - E_{BE} - E_{WF} \tag{1}$$

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, that is, insulating or wide band gap materials, tend to charge positively over X-ray exposure time, effectively retarding the negatively charged emitted electrons, that is, lowering their E_{KE} (or equivalently, increasing their E_{BE}) by an energy amount $-E_{SQ}(t)$, where SQ indicates sample charge (Equation 2).

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

In practice, sample charging is alleviated by charge compensation (CC) mechanisms, which should compensate for the charge developed on the sample. CC is usually achieved by supplying charged particles to the sample that effectively deliver a flux of low-energy electrons to the sample.[3,4] The ideal CC should lead to charge neutralization, when the flux of electrons emitted by the sample equals the flux of electrons supplied to the sample. However, in practice, because CC compensates for an unknown charge developed at the sample that varies with time, there is always a remaining sample charge. An undercompensation leads to a positive sample charge/electron retarding potential, that is, $-E_{SQ}(t)$ in Equation (2) leading to a lower E_{KE} /higher E_{BE}, whereas an overcompensation leads to a negative sample charge/electron accelerating potential, that is, a $+E_{SQ}(t)$ in Equation (2) leading to a higher E_{KE}/lower E_{BE}. In the latter case, the excess negative sample charge can be dealt with 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, as well as crystaline phase, grain size, and morphology, (2) heterogeneity on the constitution of the sample and direction of the heterogeneity of the sample, that is, across the exposed area to X-rays (basal plane of the sample) or along cross-sections, that is, 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.[5,6] 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 nonuniform potential across the analyzed sample area (basal planes).[7,8]

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/nongrounded (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.

2 | RESULTS AND DISCUSSION

2.1 | Case I. An insulating sample: Polytetrafluoroethylene (PTFE)

PTFE is an insulating material that degrades over time under measurement by XPS.[9] 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, $-E_{SQ}(t)$ (Equation 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), for example, 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—due to an increasingly positive charge developed as the spectrum was

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

Abbreviations: CC, charge compensation; XPS, X-ray photoelectron spectroscopy.
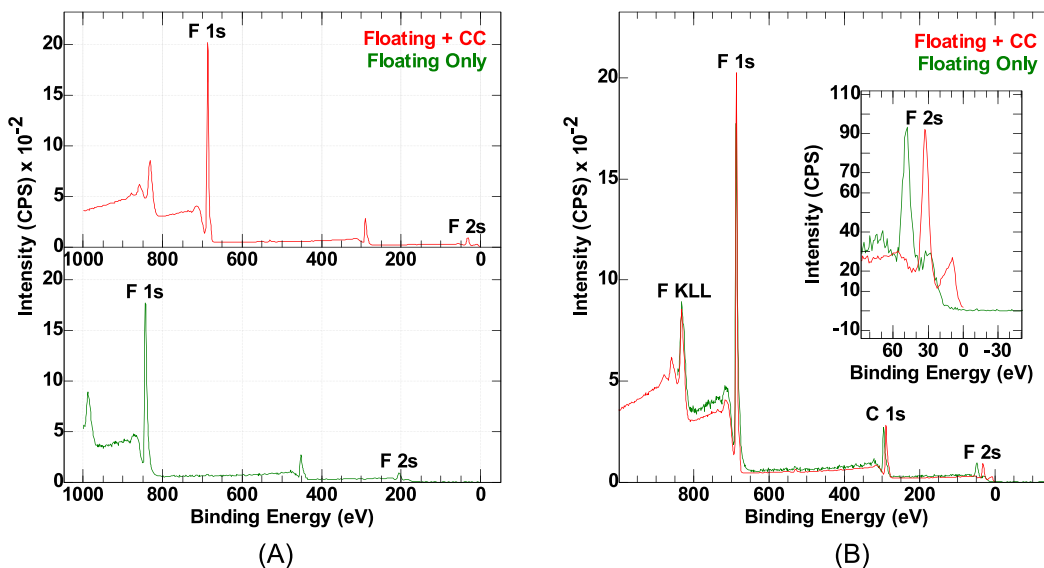
FIGURE 1 An insulating PTFE sample measured using *Floating + CC* and floating only conditions (Table 1). (A) XPS survey spectra before calibration and (B) after calibration using the maximum of the F KLL spectral signal. The inset in (B) shows the misalignment of the F 2 s spectra due to time-dependent changes in potential experienced by electrons emitted from the PTFE sample when no CC is performed. CC, charge compensation; PT-FE, polytetrafluoroethylene; XPS, X-ray photoelectron spectroscopy.

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 the sample.

2.2 | Case II. An electrically heterogeneous sample: Aluminum foil + aluminum oxide

Here we study the case of Al foil surface covered by aluminum oxide at the bottom and the top.[10] 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 aluminum 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 aluminum 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 aluminum and aluminum oxide layers, 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 aluminum 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.

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) versus heterogeneous (Al + Al oxide) electrical properties. The phenomena observed here for Al + Al oxide system are in agreement with previous literature reports.[3,12–14]
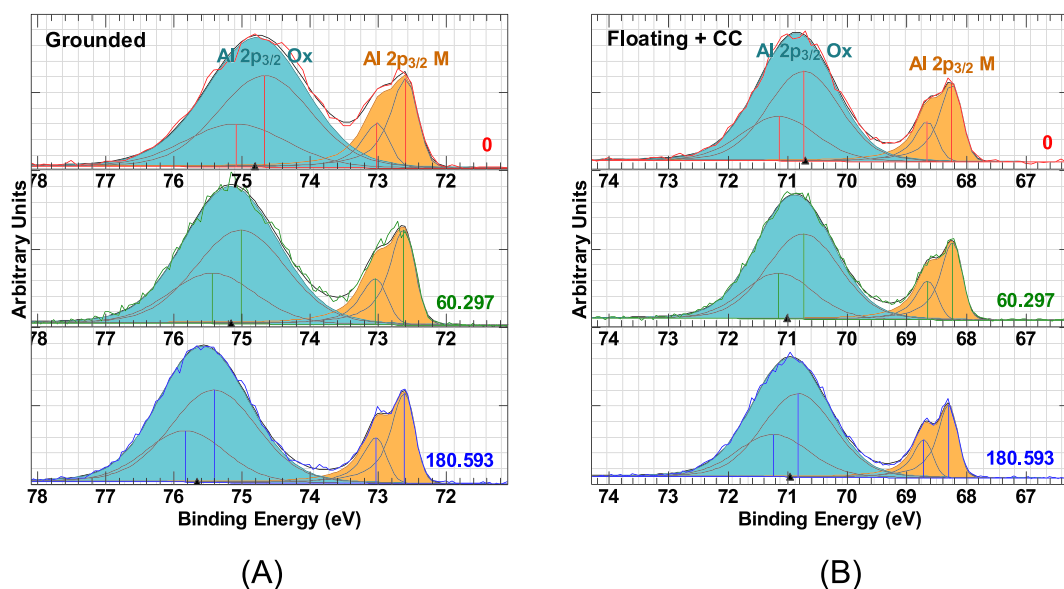
FIGURE 2 A sample of Al metal (M) with layers of aluminum oxide (Ox) at the bottom and the top. Al 2p spectra measured at increasing times (top to bottom panels) using (A) *Grounded* and (B) *Floating + CC* settings (Table 1). In (A), the Al 2p binding energy for the metal is the expected binding energy, 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 aluminum oxide shifted consistently to lower binding energy. Spectra were fitted using CasaXPS.[11]
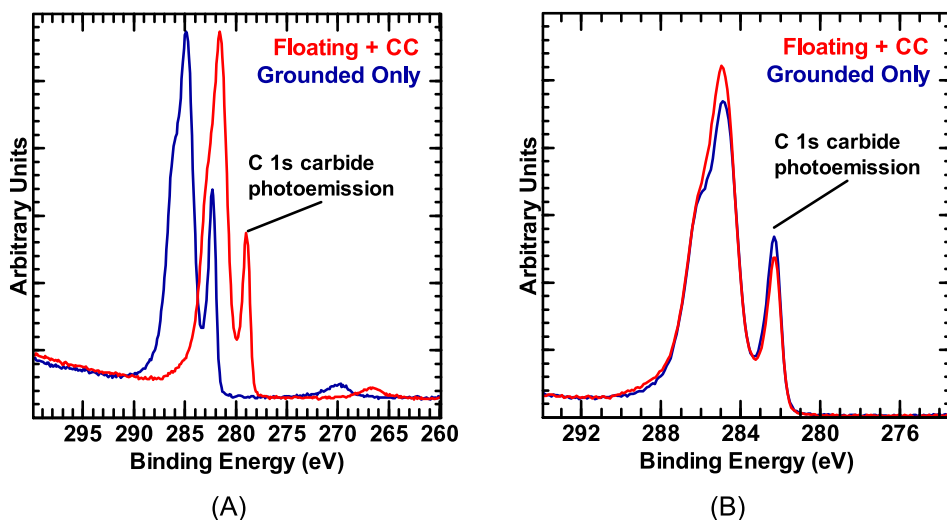
FIGURE 3 The vanadium carbide sample measured using the grounded only and the *Floating + CC* approach (Table 1). C1s spectra (A) as-acquired and (B) calibrated using as reference the E_{BE} of the Cl $2p_{3/2}$ spectral signal of the grounded spectrum.

2.3 | 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 1 s, V 2 s, O 1 s, V 2p, Cl 2p, Al 2 s, V 3 s, 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 respect to the *Grounded* spectrum. The *Grounded* spectrum seems to be effectively charge compensated as the C 1 s signal was 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, that is, 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.

FIGURE 4 MoO_3 powder sample measured repeatedly using the Grounded + CC approach (Table 1). (A) Mo $3d_{5/2}$ and (B) O 1 s spectra. The apparent binding energy shift of both spectral regions is consistent.
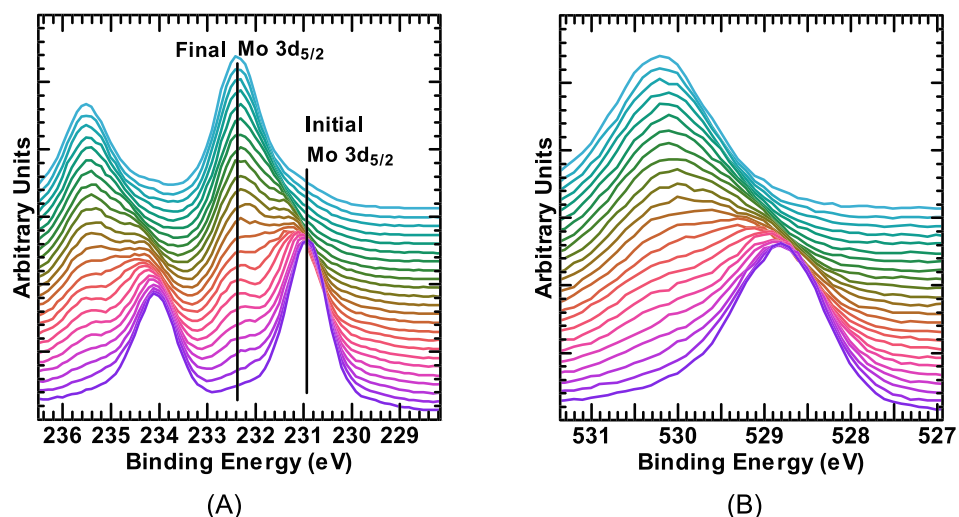
The most widely used approach for calibration of XPS data is the use of the C 1 s signal from adventitious carbon sp^3.[2,12,15,16] In this case of study, a complex C 1s envelope involving several C bonds made it difficult to unequivocally identify the C1s sp^3 signal, whereas a well-defined vanadium carbide signal at the lowest E_{BE} was 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} 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.

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

Molybdenum trioxide (MoO_3) 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.[17] This process is accelerated by sample heating.[5] However, besides X-ray-induced spectral changes, XPS spectra distortions are also introduced by CC processes. A MoO_3 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 $3d_{5/2}$ 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 CC approaches of such different instruments.[3]

These E_{BE} shifts are explained as follows. MoO_3 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 CC, 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}. CC 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, other spectral changes potentially induced by sample degradation.

3 | 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 summarized as follows:

1. Pretests 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.

3. Whereas prior information about the sample physical and chemical properties 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. For the particular set of samples here analyzed, the *Floating + CC* conditions achieved effective CC. Whereas this set of samples is representative of a broad range of chemistries and most common physical properties affecting XPS measurements, the *Floating + CC* conditions cannot be generalized as a universal practice. This is especially true for unconventional samples of complex architectures. Currently, we witness a rapidly evolving field seeking the development and application of the so called heterostructures, which are constituted by nanometer-thick layers of at least two different materials assembled in a layer-by-layer fashion in vertical or horizontal architectures.[18] This brings a variety of chemistries in a single sample with different physical properties and interfaces, which surely complicates sample charging effects that need to be analyzed on the individual basis. On the other hand, the practical use of CC can be challenging and requires a fair degree of expertise on the fundamentals of charging phenomena as well as experience on technical aspects related to the suitable use of the technique. Hence, the pretesting of samples here demonstrated is recommended especially for XPS beginners.

4. Acquisition and evaluation of the survey as well as a range of narrow spectra are 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.

On the practical side, surely XPS users have to consider what best suits their needs taking into account measuring time and running costs versus accuracy and consistency of the obtained data. In addition, measurements will be conditioned by the particularities of each instrument, for example, the no availability of CC.

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); formal analysis (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).

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