Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy

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ABSTRACT

The methodology presented within this work is a result of years of interactions between many junior and senior X-ray Photoelectron Spectroscopy (XPS) users operating within the CasaXPS spectral processing and interpretation program framework. In particular, discussions arising from a series of workshops have been a significant source for developing the overall XPS data processing concept and are the motivation for creating this work. These workshops organized by the Institut des Matériaux Jean Rouxel (IMN), Nantes gather both experienced and novice users of XPS for a week of discourse in conceptual experiment design and the resulting data processing. However, the framework constructed and utilized within these workshops encouraged the dissemination of knowledge beyond XPS data analysis and emphasized the importance of a multi-disciplinary collaborative approach to surface analysis problem-solving. The material presented here embodies data treatment originating from data made available to the first CNRS Thematic Workshop presented at Roscoff 2013. The methodology described here has evolved over the subsequent workshops in 2016 and 2019 and currently represents the philosophy used in CasaXPS spectral data processing paradigm.

1. Introduction

X-ray Photoelectron Spectroscopy (XPS) is utilized to provide a chemical composition of complex materials that range from inorganic to biological materials under UHV conditions with recent developments in the instrumentation allowing to operate under elevated pressures or moist environments [1–5]. The ensuing data interpretation of the complex spectral lines has been developing for decades with recent advancements made in operator bias-free methods [6–8] as well as understanding and quantifying the underlying (un)systematic errors [9,10] as well as developing the overall experiment planning, data acquisition and interpretation strategies [11,12]. The discussion that follows is an example analysis for molybdenum sulfate developed as part of the CasaXPS user group aimed at developing a holistic methodology for XPS analysis while calculating the amount of molybdenum measured by XPS from a particular sample. This example has been chosen because

creating a peak model for Mo 3d and S 2s is one of the best options available for estimating the intensity of photoemission from molybdenum.

Before describing a detailed analysis for a relatively simple XPS measurement, it is worth discussing an overall experimental planning and implementation flow. The first and most important part of data treatment is to ensure a measurement includes all relevant spectra necessary to understand a sample. Secondly, when attempting to analyze data, the interpretation of a spectrum is dependent on understanding how this particular spectrum relates to other spectra measured at the same time as the spectrum. Therefore, receiving a complete set of data for analysis is the most important step on the path to understanding a sample. While a measurement by XPS is typically aimed at understanding a sample surface, it is also worth bearing in mind the experiment is an investigation into the interaction of a material modified by photoemission in a low-pressure environment. The question of what happens to a sample when photoemission occurs should be considered for all samples, but is most important for insulating samples, as the measurement of such samples requires complex mechanisms for replenishing photo-emitted electrons to the sample. Indeed, any interaction of the sample with components of an instrument may influence XPS data. The act of cleaning a sample using an ion beam also represents an intervention in sample composition using Ar^+ beam [13], the effects of which on the sample must be considered when interpreting spectra. Finally, the advantage of understanding the physics of XPS when measuring a sample should not be underestimated. Similarly, the advantages of understanding the material properties of a sample are equally important. It is, therefore, necessary to have available, persons with knowledge of both.

Once XPS data are obtained, interpretation of the data is equally as important as the overall analysis process, and in fact, should be considered an integral part of the analysis workflow. Analysis of initial measurements is often the route by which future measurements are designed that ultimately allows a scientifically meaningful outcome. Thus in practice, there are several bodies of knowledge base essential for any XPS work, namely, (a) knowledge of XPS instrumentation, (b) knowledge of the sample and (c) knowledge of how to analyze data. While it is true that there are many examples of analysis by XPS for which a complete knowledge in all three areas is not necessary, more involved uses of XPS are best served by appreciating the need for all three areas of knowledge. In this sense, we proposed that XPS is a team activity with the knowledge of the overall analysis procedure best shared across several people to arrive at accurate conclusions. Data treatment technology is often shared between both a material scientist and the instrument expert, but both rely, to a greater or lesser extent, on the support of others within their research field, the instrument vendors and designers of data analysis software. Collaboration is therefore an important part of working with XPS.

In the following sections, at least three types of the knowledge base, integral to the XPS experiment, will be considered in the context of a specific set of data. XPS spectra discussed below were measured using a Kratos Axis Ultra at the University of Manchester [14] from a molybdenum sulfate sample. Data exported from the instrument-native file format to ISO 14,976 (VAMAS) format [15] are analyzed using CasaXPS. CasaXPS data analysis software was designed to process spectra and images using the ISO 14,976 file format. The software was first released in 1999 and has been developed over subsequent years to support the conversion of data formats from a wide variety of sources into ISO 14,976 formatted data. One of the themes of the CNRS Roscoff workshops was the analysis of data in CasaXPS for the reason that users of different instruments from different manufacturers can apply the same data analysis techniques in the same software to make sense of samples, exchange ideas and exchange data with ease envisaged by the original VAMAS project. One of the outcomes for these workshops is the creation of videos that can be viewed via the CasaXPS Casa Software YouTube channel [16], Prof. Mark Biesinger's YouTube channel [17]. Corrections

to photoemission intensities are performed via Scofield cross-sections [18], National Physical Laboratory transmission correction [19], escape depth correction based on effective attenuation [20] and angular distribution correction assuming an angle between the X-ray source and the direction of collection equal to $60°$.

2. Instrumentation

The first step to understanding the influence of instrumentation on spectra is obtaining information about the specific instrument used to measure the sample. Spectra necessarily include shapes that are characteristic of a specific instrument. Even instruments of the same make and model can generate different spectra, depending on settings and instrument configuration. The instrument influences shape because the instrument's ability to record electrons changes with the kinetic energy of the recorded electron. These variations are referred to as transmission for an instrument and are most apparent in wide scan spectra, where photoemission signal is measured over a large energy range, displaying all available photoemission peaks for a material. The influence of transmission is significant to relative intensities in photoemission peaks and also the line-shapes seen in the inelastically scattered photoemission signal that appears as background to photoemission peaks.

In addition to transmission, a specific instrument will generate photoemission peaks with shapes that are dependent on the instrument and operating mode used to measure spectra. Electrons emitted from a sample are transferred from the sample to a detector by a set of lenses [21]. The characteristics of these lenses, how these lenses are tuned and how these lenses steer electrons through apertures within the lens system, alter the shape of the recorded photoemission peaks. From the data analysis perspective, in an ideal instrument, the transmission would be flat. A flat-transmission response is a necessary condition to ensure that both the size of the analysis area and the angular acceptance of electrons remain constant during a measurement, without dependency on electron-energy. In the absence of flat transmission response, a comparison of photoemission peaks requires a sample that is homogeneous in the area and homogeneous in-depth distribution. Knowledge of the true transmission is therefore useful when understanding limitations imposed by an instrument on interpreting relative intensities of photoemission peaks.

Similarly, line shapes for photoemission peaks are specific to the pass energy, aperture widths and energy distribution within the X-ray source. The width for a peak measured by a specific instrument is also limited by these factors. Therefore, attempting to model a photoemission signal, using a synthetic component that is narrower than what might be possible for an instrument, can be avoided when one knows the limitations of a particular operating mode.

For the data considered here, pertinent information about the instrument is discussed to illustrate the types of considerations one might address when analyzing spectra from the instrument in question. These discussion points are not intended to be exhaustive but are included to demonstrate the benefits of information within a VAMAS file compiled with experimental context. The instrument used to measure the data presented here is a Kratos Axis Ultra. Spectra are measured using a lens mode referred to as Hybrid mode, with a pass energy of 40 eV for survey data and a pass energy of 20 eV for narrow scan data. In both cases the aperture arrangement used to prepare electrons for entry into the energy filter hemispherical lens element (HSA) are two slots positioned at the entrance to the HSA and within the transfer lens column. The arrangement of apertures is important because it influences both transmission and energy resolution when spectra are collected. Not all information relevant to this experiment is included in the VAMAS file. For example, the state of an iris at the bottom of the lens column is not recorded in the file. However, the use of Hybrid mode and the shape of the transmission curve added to the VAMAS file imply the angular acceptance iris is fully open.

The size of an angular acceptance iris is important for quantification

by XPS. The iris is located close to the sample and is designed to limit the solid angle of photo emitted electrons entering the lens system. Limiting the solid angle restricts the emission directions that are accepted into the analyzer and give rise to the measured spectrum. The solid angle, limited by the size of the angular acceptance iris, and depending on lens mode, may change with the kinetic energy of electrons. Thus, the transmission may deviate from a flat response as the number of electrons recorded changes, due to a change in the solid angle, with kinetic energy. Another aspect to consider is that, to some extent, a change in acceptance angle changes the volume within the sample from which electrons are collected, since probing depth depends on emission angle. Both have implications for the quantification of heterogeneous samples.

The VAMAS file also indicates spectra were acquired making use of charge compensation. The sample is therefore assumed to be an insulating material, for which electrons leaving the surface are not replenished by electrons conducting through the material from a ground connection. While charge compensation is a feature of most modern instruments, the ability to create a uniform, steady charge state for a given sample may depend on the sample, the size of the sample, the size of the analysis area and the efficiency of the charge compensation method. The fact that charge compensation is required to obtain suitable spectra implies that there is the potential for artifacts within spectra that would not be present in spectra for a fully conducting sample connected to the ground. The detail of and interpretation of information within the VAMAS file are the foundation upon which scientific output from XPS is achieved.

3. Sample knowledge

Sample knowledge resides mostly with the person providing the sample and wishing to perform an XPS experiment. However, XPS experts often have significant input for the analysis of novel materials simply based on experience gained with similar materials. Prior knowledge about the sample is very useful to an analysis by XPS. Understanding spectra obtained from a completely random sample composition is challenging at best. Some expectation for sample composition and chemistry is a clear advantage for evaluating spectra.

However, some words of warning regarding expected sample composition are worth mentioning. A sample from the point of view of XPS is the material in the surface, limited to the top three to four attenuation lengths for electrons moving within the sample. For XPS based on X-rays with a photon energy of 1486.6 eV, for example, the depth relative to the surface interface is limited to less than 12 nm. There are few analytical techniques capable of focusing on this surface film with the surface sensitivity of nanometres. Therefore, assumptions about sample surface composition that are based on measurements performed with bulk techniques, such as Atomic Absorption Spectroscopy (AAS) or Energy Dispersive Spectroscopy (EDS), will often be inconsistent with those of XPS. Specifically, the bulk composition of a sample is not necessarily the same as surface composition, as measured by XPS.

As XPS is a surface-sensitive technique, surface contamination is important [22]. The history of a sample provides food-for-thought when interpreting the initial data. A hard polymer sample prepared by slicing with a scalpel may result in spectra that appear to be that of the stainless steel. A polymer mounted near to a silver standard and is cleaned via ion beam creates polymer spectra containing silver. A more subtle problem occurs if an instrument has previously been used to measure a fluorine-based sample. Subsequent measurements of samples may be contaminated by fluorine by simply placing these samples into the vacuum chamber. However, the most common source of contamination is adventitious carbon. Handling and storage of samples can cause great uncertainty when attempting to quantify a sample. Knowledge of the sample and its history are fundamentals by which successful data analysis is possible.

It is also advisable to seek advice or perform tests aimed at understanding how a sample responds to XPS. Some samples degrade when measured by XPS and being aware that a sample degrades would influence how measurement might be performed. For example, the choice of measurement order for narrow scan data could be important. If, for example, one of the XPS peaks changes with irradiation time, while others do not, then one would want to measure the changing peak first, to minimize radiation exposure. Another strategy to accommodate samples sensitive to radiation is to perform many repetitions using short dwell-time recording each measurement as separate spectra, then from the resulting data selectively process spectra with better signal-to-noise. Making sure the sample is stable under measurement conditions is a key test to perform before embarking on an analysis of XPS results. It is also important to ensure an analysis area is representative of a sample. Preliminary measurements at different locations on a sample are used to verify that the spectra chosen for interpretation are indeed representative of the sample.

3.1. The motivation for studying "molybdenum sulfate"

The sample knowledge used in the analysis presented here is limited. These spectra were provided as part of a set of data measured from a variety of samples for use at the first CNRS Thematic Workshop held in Roscoff 2013. These data were labeled "molybdenum sulfate", however, the survey spectrum shown in Fig. 1 indicates other elements such as Fe and Cr are also within the sample surface. While, ideally, more information about the sample would be better, in some sense the analysis of these data is typical of samples examined by XPS, namely, one objective of XPS is to assess what elements are actually within the sample as prepared.

Fortunately, these are not the only data for molybdenum available at the time of analysis, and so information about line shapes for S 2s and Mo 3d, gained by examination of additional data [8], could be utilized when constructing a peak model for the sample of interest. Ideally, these additional data would be measured using the same instrument that was used to measure the molybdenum sulfate, but the scenario explored here is closer to the reality of a typical routine XPS measurement. That is, instrument time and availability of standard samples do not permit the ideal sequence of experiments to be performed.

4. Analysis of data

The first observation [23] based on the survey measurement in Fig. 1 is the sample includes a significant proportion of carbon. If it is assumed carbon is a contamination layer uniformly distributed over the sample, then one might expect attenuation of photoemission peaks with lower kinetic energy compared to a perfectly clean sample of identical composition. It is not absolute given that uniform coverage is a good assumption for modeling the effect of carbon contamination on attenuating the other peak intensities. For example, if the surface is contaminated by carbon in the form of a set of islands of thickness greater than three attenuation lengths over a surface of the relatively clean sample, then the carbon would act as a mask blocking the signal from the sample. But on areas away from carbon islands, photoemission from the sample would appear as if from a clean surface. When presented with a heterogeneous sample, quantification by XPS is subject to many considerations that would explain why relative peak intensities deviate from the expected values. In general, the acquisition and the initial inspection of the XPS survey spectra should follow rigorous procedures and rules documented, for example, ISO standards that will allow to evaluate and correct for the contamination with adventitious carbon for thin films [24], among other first-hand evaluation methods, to make a critical decision if the data is worth processing. Upon further processing, ASTM standard for charge control and charge referencing [25] is of utmost importance to follow for reproducibility, especially for insulating samples, as summarized by Baer and coworkers [26] and reflected in the 27 papers in the recent collection focusing on the reproducibility challenges related to surface spectroscopy [27].
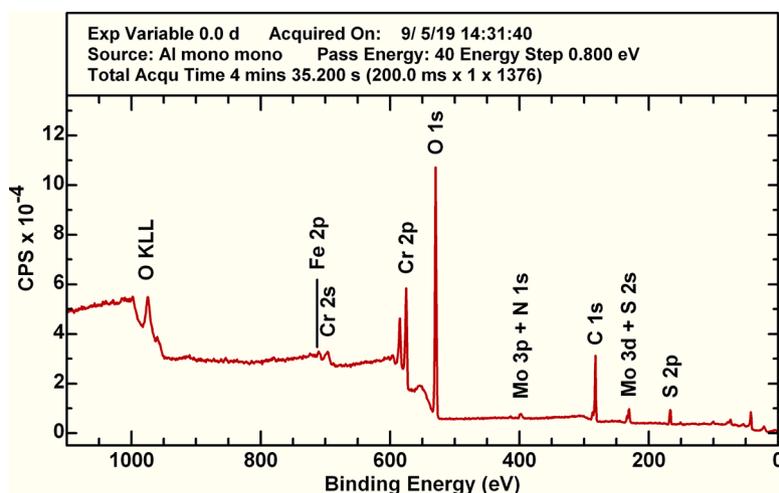
Fig. 1. Survey spectrum obtained for molybdenum sulfate sample.

The second observation from survey data shown in Fig. 1 is that the presence of molybdenum and sulfur is confirmed by the existence of photoemission peak patterns matching these elements. Photoemission from molybdenum with the highest intensity is Mo 3d. Unfortunately, there are two photoemission peaks, namely, Mo 3d and S 2s that are very close to each other in binding energy forcing the use of a peak model to separate molybdenum signal from sulfur. One might consider using other photoemission peaks of molybdenum as the means of quantifying the amount of molybdenum. Mo 3p is a possible candidate, but Mo 3p is potentially similarly compromised by an overlap with N 1 s. Using the survey spectrum, it is possible to observe the ratio for Mo $3p_{3/2}$: Mo $2p_{1/2}$ is not the expected 2:1 ratio, so the N 1 s signal may be responsible for the increased Mo $3p_{3/2}$ doublet peak. A peak model for Mo 3d and S 2s is therefore the best means of estimating the amount of molybdenum. Another reason for choosing Mo 3d/S 2s signal is the proximity of S 2p to S 2s. The intensity for S 2p is potentially of use when establishing the intensity for S 2s which must be calculated as a component in the peak model.

If the relationship between photoemission peaks from different electron configurations of the same element is used to support a peak model, then the potential problems of doing so should also be considered. The degree of error when comparing photoemission peak intensity is mitigated by choosing peaks close in energy. The reason the energy for photoemission peaks matters is as follows. XPS is a surface-sensitive technique precisely because photoelectrons moving within a solid are inelastically scattered and, given a path of travel of sufficient length, fail to emerge with the energy characteristic of an electron in a bound state. An overlayer of carbon increases the probability of inelastic scattering for electrons from molybdenum sulfate. Further, attenuation of signal due to inelastic scattering depends on kinetic energy. S 2s signal occurs at lower kinetic energy than S 2p. Therefore, due to an overlayer of carbon, the S 2s intensity relative to S 2p may be lower than expected. Since these two photoemission peaks are close in kinetic energy, the intensity ratio for photoemission at these two energies is less prone to error compared to peaks farther away in kinetic energy. Nevertheless, overlayer contamination poses a problem for such comparisons of peak intensities.

The analysis of these data would be easier if the carbon contamination were not present. Fortunately, there is evidence within these data shown in Fig. 1 that carbon does not form a thin layer over molybdenum sulfate. The evidence is based on the background associated with Mo 3d/ S 2s and S 2p. In the case of S 2p, the background does not respond to the S 2p peak but remains flat beneath the photoemission peak. Further, the background to lower kinetic energy relative to S 2p does not respond either. Thin films of carbon would result in increases in the backgrounds

of photoemission signals from buried elements, due to inelastic scattering. As this is not the case here, it appears sulfur is at the surface and even possibly mounted on top of the carbon.

In the analysis that follows, the assumption is that contamination is not a uniform film over the sample. Hence a comparison of S 2s to S 2p intensities is appropriate. The assumption may well be incorrect, but the steps described here are aimed at illustrating what is possible provided the necessary verification of sample cleanliness is performed and quantification calculations are reliable.

The final routine check that should be performed is to examine narrow scan data for abnormal shapes that might indicate charge-compensation failed to arrive at a uniform steady-state potential for the sample. High-resolution data are most sensitive to varying potential at the surface and narrow photoemission peaks are also useful when looking for a non-uniform potential steady state. Repeat measurements of the sample can improve confidence in charge compensation as these should be used to look for variation in separation of photoemission peaks at opposite ends of the energy scale in survey data. If the separation in the energy of a low kinetic-energy peak from a high kinetic-energy peak changes between repetitions, then the charge compensation may not have achieved a steady-state potential even though photoemission peaks appear to be well-formed.

The discussion now proceeds to assume all necessary checks have been performed, and spectra are without artifacts of significance.

4.1. Use of known samples when creating peak models

The most probable oxidation state of molybdenum cation is 6+ due to its stability as in molybdenum trioxide. Therefore a reasonable first assumption is Mo 3d spectra obtained from MoO_3 will be an approximation to the doublet peak due to Mo 3d emitted from molybdenum sulfate. Mo 3d spectra measured from samples containing molybdenum trioxide, with and without sulfur, are part of a library of data [8] available at the time these molybdenum sulfate spectra were collected. It is therefore possible to gauge the character of line shapes and relationships between peaks from both Mo 3d and S 2s. Luckily, these library data included examples where sulfur was both abundant and sparse. Therefore, in Figs. 2 and 3 spectra measured from these two extremes are fitted as a means of estimating fitting parameter relationships between Mo 3d doublet components and, equally as important, the line shape for a component representing S 2s.

These data allowed the relationship between doublet components in Mo 3d to be established. Constraints based on the fit to these data are used to model data in Figs. 3 and 4. Line shapes defined by LA(1,n) are numerically integrated Voigt functions. The parameter n is an integer
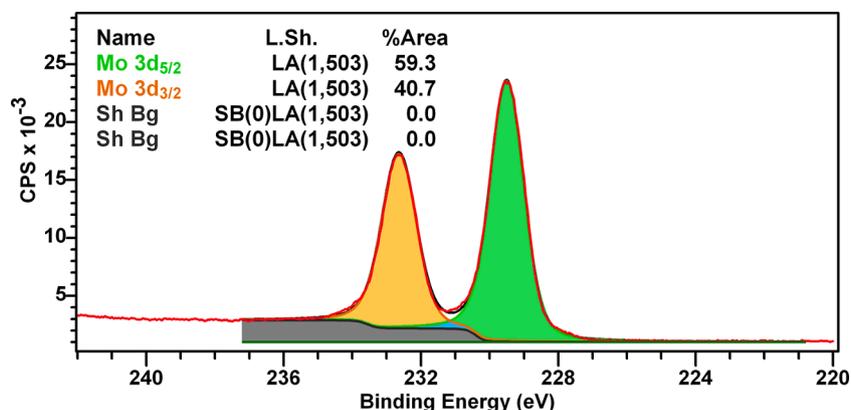
Fig. 2. Mo 3d doublet measured from molybdenum trioxide at a point on the sample where there was no evidence of sulfur. A component used in a peak model to accommodate a Shirley background shape is constructed from the bell-shaped line-shape LA(1,503) by applying a prefix SB(0) to the line-shape LA(1,503).
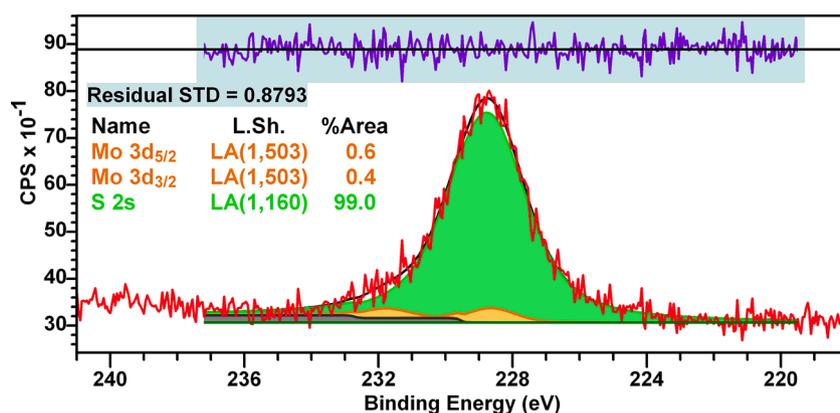

Fig. 3. Mo 3d spectrum from molybdenum trioxide sample at a location on the sample where molybdenum was mostly absent but sulfur appeared relatively abundant. These data form the basis for asserting S 2s is reasonably modeled using a pronounced Lorentzian Voigt function LA(1,160).

value specifying the relative width of a Gaussian and Lorentzian used to construct the Voigt line shape. Background intensity changes, due to Mo 3d emission, are accounted for by applying Shirley background SB(0) sigmoid components to the bell-shaped line shape LA(1,503) located concerning Mo 3d zero-loss signal. Both bell-shaped LA curves and components representative of the background may be optimized to obtain peak models that reproduce data envelopes.

Fortunately, the line shapes for these two photoemission peaks Mo 3d and S 2s are significantly different. Despite these differences in shape, Mo $3d_{5/2}$ and S 2s are highly correlated, which is never helpful when fitting components in a peak model to data. The model shown in Fig. 3 is heavily weighted in favor of S 2s. Therefore, while confidence in the relative proportions of Mo and S for these data is low, in terms of line shapes for S 2s these data in Fig. 3 serve to provide an estimate for the S 2s line shape. The essential shape for S 2s is seen to be Lorentzian in nature, which is consistent with the shape observed for the peaks in Fig. 4a. The selection of line shape based on data in Fig. 3 can be made with reasonably high confidence. Nevertheless, as a consequence of these library data, based on Mo 3d determined from data in Fig. 2 and the line shape for S 2s in Fig. 3, a peak model is constructed and applied to data of interest in Fig. 4a.

The peak model in Fig. 4a, under constraints defined via other means, as described above, offers good precision when estimating the amount of substance for molybdenum and sulfur. Accuracy for these quantities is less certain, but confidence in the accuracy is enhanced by comparing the intensity for S 2s to the intensity for S 2p, which is isolated and can be estimated using simple integration over an energy interval (Fig. 4a) and leads to 50:50 ratio between both corrected areas.

There is however always uncertainty about the accuracy of XPS quantities owing to instrumental factors, uncertainty in sensitivity factors and other unknowns such as the true background created by inelastic scattering of electrons. The relative areas for S 2s and S 2p shown in Fig. 4a provide confidence for the use of the peak model as shown, but achieving 50:50 for the corrected areas of these two photoemission peaks from sulfur is not absolute proof the peak model is accurate.

This issue of accuracy is illustrated by observing that the relative proportions of the S 2s component to the area calculated by integration from the S 2p signal can be made to change by altering the Gaussian width used in the convolution integral from which the S 2s line shape is formed. Generally speaking, changes in shape to any synthetic line shape used in a peak model may alter the relationship between component areas, and therefore, quantification outcomes.

The fact that altering line shapes alters quantification is the main reason it is important to establish the appropriate line shape for a given photoemission mechanism by means other than mathematical optimization. To be precise, line shape parameters should not be selected by optimization on a case-by-case basis. The steps illustrated here involve selecting the line shape for S 2s based on multiple sets of data and attempting to ensure the correct relationship to S 2p. Once line shapes are selected, the line shapes in a peak model should not be altered without extremely good reasons based on science rather than the mathematics of optimization.

While precision in measuring molybdenum via the peak model in Fig. 4a is acceptable, the relative intensity for molybdenum to sulfur determined by this method requires explanation. The meaning for these components must be interpreted in the context of the survey spectrum in
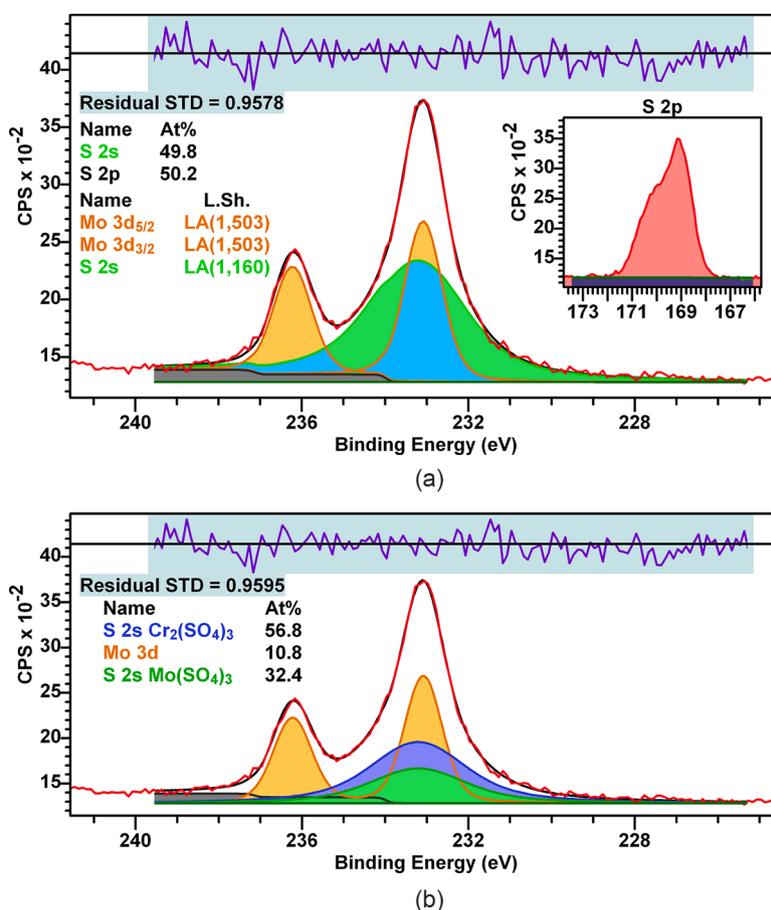
Fig. 4. (a) The peak model was constructed based on data in Figs. 2 and 3, aimed at measuring the amount of molybdenum in the sample of interest. Correlating the ratio of peak intensity for S 2s and S 2p, allowing for corrections necessary to make a fair comparison, provides supporting evidence for the use of the line shape LA (1,160) selected for S 2s. (b) the peak model that accounts for the complexity of the sample, e.g. presence of chromium, as evidenced by Fig. 1.

Fig. 1. The survey spectrum includes photoemission from chromium of significance, the importance of which is emphasized by the observation that the analysis in Fig. 4a does not return the expected ratio (1:3) between molybdenum and sulfur for molybdenum sulfate. One explanation for an excess of sulfur relative to molybdenum when comparing the ratio for components assigned to Mo 3d and S 2s is that the sulfate ion is present within the sample coordinated to other elements. After reviewing survey data in Fig. 1, the most likely candidate other than molybdenum is chromium. Therefore the model shown in Fig. 4a is best described as suitable for analyzing samples which include Mo^{6+} and SO_4^{2-}. Further spectral interpretation can be obtained by using survey spectra in Fig. 1 or the corresponding high-resolution spectra to obtain the amount of chromium on the surface and account for that during the quantification. An example of this is shown in Fig. 4b where the S 2s peak is now a sum of two components, namely $Cr_2(SO_4)_3$ and $Mo(SO_4)_3$. Since Fig. 1 also indicates in the real-life samples measurable amounts of iron, quantification may be expanded beyond this example while maintaining the correct ratio of Mo 3d doublet peaks.

Quantification of a sample based on survey measurements can provide important evidence to support analysis by peak model. However, in this example the survey spectrum suggests the sample, as far as XPS is concerned, is potentially heterogeneous and given the origin of these data, we have no understanding of the role played by carbon in the chemistry of the sample. Carbon seen in Fig. 1 may be surface contamination which alters methods used for quantification [28]. Both of these observations mean quantification based on sensitivity factors generally applicable to homogeneous samples when applied to samples with less well-defined composition is prone to error [23]. Nevertheless, the survey spectrum used in a qualitative sense is important to interpreting the

peak model in Figs. 4a and b. The following section is an example of where the sample is unavoidably heterogeneous. Hence the issues discussed above are relevant to samples of the nature presented below.

5. Implications of the constructed model

The peak model shown in Fig. 4 may appear uninteresting from a material science perspective. However, studies of wear tracks on samples of tribological origin present more challenging problems for XPS analysis and the use of peak fitting data envelopes is essential to such research. Results from a tribology study, analyzed by XPS imaging, are presented in Fig. 5. The images in Fig. 5 are the result of data treatment applied to a set of images acquired over a range of energies corresponding to the spectra in Fig. 6. In particular, these images are constructed by partitioning the signal at each pixel into spectra shown in Fig. 6. An analysis of these spectra in Fig. 6 requires an understanding of Mo 3d/S 2s gained by considering materials such as molybdenum trisulfate, molybdenum disulfide, molybdenum trioxide and molybdenum dioxide. Without an appreciation for the peak model in Fig. 4, it would be easy to overlook the possibility that these data in Fig. 6 may include the S 2s signal within the shapes one might think are characteristic of MoO_3 in a 6+ oxidation state only.

One important point that should be highlighted is that the analysis of imaging data sets does more than showing the spatial distribution of chemical phases, but also provides information about possible charge compensation differences over the analysis area. The spectrum in Fig. 6 labeled *Mo 3d/S 2 s 6+ Rich* includes a feature labeled A which appears to be residual molybdenum disulfide (4+) located on the sample where molybdenum 6+ is dominant. The recorded energy for the feature
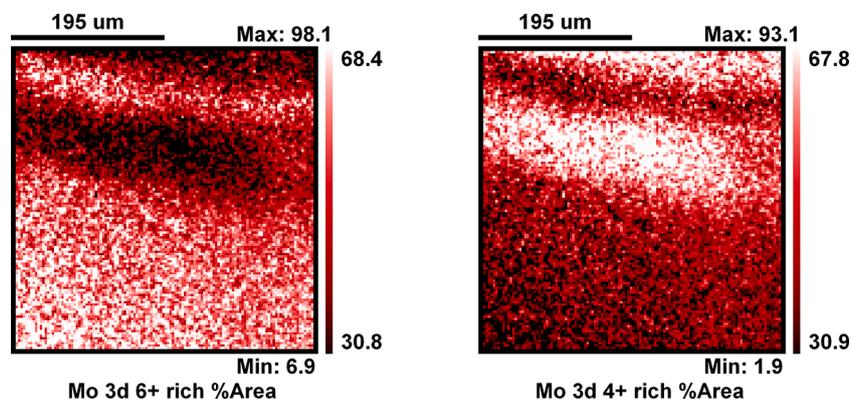
Fig. 5. XPS images measured from a wear track, the chemistry of which requires the analysis of spectral shapes seen in Fig. 6. These images are formed from a data set consisting of a set of XPS images measured sequentially over an energy interval corresponding to the spectra shown in Fig. 6. Spectral information at each pixel location is fitted using the two spectra in Fig. 6 and the relative contributions of these two spectra at each pixel are used to construct these two images.
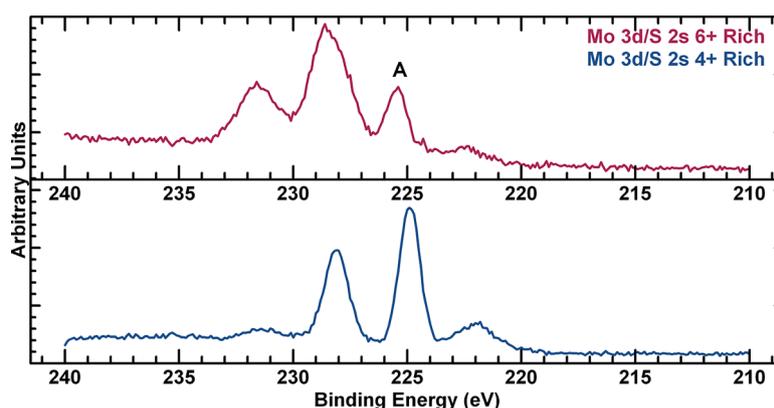

Fig. 6. Spectra derived from a representative spectromicroscopy data set. These two spectral envelopes are characteristic of two phases in material properties associated with a wear track. Analysis of these spectroscopic shapes requires an understanding of both molybdenum sulfide and molybdenum sulfate.

labeled A is offset in energy relative to peaks for the same material from locations where the molybdenum disulfide is dominant. A shift of this nature may well be related to charge compensation variation between zones on the sample, with different material properties. The purpose of this example is to emphasize that good knowledge of the sample history together with the instrument operator engagement before and during the data acquisition, as well as data evaluation stages, are key points to achieve the most reliable interpretation of XPS spectra.

These interactions are summarized in Fig. 7. In particular, the knowledge base available to an investigator consists of that acquired by an expert operator via interactions with the available complex information system. In particular:

- prior research experience, combined with research publications as well as available internet databases, are typically used to inform the planning stages of the experiments. This also involves evaluating if XPS is the only instrument that can provide the full story or other surface science imaging and spectroscopy techniques, such as Scanning Tunneling Microscopy (STM), Secondary Ion Mass Spectrometry (SIMS), Transmission Electron Microscopy (TEM) or Scanning Electron Microscopy (SEM), alternatively should be used alone or to complement XPS via a correlative approach [29];
- existing researcher expertise can be used to prepare series of samples using well-established synthesis procedures using *ex-situ* methods concerning XPS;
- expert operators typically provide their inputs or collect the information on the sample preparation, necessary for the initial spectral analysis;

- manufacturer established procedures typically are followed by the operator to maintain the instrument at the optimized performance by performing routine checks and any calibration necessary to ensure the acquired data is void of instrumental artifacts;
- the available resources, including instrument manufacturer and expert led courses, such as those by CasaXPS user base in Roscoff, France, as well as databases maintained by academic institutions, should be utilized during all stages of spectral analysis including wide scan and high-resolution scans, evaluate the validity of the data and if needed, to disqualify it. Peer-review publications then act as the main source of comparison for discussing the findings and eventually contributing to the growing knowledge base;
- it needs to be stressed that even with a prior sample knowledge a wide scan needs to be acquired and thoroughly examined while the resulting publications should include it at least in the supplemental material. This would identify the (un)expected element and their atomic composition in the surface region probed by XPS. Additionally, the corresponding information obtained from the shape of the background will elucidate buried interfaces while plasmon and shake-up information will suggest the related electronic structure phenomena;
- if possible, XPS spectral imaging is suggested to determine any elemental distribution and changes in charge or oxidation state to evaluate the need and effectiveness of the charge neutralization. The high-resolution spectra are typically selected and acquired by the operator, at least one per element, for detailed chemical composition and binding information. It is important to apply an iterative process to the peak models by varying the peak shape, the background shape
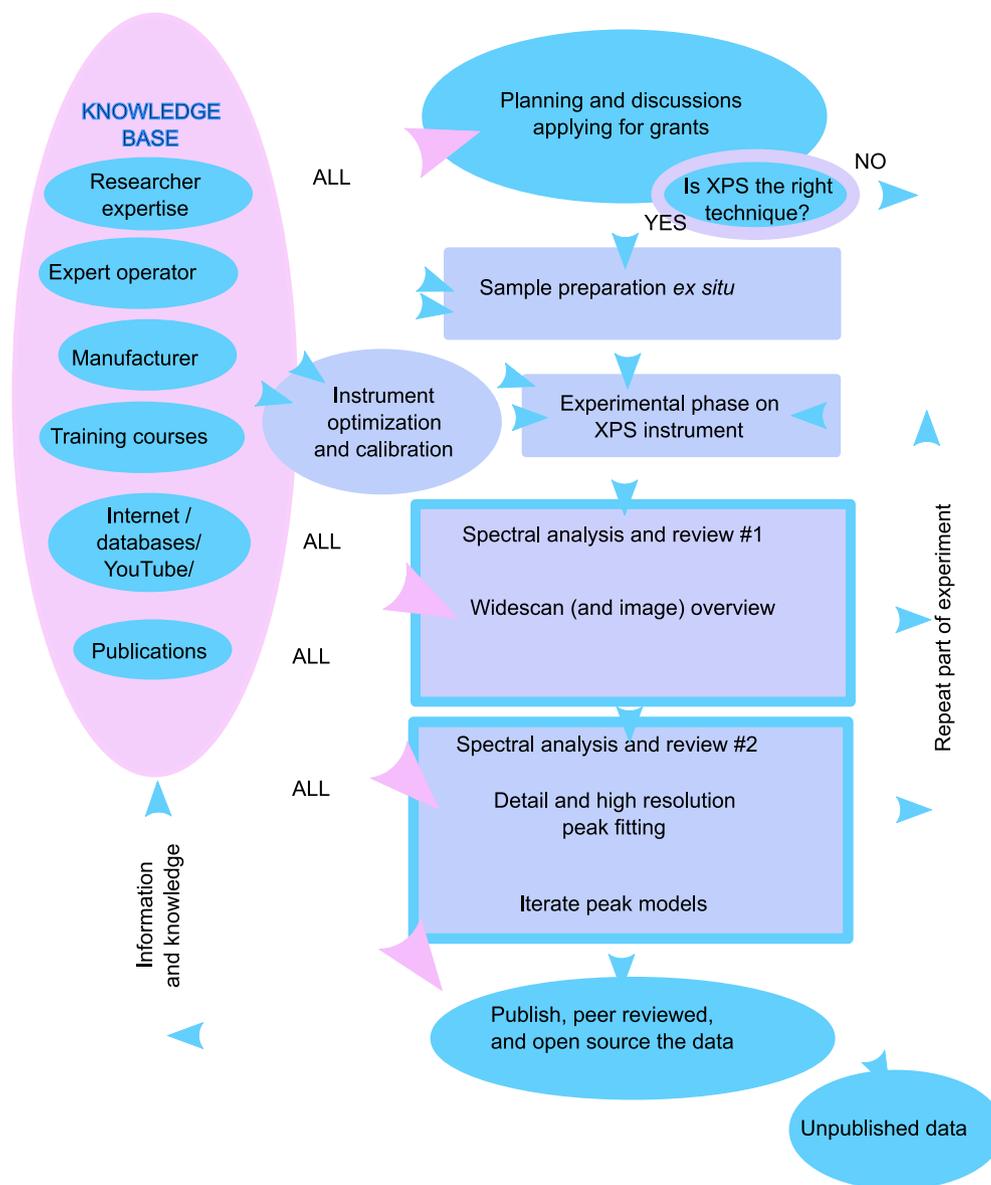
Fig. 7. A conceptual workflow of the XPS experiment that includes knowledge acquisition, storage/retrieval and sharing as well as experiment conceptualization, planning, implementation. The size of the boxes represents an approximate time/effort dedicated to each phase of the experiment.

as well as the background averaging until reliable information is obtained that can be published in peer-reviewed work.

- the data has to be scrutinized and reconciled where only reliable and reproducible peak models need to be applied for publication and the remaining data should be stored as unpublished until complementary information becomes available.

6. Conclusion

Analysis of XPS data is best performed by making use of spectroscopic data coupled with context for such data. Through the use of a specific example, general strategies for constructing peak models and the interpretation of data are presented. The focus of these discussions is to show how gathering information from data is enhanced by making use of knowledge that often resides in other researchers and that advancing science through XPS is best performed with support from other pools of knowledge. A collaboration between a researcher, instrument experts (both internal and instrument manufacturers) and experts in data treatment is the basis for successful outcomes of research that makes use of XPS. In the absence of this ideal scenario, gatherings in

the format of workshops described here provide a good approximation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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