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Practical Guides for X-Ray Photoelectron Spectroscopy (XPS): First Steps in planning, conducting and reporting XPS measurements

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Abstract

Over the past three decades, the widespread utility and applicability of X-ray photoelectron spectroscopy (XPS) in research and applications has made it the most popular and widely used method of surface analysis. Associated with this increased use has been an increase in the number of new or inexperienced users which has led to erroneous uses and misapplications of the method. This article is the first in a series of guides assembled by a committee of experienced XPS practitioners that are intended to assist inexperienced users by providing information about good practices in the use of XPS. This first guide outlines steps appropriate for determining whether XPS is capable of obtaining the desired information, identifies issues relevant to planning, conducting and reporting an XPS measurement, and identifies sources of practical information for conducting XPS measurements. Many of the topics and questions addressed in this article also apply to other surface-analysis techniques.

I. INTRODUCTION

More than half of the scientists responding to a survey that was published in 2016 indicated that there was a “significant reproducibility crisis” in science and another 38 % indicated that there was a slight reproducibility crisis.[1] Although such problems are generally thought to exist mainly in clinical or psychological studies, there is evidence that there are significant issues related to reproducibility and replication in most areas of science including those of importance to the American Vacuum Society (AVS).[1–4] The nature and causes of poor reproducibility appear to have many sources, but among them is the availability of a growing suite of automated or semi-automated experimental and computational tools in many research projects.[4]

Over the past three decades, the use of X-ray photoelectron spectroscopy (XPS) has grown and it is now the most commonly applied method of surface analysis.[5] XPS has become essential for many types of research, expanding from chemistry and materials science into many other areas including those associated with environmental,[6, 7] atmospheric,[8] and biological systems.[7, 9, 10] The rapid growth in the use of XPS is due to the importance of surfaces, very thin films, and interfaces in many areas of science and technology, the ease of operation of XPS instruments, the *perceived* simplicity of data interpretation, the ability to analyze a wide variety of samples and the provision of desired information. It was recognized about 20 years ago that, as XPS matured, the reliable use of XPS would likely be constrained by the availability of XPS experts and expertise among the many users of the technique.[11, 12] To a significant degree, this concern has become reality. It is clear to experienced XPS users that in many publications where XPS use is reported, the information is limited in some way and that too often the XPS data reported are incomplete or misinterpreted. These issues are sometimes complicated by historic differences in instrument capabilities and calibration, and the spread of binding-energy information in available XPS databases.[13]

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There are many steps involved in appropriately setting up and verifying instrument performance for a particular experimental objective, choosing suitable data-acquisition strategies, extracting the desired information from what can be complex data, and preparing a satisfactory report. Reproducibility issues related to both instrument design and operation and experimental procedures are not new. Interlaboratory-comparison studies conducted starting in the late 1970s[14, 15] demonstrated that XPS measurements, first on materials commonly used as catalysts and then on metals, were not reproducible from laboratory to laboratory. Through the efforts of many people including instrument vendors, researchers, national standards laboratories and standards committees, it is now possible to operate instruments in highly reproducible and reliable ways. Practical guides for effective and efficient XPS analyses have been developed by ASTM Committee E-42 on Surface Analysis[16, 17] and by Technical Committee 201 (TC 201) of the International Organization for Standardization.[11, 18–20] Although the information needed to make useful and reproducible XPS measurements is available, a significant number of new and less experienced XPS users (and often journal reviewers) are fooled by the easy use of instrumental software and are often not aware of the steps and care needed to produce reliable XPS data for specific analytical purposes.

A. XPS guides

This article introduces a series of XPS guides and tutorials that are being assembled by a committee of experienced practitioners to share best practices in the use of the technique. The first document to appear was a tutorial on interpretation of XPS survey spectra.[21] Although certainly not the only reason or even a primary cause, the misuse and misinterpretation of XPS data contribute to reproducibility issues in the scientific literature. We note that the U.S. National Academies have established a study group to explore the issues of reproducibility and replication in scientific and engineering research.[22] Among the objectives of the study group is an effort to highlight examples of good practices. The AVS and its flagship journals (Journal of Vacuum Science and Technology (JVST) A and B, BioInterphases and Surface Science Spectra) recognize the importance of data reproducibility on research quality and JVST is preparing to publish a series of practical XPS guides. The intent is to provide short digestible articles that provide or point to information about protocols, guides, and good practices that can enable XPS users with different educational levels and experience to apply XPS appropriately to the problems of interest to them. Some of these papers may also serve as quality guidelines for journal editors and reviewers. Similar guides may later be developed for other measurement techniques.

The present article is the first in a series of guides planned for this journal. This guide identifies sources of information for conducting XPS measurements and examines questions that should be asked when determining if XPS is the best or even an appropriate technique for obtaining the desired information about a specimen or problem. Many of the topics and questions addressed in this article apply to other surface-analysis techniques such as Auger-electron spectroscopy (AES) and secondary-ion mass spectrometry (SIMS). XPS was chosen to start this series because of its wide use.[5]

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B. Multiple Stages of XPS Experiments and Applications

Many factors contribute to the successful and reliable application of XPS. There are also multiple ways that XPS can be applied to address problems of varying complexity. Failures of different types may occur at any step in the process including, but not limited to: deciding to use XPS and preparing a sample for analysis; selecting data collection strategies, data interpretation, and reporting the results. The ultimate goal of any analysis is to obtain reliable and useful information that answers the analytical question. Above all, this requires an analyst to know the analytical question, i.e., what is the purpose of this particular analysis? The planned guides will examine other questions or issues that often arise in different ways at various stages of planning, executing and reporting an XPS analysis. Some common questions and issues are listed below and are shown with examples of related issues or questions in Table I.

1. Where can I find the information I need about XPS?
2. Can XPS provide the information I need?
3. Planning measurements.
4. Making XPS measurements.
5. Extracting desired information from the data.
6. What needs to be recorded and reported (e.g., in a report or a journal publication)?

This guide addresses the first two topics on this list by describing sources of XPS information and identifying questions that can help to determine if XPS can meet the analysis objectives.

II. Where can I find the information I need about XPS?

A. Information that XPS can provide

XPS has become the most widely used surface-analysis tool because all elements, with the exceptions of hydrogen and helium, can be identified on sample surfaces from the binding energies of photoelectrons emitted during X-ray excitation. Tabulations of electron binding energies of the elements enable elemental identification, and small shifts, typically a few eV, in those binding energies from those of pure elements and other features in the spectra can provide information about the chemical states of the elements of interest. The relative amounts of the detected elements within the analysis volume can, in principle, be extracted from the intensities of the photoelectron peaks if the sample is assumed to be homogeneous over the XPS sampling volume.[14] With knowledge of XPS information depths, the application of ion sputtering, imaging and/or computational approaches, it may be possible to obtain information about the thickness of thin films and elemental distributions near the surface for inhomogeneous samples. Information about the physical processes involved and application of XPS modeling programs or algorithms make it possible to relate in some detail expected distributions of species near a sample surface with the measured results.[5, 23–28] The valence-band region can often provide additional information about subtle chemical differences not found in the core region.[29, 30]

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B. Sources of XPS information

A great deal of information has been published about XPS, the information it provides and how to apply it to specific types of problems. These sources range fromvery short introductions to surface-analysis methods[31, 32] to introductory monographs,[33, 34] extended volumes,[35, 36] and journal articles covering specific topics such as sample preparation,[37] quantification,[38] data analysis,[39] curve fitting,[40–42] spectral interpretation,[43] electron transport and path lengths,[44–46] and information available from XPS valence-band spectra.[29,30] Books and journal articles also focus on specific applications of XPS that include materials science,[43, 47, 48] nanoparticles,[9, 49] corrosion,[50] biological samples,[9, 10] and environmental surfaces.[7, 51] A sampling of the areas for which guides and standards have been developed for XPS by ASTM Committee E-42 on Surface Analysis[16, 17] and ISO/TC 201 on Surface Chemical Analysis[11, 18, 19] is shown in Table II. Summaries of many ISO/TC 201 standards and guides have been published.[52–58] Crist[13] provides a list of the significant number of XPS handbooks and databases, noting as well some of their challenges and inconsistencies.

The National Institute of Standards and Technology (NIST) provides several types of XPS-related data including electron inelastic-mean-free path and effective-attenuation length data bases[5, 59] and a useful program for simulation of XPS spectra (Simulation of Electron Spectra for Surface Analysis (SESSA)).[24, 25] A variety of other software related to XPS peak fitting or analysis is available.[5, 23, 26–28] A great deal of information about XPS can be found online, including webinar-tutorials,[43, 60, 61] and other collections of related information.[48, 62] For those who might like to interact with experienced XPS users directly, various organizations offer short courses on XPS and other surface-analysis methods.[63, 64] Surface Science Spectra is a peer-reviewed journal/database that contains hundreds of vetted and reviewed spectra. Instrument vendors and others have tutorials, databases and other useful information.[62, 64, 65]

C. Good methodology is necessary, but not always sufficient

The ability to obtain XPS data of high quality and reproducibility is now well established, documented and included in guides and standards,[11, 1418, 66] but, as noted above, this was not always the case. Through considerable efforts of many researchers, instrument vendors, and standards committees, the situation had significantly improved such that in 2003 Powell[66] could report major progress in reducing the uncertainties in XPS measurements.

Unfortunately, it is not always possible to equate measurement reproducibility for reference materials or model samples with the ability to reproducibly extract useful information on ‘real’ samples. The ability to make repeatable and accurate measurements on ideally flat surfaces remains critical for instrument and method development. However, many of the surfaces of current interest are much more complicated in topography, chemistry or both. Many “real” samples are also subject to handling[37]or probe damage,[67, 68] have information obscured by contamination, may experience surface charging during analysis, and the desired information may not be obtained using the standard methods often used to analyze or quantify XPS data. The default method commonly applied for quantifying the elements present in the XPS analysis volume does not consider the effects of layered surface

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structures or sample topography. The default approach assumes a homogenous distribution of the detected elements, which is almost never the case within a few atoms depth into the surface and rarely the case laterally across the analysed area of many important materials. Nano-objects, as one example, are of increasing importance in multiple areas of science and technology, but meaningful comparison of the composition of the surface of nano-objects- especially if they are of different sizes - requires consideration of object shape and size in the analysis.[9, 69, 70]

III. Can XPS provide the information I need?

The senior XPS analyst at the Environmental Molecular Sciences Laboratory of the US Department of Energy User Facility, Mark Engelhard, sometimes gets samples placed on his chair in the laboratory with the request, “please make XPS measurements on these samples.” When that is the only information provided, it is somewhat like getting into a taxi and asking the driver to take you someplace without saying where. Most meaningful XPS measurements are conducted with specific questions in mind. If there is a concern for a particular type of impurity on the surface (or near the surface) of a material, it can be important for the analyst to design the experiment/measurement to optimize the ability to detect that element. Experimental optimization considers many factors including the nature of the desired information, specimen history, methods of preparing a specimen for analysis, sample topography, sensitivity to damage,[67] likelihood of sample charging, needed elemental sensitivity, possible interference of peaks from other elements in the sample,[71, 72] possible presence of confusing contamination, and depth/location of the region of interest. Detailed communication between the owner of the sample/issue/problem and the XPS analyst is often the most critical aspect, and if not performed will often lead to a “second go round”.

We now address the following questions from topic 2 in Section I.B and Table I.

A. What information do I need from an XPS analysis?

An assessment of the desired or needed information should determine first if XPS is an appropriate method and second if the sample is in a condition or form such that the needed information can be obtained. Is the needed information qualitative (e.g., whether an element or chemical state is present), quantitative (e.g., what is the composition of particular phases or the nature of the sample morphology)[73, 74] or comparative (e.g. examining surfaces of “good” and “bad” samples or looking for other surface compositional differences)? Sometimes surface enrichment or depletion is the desired information. In such cases, information about the bulk composition may also be needed. When chemical-state information is desired, it is important to consider if it is possible to distinguish among likely chemical states and if environmental conditions, required sample handling or the measurement process (vacuum, X-ray, electron or ion beam exposure) might destroy the desired information.

The fitting of XPS photoelectron spectra is often used to determine the relative amounts of different chemical states contributing to a spectrum. It may also be useful in helping separate overlapping peaks when there are peak interferences. Unfortunately, peak fitting is often

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done without considering the likely chemistry of the sample and the physics of the XPS process, and the results are often not reported in adequate detail. It is important to remember that the objective is to extract chemical information from a spectrum, not necessarily simply getting a good fit to this spectrum. Figure 1 (with details in the Appendix) provide examples of chemically meaningful and meaningless fits to a nickel spectrum.

Consideration of the potential use of XPS includes evaluation of possible or alternative approaches to obtaining the desired information. Might other types of analytical approaches provide the needed information more rapidly, at lower cost and/or with less sample preparation than for XPS?[75–77]

B. Is the form or nature of the sample compatible with XPS?

Because of the surface sensitivity of XPS, appropriate preparation and handling is essential to avoid destroying the desired information or adding unwanted contamination[37] A series of ISO standards describing appropriate sample handling practices has been prepared.[78–81] In some cases, surface contamination may cover the surface of interest, but solvent and other processes may also remove surface molecules or alter their chemical states.[79, 80] An example of the impact that sample preparation can have on spectra is shown by example in Figure 2 where the thickness of an oxide layer on iron nanoparticles increases quickly when the particles are exposed to air.

Most laboratory XPS instrument are designed to achieve ultra-high-vacuum conditions to keep the surface from being contaminated during analysis. If the sample is not vacuum compatible, it may need to be cooled[82] or analyzed in an environmental near-ambient pressure XPS system, noting that the sensitivity of such instruments is significantly worse than for an equivalent UHV instrument.[83] If the depth of analysis needs to be larger then a higher energy X-ray source may be required.[84] A variety of in-spectrometer processing treatments[14, 37] may also be used to clean, fracture, heat, or cool the sample, deposit films, or chemically modify (process) the sample of interest.

The sample size requirements are instrument dependent. The maximum sample size that can be analyzed in most XPS instruments is on the order of 20 cm^2 and often on the order of a few cm^2. Allowed sample heights are also instrument dependent, but typically are < 25 mm. Larger samples would need to be cut to size in some way without destroying the region or chemical species of interest or possibly involve the use or development of a custom sample holder.[79, 80]

C. Does XPS have the needed sensitivity? Might peak interferences complicate analysis?

The nominal sensitivity of XPS is often stated to be ≈ 0.1 atomic %. However, the elemental sensitivity factors for various elements can differ by as much as a factor of ≈100. The sensitivity will depend on the specific element to be detected, the matrix material, the depth distribution of the element of interest, and possible interferences from other elements in the sample. Shard has developed some relatively simple charts to help determine detection limits (considering several factors including the impact of peak interferences for specific elemental combinations) and these have been extended by Hill *et al.*[72, 85] Another approach to

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detection limits involves the use of computer simulations to model electron emission from the sample.[71,51,85]

It must always be remembered that the measured intensity of a photoelectron peak decreases approximately exponentially with depth of the emitting atoms from the surface. The actual intensity for any given analysis, however, depends on both the material and measurement configuration, which can mean that 95% of the total intensity may come from a depth as small as 1 nm depth or as large as 10 nm for routine laboratory-based instruments. The composition of this surface/near-surface region generally differs from the bulk of the material. Because some species can be enriched in the surface, the bulk composition of a material is rarely a reliable guide as to what can be observed on the surface. An element might be below the detection limit if the element was uniformly distributed in the sample, but might be detected if that element was concentrated on the surface. Similarly, some species may be depleted on the surface and not be observed even when the amount in the bulk material is greater than the XPS detection limit. Surface contamination can obscure material on the surface. In some cases, surface contamination such as so-called adventitious carbon can be removed without significantly modifying other aspects of the sample surface.

D. Does XPS have the depth and lateral resolution needed? Would I need to apply ion sputtering?

The lateral resolution of XPS varies with the instrument, but for most laboratory instruments the region of analysis usually needs to be > 1 μm in size and detailed chemical analysis usually requires sizes ≈ 10 μm or larger.[86–88]

As noted above, XPS is typically most sensitive to the outermost 1 nm to 10 nm of a material with laboratory instruments commonly equipped with Al or Mg Kα X-ray sources. If the region of interest is deeper in the material, the analyst has two options. First, XPS can be performed with higher X-ray energies, either with use of other X-ray sources that provide higher energies than normally used in laboratory instruments (e.g., Ag Lα, Cr Kα, or Ga Kα) or with synchrotron radiation, i.e., use of so-called hard XPS or HAXPES.[84] A major advantage of using synchrotron radiation is that the X-ray energy can be tuned to provide optimal surface sensitivity for a particular sample. However, it should be noted that quantitative analysis from synchrotron XPS is far from simple due to factors such as X-ray polarization and uncalibrated electron spectrometers at nonstandard geometries to the incoming X-rays. Suitable reference sample data taken at each photon energy and each electron spectrometer setting, as well as substantial expertise are required if meaningful results are to be obtained. Second, sputter depth profiling could be applied. An increasing variety of ion beams, including various types of cluster sources, allow depth profiling of organic and inorganic layers. However, successful profiling, without significant sputter-induced artifacts, depends on the combination of the ion beam used and the type of sample material.[89–91] For a given X-ray energy, greater surface sensitivity can be achieved on relatively flat samples by detecting photoelectrons at more grazing emission angles.

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E. How might XPS measurements be conducted in a manner that obtains the desired information?

A range of considerations go into actually planning how to get useful information from a sample. These include where and how a sample would be prepared, packaged or transported? The nature of sample handling, the time between preparation and analysis, and environmental factors can all impact an analysis.[49, 92, 93] Some samples require handling in a glove box,[92, 94] some may require heating in vacuum to get to the desired state,[92, 95] while others may need cooling to avoid sample alteration or probe damage.[6, 96] XPS data can also be collected in a variety of modes, each with relevant protocols and considerations,[11] including survey (wide scan) spectra, selected-region high energy resolution (narrow scan) spectra, imaging,[88, 97] angle resolved[98] and sometimes the use of ion sputtering for depth profiling.[35] Are reference data or standard materials needed to ensure useful data? What type of data analysis will be needed to get the desired information from XPS spectra?[60, 99] Would modeling of the system to generate expected data be useful prior to data collection?

IV. Summary

We seek to raise awareness that reliable and reproducible XPS results depend upon the use of appropriate practices. This, the first of a series of planned guides in this journal on best practices for XPS measurements, identifies several stages of planning and executing an XPS measurement and analyzing and reporting the results. Problems impacting the quality and reproducibility of XPS results can occur at each stage. We recommend identifying specific analysis objectives for an XPS measurement as an important starting point. Typical questions that should be asked before undertaking an XPS analysis were described and sources of information and guidance on the use of XPS for different types of applications were identifed.

Topics planned for inclusion in this series of articles include: sample preparation, instrument set up and performance checks, spectral interpretation, quantification, fitting spectra, sample damage, sample charging, quantitative 2D image analysis, and sample morphologies (i.e., lateral and depth distributions of elements or chemical species). It should be apparent to the reader that although this article addresses issues with XPS analysis, the framework outline is relevant for many types of analysis. Researchers should also consider repeatability and reproducibility when they are fabricating samples/devices.

ACKNOWLEDGMENTS

The planned series of guides and tutorials is being developed as part of an AVS response to reproducibility issues appearing in many areas of science. It is one of several activities being initiated under the guidance of the Reproducibility Subcommittee of the AVS Recommended Practices Committee. It is appropriate to acknowledge the major contributions of members and task leaders of ASTM Committee E-42 on Surface Analysis and ISO Technical Committee 201 on Surface Chemical Analysis.

Appendix –: Examples of appropriate and inappropriate use of curve fitting

The peak fits in Fig 1 are intended to demonstrate the difference between fitting the envelope of a spectrum as well as possible versus using chemical insight to extract chemical information from the spectrum. Too often fit assumptions and parameters are not adequately

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reported in publications. A recent paper[100] and a planned guide will more fully discuss good practices related to fitting XPS spectra and in reporting fit data.

A peak fit using chemically meaningful peak widths, positions, relative peak intensities and background based on known relationships among related peaks is shown in Fig. 1a. The fit in Figure 1b does not include information about the chemical species involved, meaningful peak widths, background or appropriate binding energies.

Spectral details and chemically meaningful fit

The example shows the Ni $2p_{3/2}$ region of a sample of nickel metal that has been sputtered to remove any oxide. The sample was run on a VSW HA100 spectrometer[101] using achromatic Mg Kα X-radiation with a power of 300 W. The spectrum was recorded in the fixed analyzer transmission mode with a pass energy of 25 eV. The spectrum was originally run over a 40 eV range to cover the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ regions, the peak fit covered the full range of collected data. Fig. 1a, based upon the fit to the 40eV range has been cut down to 20 eV to show only the Ni $2p_{3/2}$ region. The spectrum was part of a study published many years ago.[102]

Figure 1a shows three clearly identifiable features shown as A, B, and C. Feature A is the Ni $2p_{3/2}$ region, feature B is a satellite associated with the Ni $2p_{3/2}$ region, and feature C is the Ni $2p_{1/2}$ peak excited by $K\alpha_3\alpha_4$ X-ray satellite radiation arising as a result of the unmonochromatized X-radiation used. This fit to the 40 eV range fitted both the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ regions using a Voigt function (a convolution of the Gaussian and the Lorentzian curve shapes)[103] with the parameters in Table III.

The Ni $2p_{1/2}$ region (not shown in the figure) was observed to be broader than the Ni $2p_{3/2}$ region, a phenomena that can be explained by Coster-Kronig broadening of the higher binding energy spin-orbit component. The fit was carried out so that the area ratio of the nickel spin orbit doublets was fixed at 2.0 and the width of the Ni $2p_{3/2}$ region was set to be 70% of that of the Ni $2p_{1/2}$ region to account for broadening of the higher binding energy spin-orbit-split component. The fit also included the satellite peak associated with the metal. An iterative Shirley non-linear background[104] was fitted to the region in two segments separated at 14.45 eV from the start of the full 40 eV region. The choice of background is very important and the iterative Shirley background chosen here, applied in both Ni 2p regions, gave the correct area ratio (1:2) for the two spin-orbit split Ni 2p peaks.

Rationale for choosing the Ni $2p_{3/2}$ region

The Ni $2p_{3/2}$ region is the most intense feature of the nickel metal spectrum so it is normal for this region to be used for the study of nickel systems. The spectrum was collected using achromatic X-radiation as this provides a particular challenge because the Mg Kα X-radiation has photoelectron peaks from Kα3α4 X-ray satellite radiation for the Ni $2p_{1/2}$ peak which gives rise to peaks in the Ni $2p_{3/2}$ region. An inexperienced operator might only record the Ni $2p_{3/2}$ region and not be aware of the features arising from the $K\alpha_3\alpha_4$ X-ray satellite features arising from an unrecorded Ni $2p_{1/2}$ region. There is a nickel satellite feature at around 6 eV higher binding energy than the Ni $2p_{3/2}$ peak (C), but there is also

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considerable intensity from the peaks from $K\alpha_3\alpha_4$ X-ray satellite radiation for the Ni $2p_{1/2}$ peak.

The fit in Fig. 1a is a good fit with a reduced chi-squared value of 3.8730 (Ref. 105) for the full 40 eV region. There is a small mismatch around 854.5 eV on the high binding energy side of the Ni $2p_{3/2}$ peak. This is probably due to conduction-band interaction, but in fitting the whole 40 eV region a good fit could not be obtained by including an exponential tail to represent conduction-band interaction on both the Ni $2p_{1/2}$ and the Ni $2p_{3/2}$ peaks.

Is there any oxidized species present?

The O 1s region (Figure 3) shows a weak feature, but its binding energy around 539 eV is outside the region where O 1s features are normally seen (519 eV to 533 eV). This weak feature is not from oxygen but is an $L_2M_{2,3}M_{2,3}$ nickel Auger feature. In earlier work, one could see a true O 1s signal appear after the etched nickel metal is exposed to water in an anaerobic cell.[102] So there is no oxygen present, but the inexperienced operator might assume that the $L_2M_{2,3}M_{2,3}$ nickel Auger feature is an O 1s feature, and then fit the features A and B in Fig. 1(a) as being due to an oxidized nickel species.

The inexperienced operator fit

For the fit in Fig 1b it is assumed that an inexperienced operator makes the following major errors or invalid assumptions:

1. The Ni $2p_{3/2}$ region and O1s region are the only regions of relevance for determining the chemical state of nickel in the sample.
2. The $L_2M_{2,3}M_{2,3}$ nickel Auger feature is not a nickel feature but due to O1s features arising from surface nickel oxidized species.
3. The spectral region in the Figure represents nickel metal and a shifted peak that is composed of a number of overlapping peaks arising from oxidized nickel.
4. A linear background is fine for fitting this XPS spectrum. It makes things simpler.
5. No need to use more complicated functions, the spectrum can be fitted using Gaussian functions, even though the physics of the process requires a convolution of a Gaussian and a Lorentzian.
6. Assumes that the features shown as A and B in Figure 1a are caused by a series of chemically shifted peaks due to different oxidized nickel species (oxide 854.2 eV, hydroxide $Ni(OH)_2$ 862.9 eV and surface species, etc.).[102]

Figure 1b shows the inappropriate fit to the region. The fit of peak shape is satisfactory but not great. The reduced chi-squared for the fit is 13.3011 for the 20 eV region. The fit shows a metal peak and six peaks attributed by the inexperienced operator to oxidized nickel species shown in Table IV.

Just about everything is wrong with this fit:

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1. There is actually no oxidized nickel species, so the fitting of six species to oxidized nickel is completely wrong.
2. The use of a linear sloping background rather than a more accepted background such as iterative background of Figure 1a gives a much greater intensity to the regions A and B identified in Figure 1a, thus allowing the fitting of the six “oxidized” species in Figure 1b.
3. Many of the “oxidized” species in Figure 1b have binding energies that are not known for nickel.
4. Gaussian peaks are not appropriate for curve fitting, some Lorentzian character is found in every XPS spectrum. In particular the metal peak is known to have considerable Lorentzian character. This incorrect fit illustrates that given enough Gaussian functions one can fit almost anything.
5. The considerable intensity from the $K\alpha_3\alpha_4$ X-ray satellite radiation for the Ni $2p_{1/2}$ peak has been ignored.

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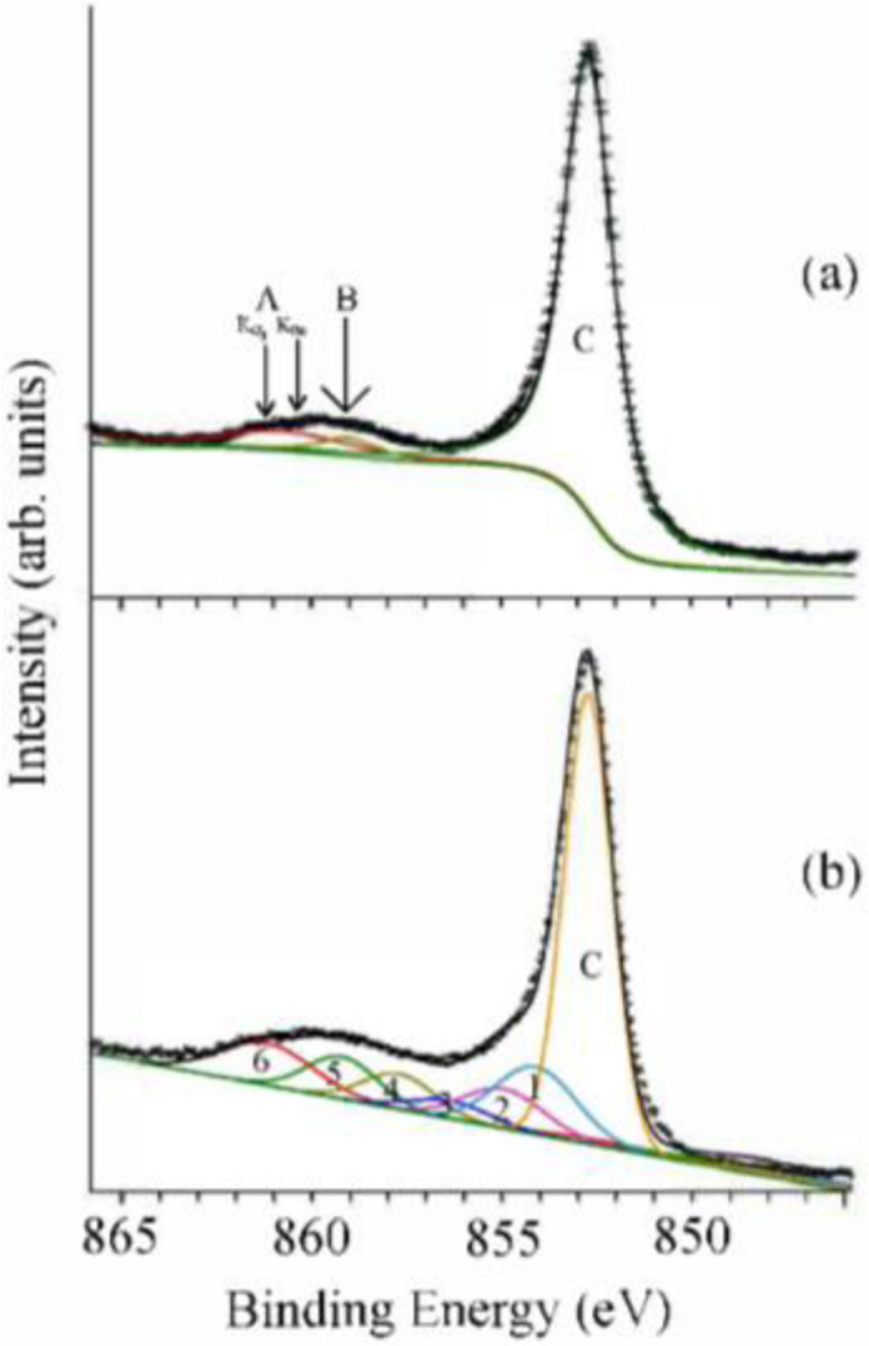

Figure 1.

A frequent area of analysis failure involves fitting XPS spectra without consideration of physics and chemistry of the spectrum. The Figure shows the Ni $2p_{3/2}$ region of a sample of nickel metal that has been etched to remove any oxide. Peak C is the Ni $2p_{3/2}$ photoelectron peak. Information about other peaks appearing in the figure are described in the appendix. Fig. 2a shows the case of a fit using chemically meaningful peak widths and positions and relative peak intensities based on known relationships among related peaks. Fig. 2b shows a fit which does not consider known information about the chemical species involved,

meaningful peak widths, or appropriate binding energies. Often fits are presented in the literature without either fit details or the rationale of the approach to fitting and peak fit parameters. Discussions of the two approaches in these two fits is provided as an appendix. Data from ref 101.

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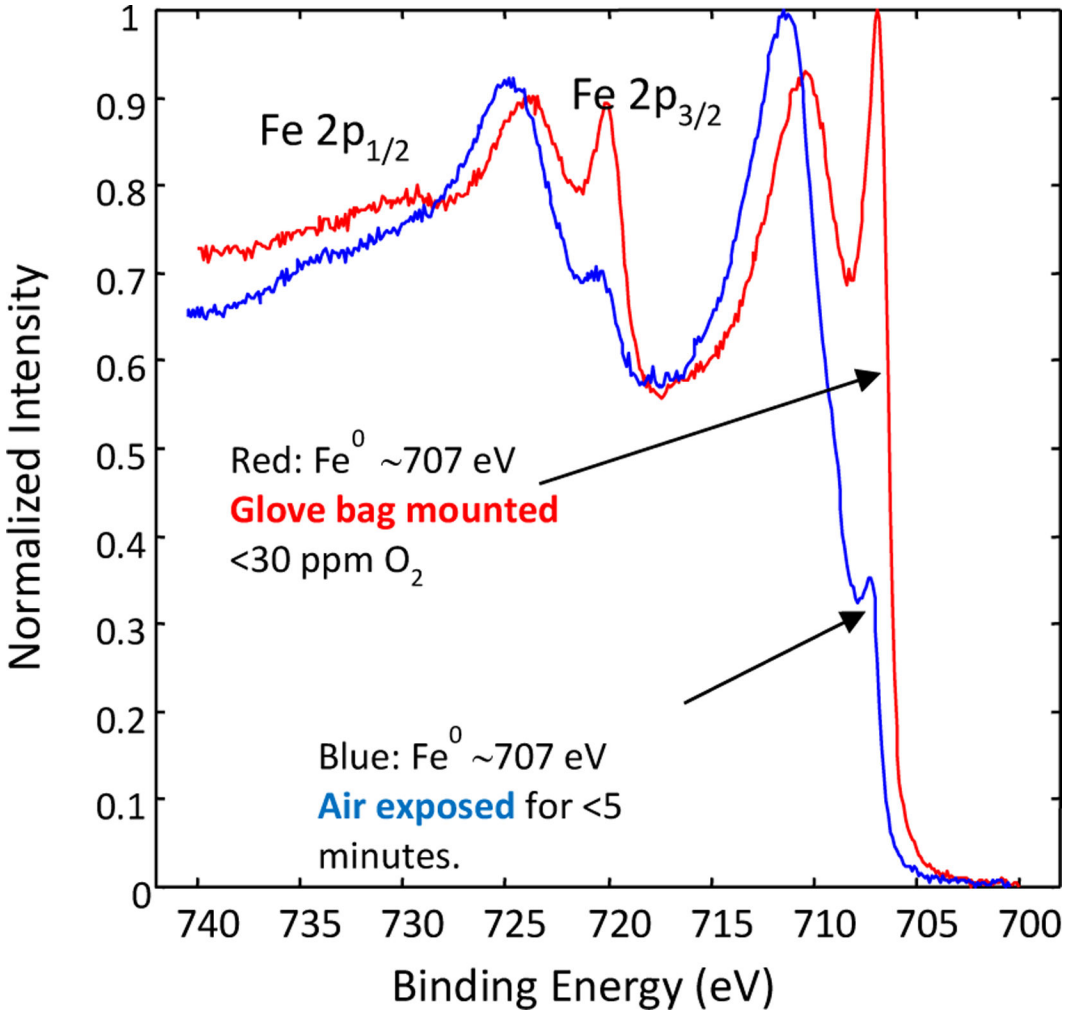

Figure 2.

Handling, preparation and mounting of samples can affect the information obtained from an XPS measurement. When iron metal-core oxide-shell nanoparticles are removed from their initial packaging and mounted for XPS in a glove-bag connected to the spectrometer, a relatively strong Fe0 peak (~707 eV) from particle metal cores is observed in addition to an oxide peak (~710–711 eV). If particles are exposed to air for less than five minutes, the Fe0 peak is significantly decreased relative to that from the oxidized Fe shell. Reprinted with permission from Chapter 2.1 of *Characterization of Nanoparticles: Measurement Procedures for Nanoparticles*, edited by W. E. S. Unger, A. G. Shard and V.-D. Hodoroaba (Elsevier, Oxford, 2019) ref 92. Copyright Elsevier.

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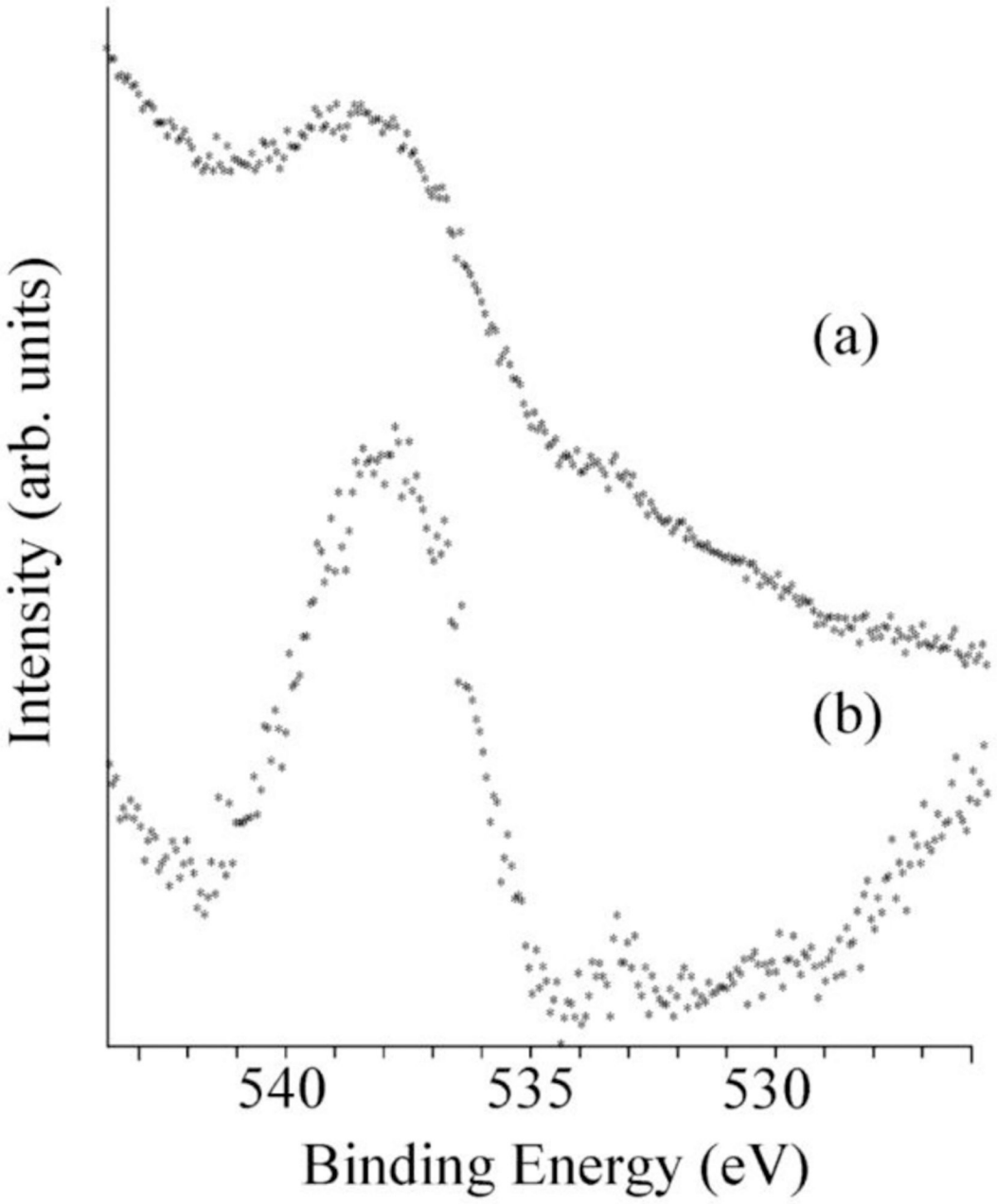

Figure 3.

O 1s regions of sputter etched Ni. The peak observed is not from O but an L $_2$M$_{2,3}$M$_{2,3}$ nickel Auger peak. The original data is shown in (a) and the data with a linear sloping background removed is shown in (b). Data replotted from Ref 102.

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Table I.

Stages of an XPS measurement, information sources and example issues or questions at each stage

1) Where can I find the information I need about XPS?
• Introductory articles and monographs • Comprehensive volumes • Journal articles covering specific topics (e.g. peak fitting, quantification, sample preparation) • Books and journal articles covering specific applications (e.g. • Guides and standards • Handbooks and datas bases • Simulation and analysis software • Web based seminars, tutorials and data bases
2) Can XPS provide the information I need?
• What information do I need from an XPS analysis? • Is the form or nature of the sample compatible with XPS? – Has the sample been handled or treated in a way compatible with getting the needed information from XPS, or has a contamination layer been introduced? – Is the size compatible with the XPS instruments available? – Can routine laboratory-based XPS measurements meet the measurement needs or is special-purpose instrumentation required (e.g., XPS with synchrotron radiation, near ambient pressure XPS, or XPS with special environmental chambers)? • Does XPS have the needed sensitivity? Might peak interferences complicate analysis? • Does XPS have the depth and lateral resolution needed? – Would I need to apply ion sputtering, plasma cleaning, angle-resolved XPS or use XPS with high-energy X-rays to get the information I need? – Does the sample need to be cleaned in some way to allow the desired information to be acquired? • How might the XPS measurements be conducted in order get the desired information (angle-resolved measurements, imaging, heating, cooling, environmental conditions, standard samples, sample handling and preparation)?
3) Planning an XPS measurement
• What are the analysis objectives and what is the approach for meeting them? • What type of sample-preparation method is needed? • Data collection plan: what types of spectra will need to be collected? – Can most information be obtained from the needed survey spectrum? – Are high-energy-resolution spectra from core regions needed? – Is there a need for angle-resolved XPS, sputter depth profiling, imaging or other special approaches? – Appropriate statistics and replication of measurements. – Will modeling of spectra be needed and does that impact the data to be collected? • Instrument set up, performance verification and check on calibration status. • Standard samples to be run.
4) Making an XPS measurement
• Following a data-collection plan. • How much data to collect (adequate statistics and reproducibility)? • Checking for possible specimen damage from the X-ray source or charge neutralization system. • Is charging occurring? Taking actions to minimize or control.

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- Are measurements consistent and reproducible?

5) **Extracting desired information from the data**

- Approach to data analysis.
- Peak identification and spectral interpretation.
- Charge correction.
- Chemical-state information.
- Peak fitting (Figure 1 shows an example of issues related to fitting of spectra along with the Appendix for accompanying details).
- Quantification and/or application of spectral models?
- Modeling and interpreting the valence-band region?
- Evaluating completeness of information and possible need for more data.

6) **What needs to be recorded and reported (e.g., in a report or a journal publication)**

- Information needed for others to reproduce the results.
- Sample information, including preparation.
- Instrument information, including calibration.
- Analysis and/or modeling details.
- Use of consistent terminology.

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Table II.

Topical Areas and Related Standards and Guides for XPS Analysis *

Instrument Guides Calibrations and Checks	ASTM Guide or Standard	ISO Standard	Other Resource
Analysis Guidelines and Guide to Standards	E2735	10810	
Surface Terminology		18115 Part 1 **	
General System Check &		15470	
Instrument Performance		16129	
Sample Preparation and Handling	E1829, E1078	20579 Parts 1 to 4 [Formerly 18116 and 18117]	
Binding Energy	E2108, E1523	15472, 19318	
Intensity Repeatability and Constancy		24237	
Intensity/Energy			NPL software ***
Response Function			
Linearity of Intensity		21270, 18118	
Scale			
Peak Intensities	E995	18392, 20903	
Background, Fitting and Damage		19830, 18554	
Quantification-Sensitivity		18118, 19668	
Factors, Detection Limits			
Ion Gun and Sputter	E1577, E1127	15969, 22335	
Rate, Film Thickness	E1634	14606, 14701	
Depth Resolution	E1127, E1577	14606	BCR261 ****
	E1634, E1636		NIST SRM 2135c *****
Charge Control and Referencing	E1523	19318	
Analysis Area	E1217	19319	
Lateral Resolution		18515	
Data Reporting	E996	20579–4, 13424	

* Adapted from Table 1 of ASTM Standard E2735–14.

** This terminology is available at no cost at https://www.avs.org/Technical-Library/Technical-Resources

*** http://www.npl.co.uk/science-technology/surface-and-nanoanalysis/services/calibration-softwareand-reference-materials-for-electron-spectrometers.

**** European Institute for Reference Materials and Measurements, BCR261, certified reference material.

***** National Institute of Standards and Technology, NIST-SRM 2135c Ni/Cr Thin Film Depth Profile Standard, https://www-s.ni99st.gov/srmors/view_detail.cfm?srm=2135c.

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Table III

Fitting parameters for 40eV wide Ni $2p_{1/2}$ and Ni $2p_{3/2}$ regions*

Region	Voigt FWHM	Gaussian FWHM	Lorentzian FWHM	Binding Energy(eV)	Area Ratio
Ni $2p_{1/2}$ (not shown in Fig 1)	2.277	1.300	1.500	869.80	1.000
Ni $2p_{3/2}$ sat. (B)	1.940	1.185	1.185	859.18	0.047
Ni $2p_{3/2}$ (C)	1.594	0.910	1.050	852.70	2.000

*See ref 103 for discussion of the various FWHM values

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Table IV.

Peaks identified by an inexperienced analyst assumed to be associated to one metal and six oxide peaks

Peak Fig. 1b	Assumed Identification	Binding Energy [ev]	Comments
C	Metal	852.7	Correctly identifed
1	Oxide 1	854.1	Close to the actual binding energy of NiO
2	Oxide 2	854.9	“New” surface species
3	Oxide 3	856.3	Close to the actual binding energy of $Ni(OH)_2$
4	Oxide 4	857.7	“New” surface species
5	Oxide 5	859.2	Close to nickel metal satellite
6	Oxide 6	861.2	“New” surface species