

Applied Surface Science Division Room A211 - Session AS+BI+RA-MoM

Quantitative Surface Analysis I/Reproducibility Issues in Quantitative XPS

Moderators: Donald Baer, Pacific Northwest National Laboratory, Mark Engelhard, Pacific Northwest National Laboratory

8:20am **AS+BI+RA-MoM1 Improving Accuracy in Quantitation by XPS: Standards, Cross-sections, Satellite Structure, C. Richard Brundle, C.R.Brundle & Associates; P.S. Bagus, University of North Texas; B.V. Crist, XPS International LLC** **INVITED**

Determining elemental composition by XPS requires determining relative peak intensities from the elements concerned, and then normalizing using Relative Sensitivity Factors (RSF's). Such RSF's are usually generated from standard materials using the intensity from the "main" peak only and ignoring any associated satellite structure (shake-up, shake-off, and multiplet splitting components) intensity. In the seminal paper by Wagner, et al, (1) this resulted in a conclusion that the calculated Li(1s) photoionization cross-section, σ , (2) was too low by ~40%, relative to F(1s). This apparent discrepancy cast doubt on the claimed 5% accuracy of the calculated σ values for low Z elements (2). We show that this is incorrect. The discrepancy is due, primarily, to the fact that Li(1s) loses almost zero intensity from the main peak into associated satellites, whereas for F1s it is substantial, *spreading over 100eV to lower KE*. A calculated σ always refers to the *total* intensity of photoemission from the orbital concerned, including any intrinsic satellite structure. In addition, the experimental Li(1s) peak intensity in Wagner, et al. (1) was actually *overestimated*, owing to inclusion of overlapping satellite structure spreading from the nearby F(2s) peak. For the 1s intensities of the first row elements, a crude theoretical approximation predicts the total intensity lost from the "main" peak to satellites quite well. It involves an exponential dependence on the number of valence shell electrons present, which for Li+ of LiF, is zero, and for F- is 6 (the filled 2p shell), yielding values of zero loss for Li+ and 20-30% for F-. Full *ab initio* quantum calculations for these ions support the crude estimate (calculated Li+ losses are 1.4%; F- losses are 22.7%). In contrast to earlier claims to the contrary(3), satellite losses, for elements across the periodic table, vary widely from core-level to core level, element to element, *and most critically with the bonding situation of an element (see, for example ref 4)*. Thus any "universal" element RSF's, using main peak intensities only, though semi-quantitatively useful, are inherently limited in potential accuracy achievable, sometimes by up to a factor of 2. What is needed, for improved accuracy, are sets of RSF's appropriate to different bonding situations. Such sets would be particularly useful for the current large inexperienced XPS user base. We attempt to give guidelines.

C.D. Wagner, et al, Surf. Interface Anal. **3**, 211, 1981

J.H. Scofield, J. Elec. Spec. **8**, 129, 1976

V.G. Yarzhemsky, et al, J. Elec. Spec. **123**, 1, 2001

P. S. Bagus, E. Ilton, and C. J. Nelin, Catalysis Letters, **148**, 1785, 2018

9:00am **AS+BI+RA-MoM3 A Rigorous Approach to the Calculation of the Uncertainties in XPS Analysis, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, México; Orlando Cortazar-Martinez, CINVESTAV-Unidad Queretaro, Mexico**

One of the most important applications of X-ray photoelectron spectroscopy (XPS) is the characterization of the chemical composition of solids near the surface. However, the proper assessment of the associated uncertainties has remained an elusive problem. One of the issues is that the total uncertainty comes from various sources: the experimental data (peak intensities), parameters theoretically calculated (cross-section, mean-free-path), and parameters associated to the XPS equipment (angular and kinetic energy transmission functions).

The uncertainty on most of these parameters should be treated as systematic errors. The most important non-systematic uncertainty comes from the peak intensities [1]. It is a common practice in XPS data peak fitting to first subtract the background and then peak-fit the backgroundless data (*static* approach [2]). This approach prevents the use of the covariance matrix to calculate uncertainties because the covariance with the parameters defining the background cannot be accounted. It is only under the *active* approach [2] that it is possible to account for the covariance with the background parameters because the background is optimized in conjunction with the peak parameters. In this paper, the

assessment of the uncertainty on the peak intensities will be treated in detail, as well as the total uncertainty on the composition.

[1] A. Herrera-Gomez, A rigorous approach to the calculation of the uncertainties in XPS analysis (Internal Report), Internal Report, Internal Report. CINVESTAV-Unidad Queretaro, n.d. <http://www.gro.cinvestav.mx/~aherrera/reportesInternos/uncertaintiesXP S.pdf>.

[2] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. **46** (2014) 897–905. doi:10.1002/sia.5453.

9:20am **AS+BI+RA-MoM4 Gross Errors in XPS Peak Fitting, Matthew Linford, V. Jain, G.H. Major, Brigham Young University**

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. It is widely used in numerous areas of research and technology. Many research groups and individuals are skilled at analyzing XPS data. However, too much of what has appeared and continues to appear in the literature is of at best questionable value and accuracy. In this talk, I will discuss some of the all too common gross errors. Both correct and incorrect examples of each of the following will be shown. (i) Not plotting the data according to international convention of binding energy increasing to the left. (ii) Fitting and interpreting data that are far too noisy to be interpreted. (iii) Labeling noise as chemical components. (iv) Not showing the original data – only showing the synthetic (fit) peaks and their sum. (v) Not plotting the sum of the fit components with the original data. (vi) Having widely varying peak widths in a fit. (vii) Having the baseline completely miss the noise on either side of the peak. (viii) Not collecting data over a wide enough energy window to see a reasonable amount of baseline on both sides of the peak envelope. (ix) In a C 1s spectrum, reversing the labeling on the C-O and C=O peaks, and other mislabeling issues. The C 1s peak envelope is well understood so there shouldn't be huge mistakes here. (x) Not taking into account spin-orbit splitting when it is necessary. (xi) In a comparison of spectra, having widely differing peaks and peak positions for components that are supposed to be the same between the spectra.

9:40am **AS+BI+RA-MoM5 Improved Energy Referencing in XPS, Hagai Cohen, Weizmann Institute of Science, Israel**

Basically, energy referencing in XPS relies on an absolute reference provided at the back contact of the sample: the electrical ground. If poor connectivity is encountered between the studied surface and ground, reference signals may be used to derive correction terms for the energy scale, such as to get the proper binding energies for elements of interest. Unfortunately, in many cases this procedure fails to accurately address differential charging effects, namely local and temporal variations in the surface charge and the related electrostatic potential.

In the present work, a method for introducing a second absolute/external reference is described. The technical improvement is proven to be mandatory. It enables advanced analyses of binding energies, which refines the chemical analysis significantly. The method further reveals intriguing cases in which the x-ray induced charging does not follow the trivially expected behavior. On top of that, an access to rich electrical information is realized as soon as a second reference is introduced, thus expanding the XPS capabilities into new areas. Measurements of the inherent inner fields in semiconductors and the reliable derivation of device band diagrams, free of the beam-induced artifacts, are just a few examples to be mentioned.

10:00am **AS+BI+RA-MoM6 How to Avoid Errors in the Interpretation of XPS Data?, Andreas Thissen, P. Dietrich, SPECS Surface Nano Analysis GmbH, Germany; W.E.S. Unger, Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany), Germany**

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But

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even more, data quality becomes transparent also in times of open source publications and open data repositories.

This paper summarizes the challenges of data handling, data treatment, data storage, parameter-data correlation, expert systems for data acquisition, reporting assistance and tracking and authorization tools for sensitive data. In summary future perspectives and suggestions are discussed for improved data repeatability and data reliability.

10:40am **AS+BI+RA-MoM8 Misinterpretations in the Spectroscopic Analysis of Heterogeneous Materials and Defected Structures**, *Lisa Swartz, K. Artyushkova, J.E. Mann, B.W. Schmidt, J.G. Newman*, Physical Electronics

Analysis of samples where lateral heterogeneities can be present at a variety of scales poses a challenging spectroscopic task. In routine applications of XPS spectroscopy, the analyst is usually acquiring spectra over a large area from multiple positions on the sample and derives conclusions on “representative” chemical composition from average atomic concentrations and standard deviations. However, if lateral heterogeneities existing at the surface have smaller physical dimensions as the analysis area, the conclusions on “representative” chemical composition derived from large area spectroscopy will be erroneous. For accurate structural analysis of heterogeneous materials, it is very important to understand the scale of heterogeneity beforehand, so that the analysis areas and the size of the X-ray probe used for analysis are chosen appropriately. Often, complimentary microscopic techniques, such as SEM, are performed before XPS analysis which addresses some of this challenge but does not allow analysis over the same area.

The ability to perform small area spectroscopy for studying the heterogeneity and physical dimensions of samples is critical for obtaining accurate information on sample structure. In this talk, we will show examples of inaccurate use of large area spectroscopy and discuss the experimental approach towards selecting the relationship between the X-ray size and physical scale of defects and heterogeneities at the surface required to obtain an accurate representation of heterogeneous sample structure.

11:00am **AS+BI+RA-MoM9 Current Issues and Solutions for Reliable, Robust and Reproducible XPS Spectral Acquisition and Data Reporting**, *J.D.P. Counsell, C.J. Blomfield*, Kratos Analytical Limited, UK; **Christopher Moffitt**, Kratos Analytical Limited; *N. Gerrard, S.J. Coultas*, Kratos Analytical Limited, UK

XPS is now a truly interdisciplinary technique used in a wide variety of fields including catalysis, tribology, bioremediation and nuclear energy. With more than 1000 instruments currently in use, the ubiquitous nature of XPS means there is a greater requirement than ever for clarity regarding spectral acquisition, analysis and interpretation. The XPS user base has changed significantly – no longer the field of dedicated “technical experts” and spectroscopists – requiring instruments to be simple to use with a higher degree of automation in all parts of operation and analysis.

Here we will discuss the overall procedure for the technique specifying the critical steps in generating sound data and conclusions. Pitfalls and perils in the following steps will be briefly discussed: surface charging, beam damage, contamination, peak identification, energy calibration, quantification, peak-fitting, database usage, chemical state assignment and error reporting as will the latest methods implemented in mitigating against these issues. Worked examples and user studies will be presented to illustrate common inconsistencies.

11:20am **AS+BI+RA-MoM10 Intensity Calibration and Sensitivity Factors for XPS Instruments with Monochromatic Ag L α and Al K α Sources**, *A.G. Shard*, National Physical Laboratory, UK; *J.D.P. Counsell, Christopher Blomfield*, Kratos Analytical Limited, UK; *D.J.H. Cant*, National Physical Laboratory, UK; *E.F. Smith*, University of Nottingham, UK; *P. Navabpour*, Teer Coatings Ltd, UK

The use of monochromated Ag L α X-ray has been described previously.^{1,2} These sources have now become more widely available on commercial instruments and easier to use due to automation and the superior collection efficiency of modern analysers. To enable direct comparison between data acquired using both sources it is essential to be able have a common calibration scheme and a set of useful sensitivity factors. We employ the calibration method developed by the National Physical Laboratory for Al K α sources³ and extend this for Ag L α sources.⁴ Sensitivity factors for Ag L α and Al K α are calculated from photoionisation cross sections and electron effective attenuation lengths. These compare well to previous experimental values and data acquired from ionic liquids. The

intensity of the Ag L α source is found to be approximately 50 times lower than the Al K α source. This, coupled with generally lower photoemission efficiencies, results in noisier data or extended acquisition times. However, there are clear advantages to using the Ag L α source to analyse certain elements where additional core levels can be accessed and for many technologically important elements where interference from Auger electron peaks can be eliminated. The combination of calibrated data from both sources provides direct and easily interpreted insight into the depth distribution of chemical species. This could be particularly important for topographic samples, where angle resolved experiments are not always helpful. We also demonstrate, using thin coatings of chromium and carbon, that the inelastic background in Ag L α wide-scan spectra has a significantly increased information depth compared to Al K α .

References

1. Yates, K.; West, R. *Surf. Interface Anal.* **1983**,5 (4), 133-138.
2. Edgell, M.; Paynter, R.; Castle. *J. Electron Spectr. Rel. Phenom.* **1985**,37 (2), 241-256
3. Seah, M. P.. *J. Electron Spectr. Rel. Phenom.* **1995**,71 (3), 191-204.
4. Shard, A. G. *et al. Surf. Interface Anal.* **2019**<https://doi.org/10.1002/sia.6647>

11:40am **AS+BI+RA-MoM11 Reporting XPS Measurements and How Can We Do Better to Minimize Reproducibility Problems**, *Karen Gaskell*, University of Maryland, College Park

The level of detail and information provided in the average scientific article reporting XPS measurement and analysis varies widely. In some cases journal page limitations limit the inclusion of information such as experimental details, instrumental parameters and data sets that are required to fully describe the data collection and subsequent analysis so that it can be adequately reproduced by others. In other cases important information is simply left out. What are the minimum and preferable types of information we should include when reporting XPS results?

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