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Challenges in surface analysis

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Introduction

Many techniques have been developed since the 1960s to study the surfaces of materials. Some of them provide information on the chemical composition of surfaces and three have achieved widespread application. These three are X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS). XPS is also referred to as electron spectroscopy for chemical analysis (ESCA), and photoemission spectroscopy (PES). Histories and the backgrounds of XPS (Briggs and Grant, 2003; Kelly, 2004), AES (Burhop, 1952; Briggs and Grant, 2003) and SIMS (Benninghoven et al., 1987; Benninghoven, 2001) have been written, and these techniques continue to be developed today, providing increased sensitivity, spatial resolution, and automation. XPS and AES measure the kinetic energies of electrons leaving the surface from incident X-rays (XPS) or incident electrons (AES). Auger electrons can also be produced by other means such as X-rays, positrons (Ohdaira and Suzuki, 2013), and even ions (Grant, 2003). SIMS measures the mass spectrum (actually the mass-to-charge ratio) of positively or negatively charged ions ejected from the surface of a material following impact by energetic ions. A variation of SIMS, sputtered neutral mass spectrometry (SNMS), measures the mass spectrum of the neutral species emitted. In SNMS, ionization of the neutral species is made after they leave the surface. Other surface analysis techniques include ion scattering spectroscopy (ISS) and Rutherford backscattering spectrometry (RBS), and these have been compared with the other techniques mentioned above (Powell et al., 1991).

The most commonly used technique for surface analysis is XPS as it provides the simplest spectrum and is the easiest to quantify. XPS instruments also have a much lower cost than AES, SIMS, etc., so when groups are financially constrained, they tend towards XPS. In most cases, XPS also provides excellent information on the chemical state of surface atoms. AES can sometimes provide superior chemical information, such as the chemical state of carbon on metal surfaces (Haas et al., 1972; Hooker and Grant, 1977). While XPS and AES do not directly detect hydrogen and helium in materials, the effect of hydrogen on other elements in the surface can sometimes be observed with XPS (Smentkowski et al., 1995) and AES (Bevolo, 1985). On the other hand, SIMS can detect all elements as well as distinguish isotopes; spectra can be quite complex as large molecular fragments from the material are also formed. Isotope detection can be very useful when an oxygen beam is used for analysis, where oxygen from the surface of the material can be distinguished from the oxygen in the beam.

The number of papers published each year in AES and SIMS has been fairly constant for the past 20 years, whereas those published in XPS continue to increase. This is illustrated in Figure 1, which is plotted on a logarithmic scale to better show their growth since the early years. The publications using the terms ESCA, PES, HAXPES, NAP-XPS, ARXPS (angle resolved XPS), and ARPES (angle resolved PES) have been included along with those using XPS to compare with the other techniques. Figure 2 illustrates the use of the different terms for XPS and shows that ESCA was the preferred term in the 1960s and 1970s, but was overtaken by the term XPS in the 1980s and remains dominant. The term PES is often used

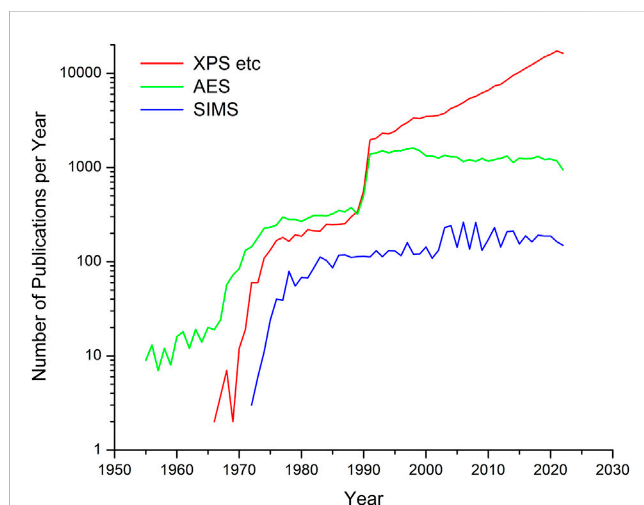

FIGURE 1
The number of publications per year as a function of calendar year for some common surface analysis methods. Note that "XPS, etc.," includes the acronyms ESCA, PES, HAXPES, NAP-XPS, ARXPS, and ARPES, and the number of papers per year has been increasing rapidly compared to the other methods. Data are from the Web of Science™.

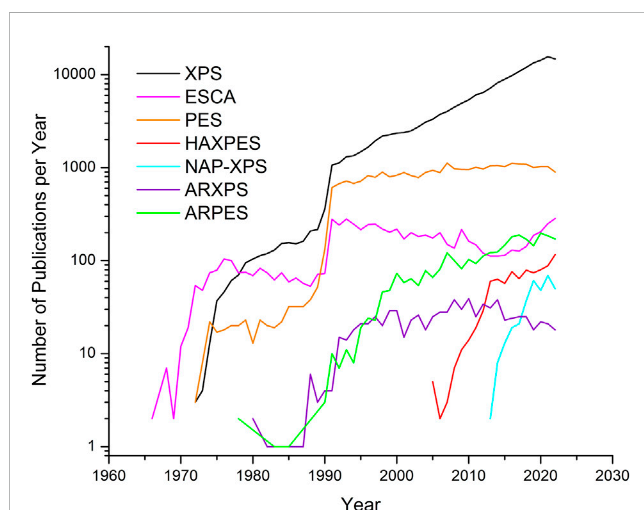

FIGURE 2
The number of publications per year as a function of calendar year for X-ray photoelectron spectroscopy, showing the number of publications using the acronyms XPS, ESCA, PES, HAXPES, NAP-XPS, ARXPS, and ARPES separately, based on the name chosen in the publication. Data are from the Web of Science™.

by those using X-rays from synchrotrons; the other terms are more specific and generally have lower numbers of publications.

Instrumentation

Surface analysis grew rapidly in the late 1960s and early 1970s with the introduction of commercial instrumentation that was largely spearheaded by industrial research laboratories (Smentkowski, 2014). Instruments for surface analysis improved in the decades that followed, and still continue to improve, especially for XPS. Spatial resolution in XPS instruments is now in the 1–10 μm region, and resolutions as low as 150 nm are obtainable at synchrotrons. Spatial resolutions are much higher for AES and SIMS instruments, as the electron and ion beams can be focused to small areas. Many instruments have a high degree of automation and can be operated remotely.

Hard X-ray photoelectron spectroscopy (HAXPES)

The number of manufacturers of commercial AES and SIMS instruments has decreased over the decades, although there is still competition between manufacturers of these instruments. Some of the early manufacturers of XPS instruments stopped making them, particularly in the 1970s and 1980s, but others remained and expanded their offerings. Additional companies have joined in manufacturing XPS instruments over the years. Today, there is good competition between manufacturers of XPS instruments, with many of them offering improved and versatile instruments. For example, hard X-ray photoelectron spectroscopy (HAXPES, also called hard X-ray photoemission spectroscopy), which was usually done using hard X-rays produced at synchrotrons, can now be done in the laboratory using silver, chromium or gallium X-ray sources instead of the usual aluminum (and magnesium) X-ray sources. The number of publications on HAXPES has reached about 100 per year, and is expected to continue to increase, particularly since the hard X-rays allow greater analysis depths and studies of deeper interfaces. Besides being able to probe higher binding energy core levels, HAXPES also reduces the effects of surface contamination, and preferential sputtering effects from ion-beam sputtering.

Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)

Some of the early XPS/ESCA instruments did not use ultra-high vacuum, and surfaces that had been cleaned *in situ* by argon ion bombardment quickly adsorbed gases from the vacuum system and were contaminated. This precluded basic research studies of the adsorption of pure gases on reactive metals, such as titanium and tungsten, in such systems. For several decades, all XPS instruments relied on ultra-high vacuum chambers. However, a great advance in XPS has been the introduction of commercial, near ambient pressure, XPS instruments (NAP-XPS). These instruments allow the chemical analysis of surfaces in reactive working environments and are well suited to studies of corrosion, microorganisms and bacteria. The number of publications on NAP-XPS has been about 50 per year for the past 5 years, and papers using NAP-XPS are especially welcome.

Software

Although acquisition software is fairly mature, allowing experiments to be put in a queue with their own acquisition

parameters and incident beam parameters, data processing software has many shortcomings. Even for XPS which has the simplest spectrum, peak identification using software is not always reliable with peaks sometimes incorrectly identified, or unable to be identified at all. Although some peak identification software claims to look for confirming peaks in a spectrum, this is not always successful. Another issue is that relative intensities of peaks from the same element or species are not checked in the software. Some manufacturers of instruments claim that their automation is so good that the specimen can be analyzed without user input (other than setting prior locations for analysis), and a composition report can be generated and printed automatically. This is often not possible and such reports often contain errors. Organizations such as ISO continue to look at methods for improving data analysis, and this is a major challenge for the manufacturers and independent software writers.

Peak fitting in XPS

Peak fitting (or curve fitting) is one of the most commonly used procedures in XPS, yet it is unfortunate that in about 40% of the papers where peak fitting is used show incorrect fitting of peaks (Major et al., 2020). This is one of the biggest challenges in the XPS field and is due to the lack of understanding about peak shapes. For example, in many metals where the photoelectron peaks are asymmetrical, users tend to add additional, unnecessary, symmetrical peaks to obtain better peak fits instead of using an appropriate asymmetrical line shape. Another issue is that constraints in peak fitting are often not used, resulting in incorrect relative intensities for doublets with well-known relative intensities, and known peak separations. On the other hand, constraints are sometimes used incorrectly such as setting the full-width at half the maximum peak height (FWHM) of doublet peaks to be identical to each other, which is often not the case. For example, the Ti $2p_{1/2}$ FWHM is about 20% larger than the FWHM of the Ti $2p_{3/2}$ peak. The challenge here is to better explain the parameters chosen in peak fitting and the justifications for them.

Publishing in the surface analysis section of Frontiers in analytical science

There is a great need for open access to papers in surface analysis, and it is the aim of this journal to meet these needs. Since the papers are published online, there is no need to curtail the presentation of the work and the discussion of the results, as is the case with most journals. This also eliminates the need for "Supplementary Material" which is accessed separately from a main paper. Research must be reproducible and details of the experiment are necessary to accomplish this goal.

Another advantage for publishing in this journal is that the papers stay alive. The publication platform allows post-publication commenting and discussion on articles even after the peer-review process. The name of the Associate Editor that handled the review process and the names of the reviewers are published with the paper.

The journal seeks high-quality papers on surface analysis including all aspects of:

- XPS (including HAXPES, synchrotron-based work, NAP-XPS and ARXPS/ARPES)
- AES
- SIMS (including D-SIMS, G-SIMS, ToF-SIMS and SNMS)
- Electron energy loss spectroscopy (EELS, REELS)
- Surface structure and diffraction
- Imaging of surface compositions
- Ion bombardment and sputtering
- Thin film and interface studies (including destructive methods such as sputter depth profiling, and non-destructive methods such as HAXPES, ARXPS, and signal backgrounds)
- Instrumentation developments
- Data processing
- Quantitative analysis
- Matrix effects, and
- Studies on metals, alloys, compounds, polymers, organic materials, semiconductors, ceramics, biomaterials, fibers, spherical particles, and nanomaterials.

Industrial applications are welcome, especially where surface analysis techniques have been used to improve products and solve manufacturing issues. Papers on surface analysis standards, and guides for using and interpreting surface analysis methods also fall within the scope of the journal. Finally, special Research Topics, such as papers presented at workshops and conferences, and collections of papers honoring esteemed careers are welcome. Let us all work together to move the surface analysis field forward.

Author contributions

The author confirms being the sole contributor of this work and has approved it for publication.

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Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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