# Chemical Analysis of Materials with X-ray Photoelectron Spectroscopy (XPS)

## Insights from XPS

X-ray Photoelectron Spectroscopy (XPS), sometimes called Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive technique capable of measuring the elemental composition of materials. In general, X-rays bombard the surface of a material, and the energy of emitted electrons is then measured by an analyser (Figure 1 a). The depth sensitivity of XPS depends on the escape depth of the electrons, which is typically between 3-10 nm.
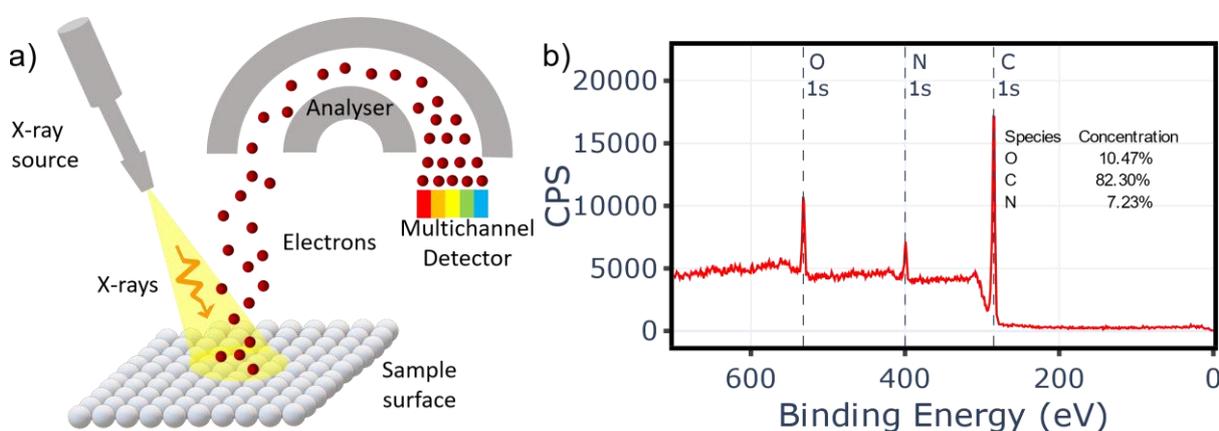


*Figure 1. a) XPS working principle. X-rays bombard a material, leading to the photoemission of electrons from the surface, which are then focused and detected by an analyser. Electrons are detected by a multichannel plate, which counts the number of electrons at different energies. b) XPS spectrum of a polymer containing carbon, oxygen and nitrogen with the corresponding concentration.*

The primary purpose of XPS is to provide quantitative information on the surface chemical composition and stoichiometry of materials (Figure 1b). For example, the formulation of alloys, the proportion between different monomers in a polymer, or composite materials such as the ratio of dispersed particles. Among all the elements, only hydrogen and helium cannot be detected with XPS.

Moreover, XPS provides nuanced chemical information unavailable to many other techniques. It is possible to distinguish between different chemical environments of the same element. For instance, XPS can not only be used to differentiate between bonding environments, e.g. C-C, C-O, and C=O, but also more complex chemical shifts arising from surface binding, intermolecular binding, or even the oxidation state of elements (e.g. the oxidation state of copper during a reaction). XPS is also sensitive to concentrations down to 0.05 % of the surface atoms[1], making it possible to precisely detect contaminations in organic and inorganic coatings or surfaces. This is frequently used, for instance, to study sample purity in semiconductor devices, metal contacts, polymer coatings, and thin molecular films.

# Working principles

As introduced above, the XPS technique works *via* the photoelectric effect. The measured electron energies are plotted as a spectrum (Figure 1b), displaying the number of electrons counted (usually counts per second, CPS) *versus* the electron energy. The measured kinetic energy of the electrons is then converted to binding energy. The binding energy of an electron is the energy required to remove it from a specific atomic orbital within a specific element, therefore providing a unique "fingerprint" for the atomic species present in a material (e.g. the C 1s, O 1s, and N 1s orbitals shown in Figure 1b). With this information, it's possible to infer the elemental composition of a sample by comparing the peaks with reference energies found in a variety of databases[2] or textbooks[3]. One common X-ray energy used in laboratory instruments is 1486.6 eV (Al K$_\alpha$), allowing measurement of elemental core lines between a range of 0 – 1486.6 eV.
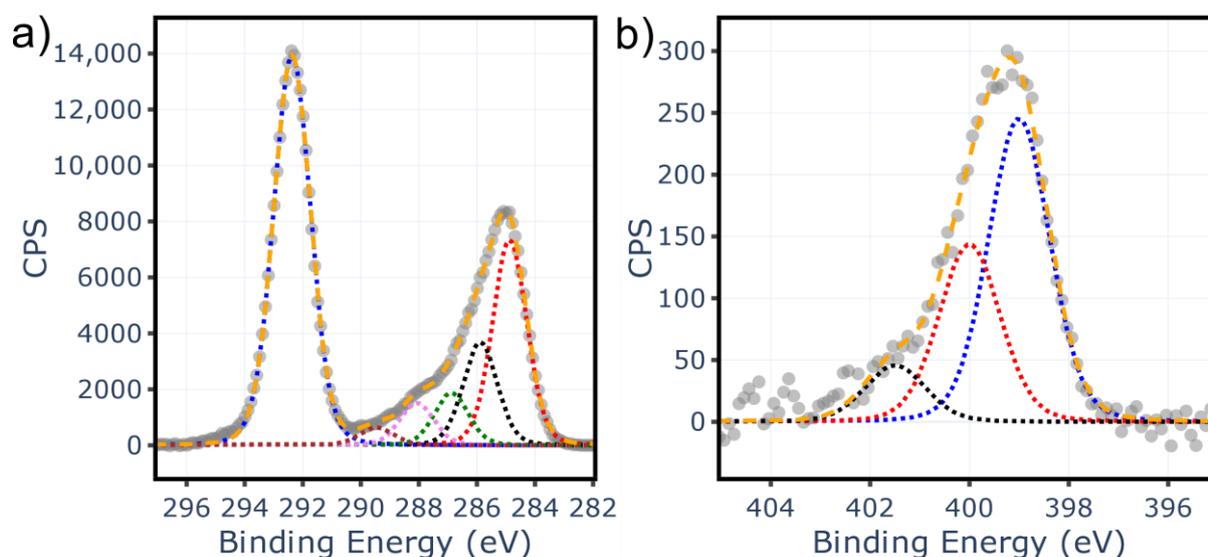


*Figure 2. a) High-resolution XPS of the C 1s peak in a sample of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) on polytetrafluoroethylene (PTFE). There are six different chemical environments C-F$_2$ (blue), O-C=O (brown), C=O (pink), C-O (green), C-N (black), and C-C/H (red). b) High-resolution XPS of the N 1s peak in a sample of TEMPO on PTFE, with three different chemical environments N-H (black), N-O (red), and N-C (blue).*

The high energy resolution of XPS affords the detection of subtle changes in the orbitals due to their chemical environment. These subtle energy changes are called chemical shifts. For instance, a single C 1s peak in 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) on polytetrafluoroethylene (PTFE) can split into several components as shown in Figure 2a. Highly electronegative atoms such as fluorine cause large shifts in energy, resulting in an entirely separate peak that can be identified as C-F$_2$ (blue). In comparison, chemical environments such as O-C=O, C=O, C-O, C-N, and C-C/H in Figure 2a, and N-H, N-O, and N-C in Figure 2b, overlap with one another. Identification of chemical environments therefore often relies on peak fitting using Gaussian functions to represent each chemical component. This process requires significant care and expertise to avoid misidentification and is a common pitfall with inexperienced users. The authors highly recommend a series of introductory papers on XPS[4], quantitative XPS[5] and peak fitting[6].

# Multi-technique capability

Laboratory XPS instruments can be fitted with a range of additional instruments providing multi-technique capability. Here we briefly summarise three methods: 3D depth profiling with argon ion milling (Figure 3a), 2D XPS imaging for mapping the chemical composition of a sample surface (Figure 3b), and temperature-programmed XPS (TP-XPS) for monitoring temperature-dependent chemical evolution (Figure 3c).
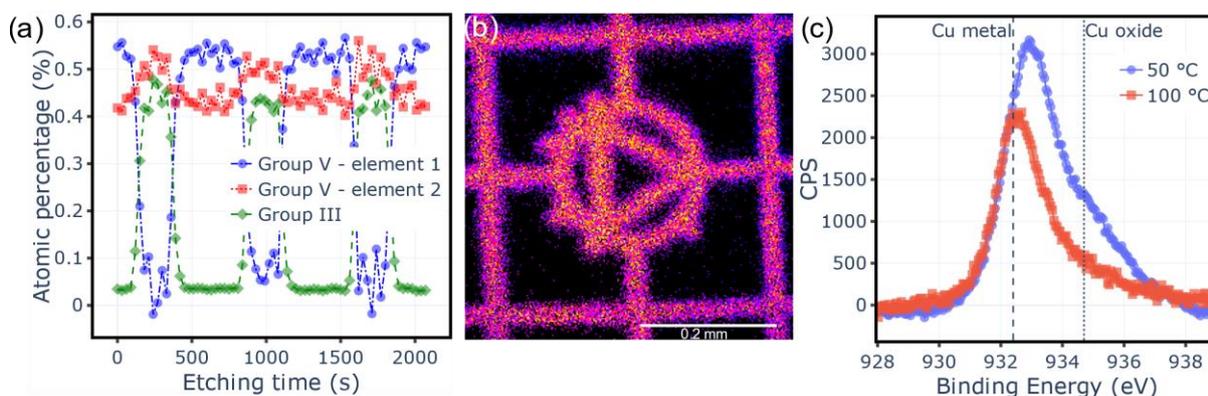


*Figure 3. (a) Depth profiling graph of a layered binary and ternary III-V semiconductor. The plot shows the atomic percentage of the group V and group III elements as a function of etching time. (b) Spatial distribution of gold in a calibration grid by XPS imaging. (c) Temperature-programmed XPS of a Cu 2p peak showing the transition from oxidised copper at 50 °C to metallic copper at 100 °C. Data for panel (a) is kindly provided by Prof. Manus Hayne.*

The surface sensitivity of XPS unlocks the possibility of depth profiling when combined with sample milling/etching. For instance, an *in situ* Gas Cluster Ion Source (GCIS) can produce $Ar_n^+$ ions capable of milling through materials with exceptional precision, down to just a few nanometres at a time. By collecting XPS in between each milling step, we obtain the chemical depth profile of the material. This is particularly useful for layered materials or interfaces (e.g. surface coatings, stacked semiconductors or buried interfaces), assessing the uniformity in the vertical direction or the thickness of the layers. An example of GCIS milling is shown in Figure 3a, which plots changes in the atomic percentage of layered III-V semiconductor material as a function of sample depth. This process is extremely precise, with an etching rate down to around 0.05 nm/s, and can be used to mill through samples of several microns thickness.

The spatial distribution of elements can also be detected in a 2D imaging mode by measuring the number of electrons photoemitted from each part of the surface plane. These measurements are relevant for patterned surfaces, devices, semiconductors, and composite materials, or to investigate the chemical uniformity of samples. One such example is given in Figure 3b, which shows an XPS map collected on a fine gold wire grid.

It is also possible to heat or cool a sample during XPS measurements using specially designed sample heating plates. This process, named temperature-programmed XPS (TP-XPS), opens the possibility of assessing the thermal stability of a sample or studying a chemical reaction as a function of temperature. One such example is given in Figure 3c, which shows a transition from Cu oxide to Cu metal due to increased temperature. These measurements are especially useful for studying heterogeneous catalysis when both the catalyst and the reactant are already on the surface.

# What kind of samples can be analysed?

XPS is suitable for analysing any polymeric, metallic, semiconductor, insulator, or ceramic material as long as it does not outgas in ultra-high vacuum (UHV). The use of XPS also encompasses the study of complex systems such as biological samples (e.g. proteins or DNA), due to the sensitivity to low amounts of material. Samples are typically solids, powders, or thin coatings. Generally, liquids cannot be studied because they outgas under UHV conditions; however, ionic liquids are a notable exception due to the negligible vapour pressure.

The typical dimensions of a sample for laboratory XPS analysis are up to 3 cm x 3 cm and a thickness of up to 2 cm, defined by the type of sample holder. Larger pieces may not fit the sample holder, but it may be possible to divide the sample into smaller specimens for separate analysis. Most XPS instruments are equipped with several sample holders to load multiple specimens in the instrument at the same time. Each measurement is confined to a small area defined by the X-ray spot size. For the instrument used in this study, this ranges from 0.35 mm x 0.7 mm down to 15 μm x 15 μm, therefore dictating the minimal dimension of the sample to be analysed.

# Cost and technical expertise

XPS offers precious information on the surface chemistry of materials. However, the high cost of the equipment and maintenance means that XPS can often only be provided by national facilities such as Harwell XPS or the Diamond Light Source, or through collaboration with universities, where instruments are often accessible for external use*. Furthermore, XPS requires skilled operators due to the complexity of the instrument's use and maintenance, as well as the data analysis.

Financial and expertise constraints imposed by XPS call for collaboration between companies and research institutions. The former would use the information to optimise their products, while the latter would benefit from exposure to real-world industrial problems and materials.

* For information on facilities at Lancaster, contact Dr Samuel Jarvis, Head of Lancaster XPS (samuel.jarvis@lancaster.ac.uk) or Alessio Quadrelli, PhD researcher (a.quadrelli@lancaster.ac.uk).

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