



# X-Ray Photoelectron Spectroscopy (XPS) Services

**X-Ray Photoelectron Spectroscopy (XPS Spectroscopy)** is also known as **Electron Spectroscopy for Chemical Analysis (ESCA)**. XPS is used to determine quantitative atomic composition and chemical bonding.

X-Ray Photoelectron Spectroscopy is a surface analysis technique used to determine quantitative atomic composition and chemical bonding. Albert Einstein's early work led to an understanding of the photoelectric effect for which he was awarded his Nobel prize in 1922. He explained that light consisted of photons of fixed energies. When light interacts with an atom, if the photon energy is higher than the minimum energy required to remove an electron from an atom, spontaneous emission of the electron from the atom would occur. It was not until the mid 1960s that the photoelectric effect was more fully developed as a surface analysis tool now known as XPS or ESCA. In XPS we refer to the minimum energy required to remove an electron from an atom as the electron binding energy,  $E_b$ . The electron binding energy  $E_b$  is related to the kinetic energy of the emitted electron  $E_k$  as follows:  $E_b = h\nu - E_k - \Phi$  where  $h\nu$  is the x-ray energy and  $\Phi$  is the instrument work function.

In general the photoelectric process is initiated by irradiating a sample with monochromatic x-rays. This results in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. Using the most common Al K $\alpha$  x-ray source, the XPS method can detect all elements other than H and He in any sample that is vacuum compatible. Although the x-rays penetrate several microns into the sample, only those photoelectrons that originate from the outer few nm are able to exit the sample without the loss of energy and contribute to the XPS peaks. Electrons which lose energy while traveling through the sample contribute to the background electron signal.

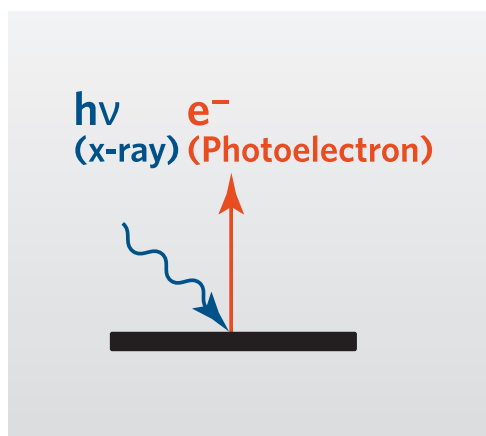


Figure 1. General schematic of the photoelectric effect.

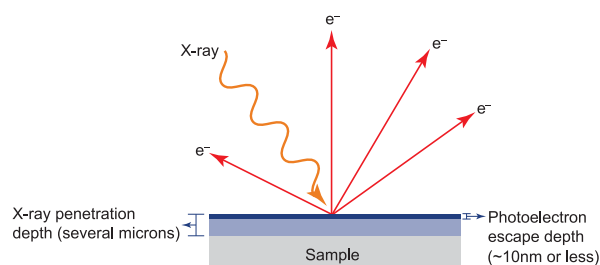
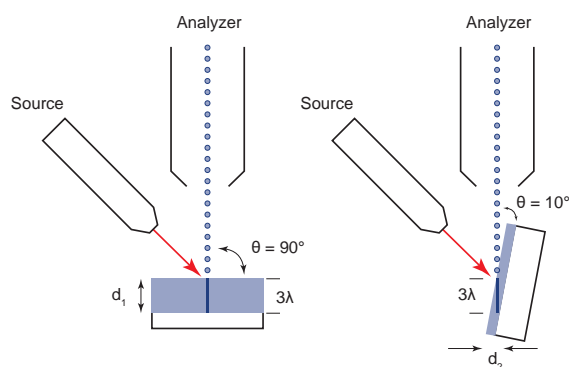


Figure 2. General schematic of how XPS works.

The XPS sampling depth is dependent on the take-off angle between the sample plane and the electron analyzer. When the take-off angle is high, e.g. 90°, the sampling depth is maximized. Conversely when the take-off angle is low, e.g. 10°, the sampling depth is minimized. The sampling depth  $d$  is most often taken as  $d = 3\lambda \sin\theta$  where  $\lambda$  is the inelastic mean free path of the measured electron within the sample matrix, and  $\theta$  is the electron take-off angle relative to the sample plane. It is important to note that electrons with different

energies will have different inelastic mean free paths: larger kinetic energies (lower binding energies) result in larger inelastic mean free paths and larger sampling depths. XPS sensitivity factors account for the sampling depth differences with different energies. Thus for samples of uniform composition within the XPS sampling depth, accurate quantification is achieved using electrons of any energy. However, if the sample is heterogeneous with the sampling depth, high quantitative accuracy requires the inspection of electrons with similar energies. Unfortunately, this is not always possible and consequently high quantitative accuracy is not always achievable.



$d = \text{Sampling Depth} \approx 3\lambda \sin\theta$   
 $d_2 < d_1$  even though  $\lambda$  is constant

Figure 3. XPS sampling depth varies with electron take-off angle.

An XPS experiment usually starts with a survey spectrum that includes the full energy range scanned with good sensitivity. From the survey spectrum, one can identify which elements are present on the sample surface. Survey spectra can also be used to quantify the detected elements. An XPS survey analysis is analogous to an AES (Auger) survey analysis.

The main differences between XPS and Auger are the ability of XPS to examine any vacuum compatible sample including insulators, and the larger analysis area in XPS. An exceptional feature of XPS is the ability to determine chemical bonding or oxidation state. This requires acquisition of high energy resolution narrow scans of specific energy regions of interest. Chemical bonding or oxidation state is derived from the peak position and peak shape. High resolution spectra can also be used to obtain higher precision quantitative analysis than can be

obtained from survey spectra.

When information is required at depths greater than a few nm, depth profile analysis is employed. In depth profile analysis the sample is sequentially examined and then material is removed by ion sputtering. This is repeated until the desired depth is reached.

For common household aluminum foil, a survey spectrum indicates the presence of O, Al, C, and Mg. The intense O peak is consistent with the native oxide on the Al metal foil. The trace of Mg is present in the alloy to increase the strength and ductility of the foil. C atoms are observed on most inorganic surfaces due to organic contaminants introduced during sample production, handling, and air exposure.

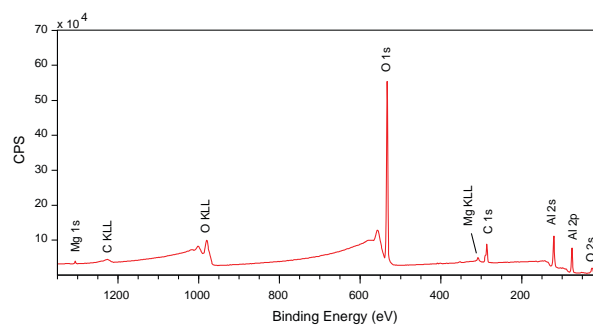


Figure 4. XPS survey spectrum of household aluminum foil.

The high energy resolution Al 2p spectrum indicates the presence of  $\text{Al}_2\text{O}_3$  (oxide) as the dominant surface species with  $\text{Al}^0$  (metal) and  $\text{AlO}_x$  (suboxide) as minor surface species. Because XPS can quantitatively determine the amounts of Al atoms in all three chemical states, XPS can be used to detect oxide thickness differences in the Å range. With proper calibration, the intensity of Al present as

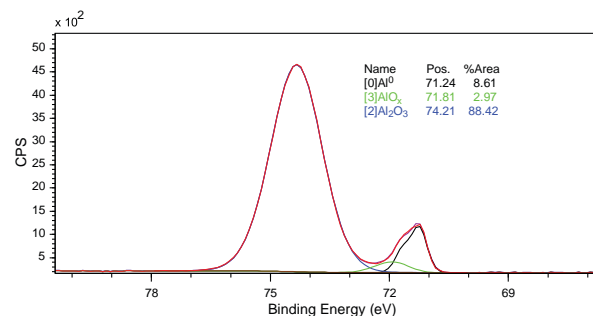


Figure 5. XPS high resolution Al 2p spectrum of household aluminum foil.

$\text{Al}_2\text{O}_3$  can be used to calculate the  $\text{Al}_2\text{O}_3$  layer thickness. In this sample the oxide was 3.6 nm thick.

As with many analytical methods, XPS has high precision (measurement reproducibility). If the sample is uniform within the sampling volume, XPS can also have high quantitative accuracy. For example, ten XPS analyses of polyethylene terephthalate (PET) film ( $\text{C}_{10}\text{H}_8\text{O}_4$ ) performed over a two month period determined average O and C concentrations of 29.3 and 70.6 atomic%, respectively. The theoretical values for PET are 28.6 and 71.4 atomic%. The precision was found to be 0.7% and 0.3% for O and C, respectively. The accuracy was found to be 2.4% and 1.1% for O and C, respectively.

## Strengths

- Chemical state identification on surfaces
- Identification of all elements except for H and He
- Quantitative analysis, including chemical state differences between samples
- Applicable for a wide variety of materials, including insulating samples (including paper, plastics, ceramics, and glass)
- Surface sensitive (1-10 nm analysis depth)
- Depth profiling for major elements (generally > 1 atomic%)
- Oxide thickness measurements

## Limitations

- Detection limits typically ~ 0.1 at%
- Smallest analytical area ~30  $\mu\text{m}$
- Limited specific organic information (no long-range bonding information)
- Sample must be UHV compatible

## Common Applications

- Identifying stains and discolorations
- Identifying surface chemistry, bonding or oxidation state
- Characterizing cleaning processes
- Analyzing the composition of powders/debris and residues/additive blooming

- Determining contaminant sources
- Examining polymer functionality before and after processing to identify and quantify surface changes
- Obtaining depth profiles of thin film stacks (both conducting and non-conducting) for matrix level constituents and contaminants (down to the low atomic% level)
- Assessing the differences in oxide thickness between samples
- Failure analysis
- Reverse Engineering

## Industry Sectors and Technologies

- [Polymers/coating](#)
- Packaging
- [Medical devices](#)
- [Pharmaceutical](#) (powders/tablets)
- [Semiconductors](#) (devices, manufacturing equipment)
- [Batteries](#)
- [Photovoltaic solar](#)
- [Optics/glass](#)
- [Metallurgy](#)

## Case Study: Validating Surface Composition and Cleanliness

The ability to manufacture products with well defined surface composition while being free of undesirable contamination is vital in many industries. XPS is

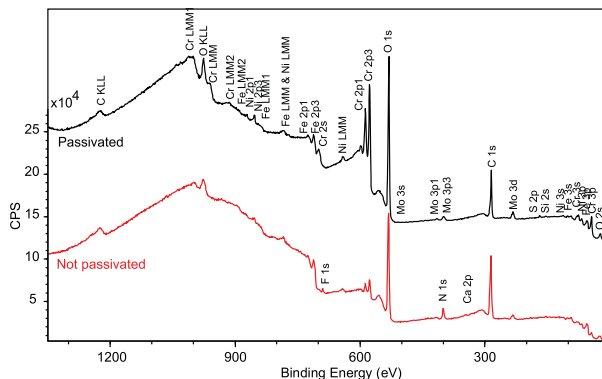


Figure 6. XPS survey spectra of passivated and non-passivated 316L stainless steel.

ideally suited to production monitoring because it can examine the surface of any vacuum compatible material be it a conductor or an insulator.

If the requirement is simply to meet a given elemental composition, then the analysis can be as simple as acquiring a survey spectrum. For example, stainless steel is often passivated to improve corrosion resistance. The primary goals are to enrich the surface with chromium by increasing the elemental ratio of chromium to iron, and to remove undesirable contaminants. Survey spectra of 316L stainless steel before and after nitric acid passivation can be used for identifying and quantifying surface composition. As seen below, nitric acid passivation increased the Cr/Fe ratio while also decreasing or removing C, N, F, and Ca surface contaminants.

Table 1. Atomic Concentrations (in atomic %)<sup>a</sup>

Sample	C	N	O	F	Si	S	Ca	Cr	Fe	Ni	Mo	Cr/Fe
Not passivated	51.0	4.1	36.5	0.4	0.5	0.2	0.2	2.6	3.3	0.4	0.6	0.8
Passivated	31.9	0.6	48.1	nd	0.6	0.5	nd	14.2	2.5	0.8	0.7	5.7

<sup>a</sup> Normalized to 100% of the elements detected. XPS does not detect H or He.

Often it is not sufficient to simply obtain elemental compositions. In many cases specific chemical bonding or oxidation states are desirable on the finished product. The primary chemical bonding goals of passivation are to produce a surface depleted in metallic iron and enriched in chromium oxide. By curve fitting the Fe and Cr high resolution spectra we can quantify the amounts of Fe and Cr in the metallic and oxide chemical states. Here we see that passivation produced a surface depleted in metallic iron and enriched in chromium oxide.

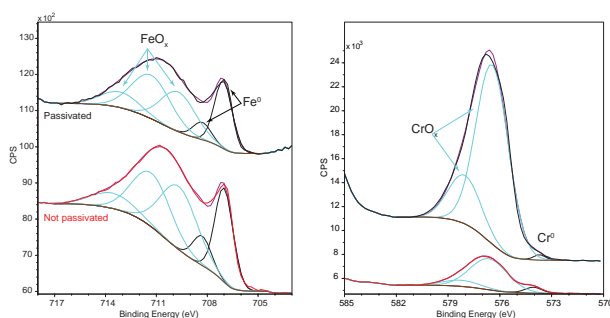


Figure 7. XPS high resolution Fe 2p<sub>3/2</sub> and Cr 2p<sub>3/2</sub> spectra of passivated and non-passivated 316L stainless steel.

Table 2. Chromium and Iron Chemical States (in atomic %)<sup>a, b</sup>

Sample	Cr <sub>metal</sub>	Cr <sub>oxide</sub>	Fe <sub>metal</sub>	Fe <sub>oxide</sub>	Cr <sub>oxide</sub> /Fe <sub>oxide</sub>
Not passivated	0.2	2.4	1.0	2.3	1.1
Passivated	0.1	14.1	0.7	1.7	8.1

<sup>a</sup> Normalized to 100% of the elements detected. XPS does not detect H or He.

<sup>b</sup> The balance of the elements are present as O, Ni, Mo, and C.

## Case Study: Type 1 Glass Vials

Type 1 glass vials are commonly used to contain pharmaceuticals because of the good chemical stability of the borosilicate glass.



Figure 8. Typical type 1 glass vials with septum caps.

A pharmaceutical manufacturer needed to determine the surface concentrations of the active pharmaceutical ingredient and excipients in spray dried multi-component formulation powders. This is a relatively straightforward analysis provided the API or excipient contains a unique element or functional group. The powders were packaged in septa sealed glass vials and shipped to EAG. As expected, XPS analysis of the powders indicated the presence of O, N, and C. However, the powders were also found to contain Si, which was not an

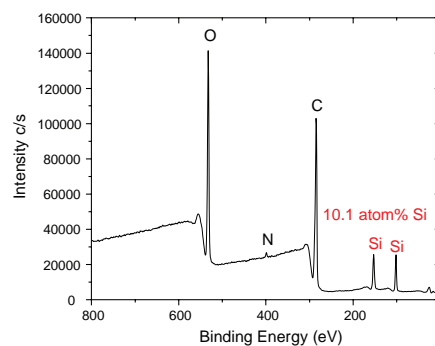


Figure 9. XPS survey spectrum of a spray dried multi-component formulation stored in a type 1 vial having a silicone septum.

expected element in the multi-component formulation.

The high resolution XPS silicon spectrum indicated that the silicon was present as a silicone. Analysis of the septum indicated it was indeed polydimethyl siloxane (PDMS). As is common with silicones, low molecular weight material from the septa migrated into the vial and consequently covered the powder. Because there are two C atoms and one O atom for each Si atom in PDMS, 10.1 atomic% Si means that 40.4 atomic% of the detected elements are due to PDMS. This equates to a PDMS layer of ~1.4nm or several monolayers. The presence of silicone greatly compromised the ability to use XPS to quantify the amount of API at the surface of the powders. It may also have caused unforeseen risks with the actual product itself. Packaging the powders with polytetrafluoroethylene (PTFE) lined silicone septa prevented PDMS contamination of the powders and permitted the study to proceed smoothly and reduced the risk of introducing foreign material to the formulation.

Type 1 glass vials were themselves found to present a problem for some reactive pharmaceutical solutions such as those with a low or high pH. Visual inspection of such vials indicated the presence of atypical particles which were subsequently determined to be lamellae shed from the glass vials themselves. During production of the vials, the base

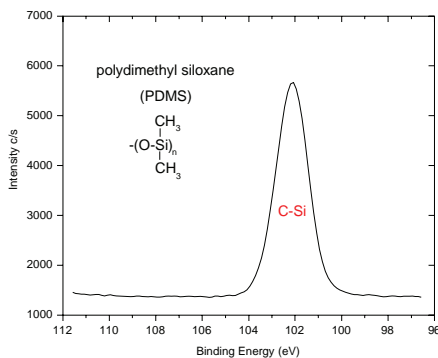


Figure 10. XPS high resolution Si 2p spectrum of a spray dried multi-component formulation stored in a type 1 vial having a silicone septum.

and neck regions are exposed to higher temperatures than the cylindrical sidewall. XPS analysis along the length of the vial revealed a depletion of  $B_2O_3$  and  $Na_2O$  in the base and neck regions. This is caused by volatilization of  $B_2O_3$  and  $Na_2O$  from the high temperature regions and subsequent condensation on the cooler sidewall.

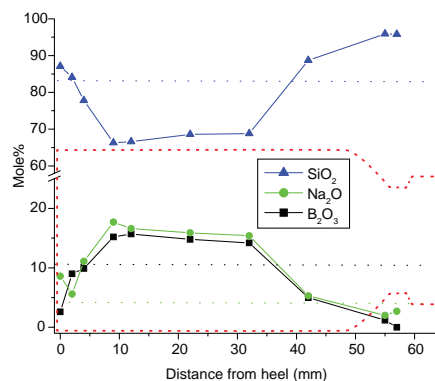


Figure 11. Measured composition of the outer surface along the length of an as-produced vial. Horizontal dotted lines represent bulk glass composition.

The depth profile of the sidewall of an as-produced (Control) vial revealed a ~70nm thick  $B_2O_3$  and  $Na_2O$  enrichment layer. Exposure of the vial to a low pH solution created a ~100nm layer depleted in  $B_2O_3$  and  $Na_2O$ . ICP-MS analysis of the solution showed elevated levels of B and Na. Exposure of a vial to a high pH solution resulted in a completely different surface. For a high pH solution, the sidewall becomes enriched in  $Al_2O_3$ . Unlike at low pH where  $B_2O_3$  and  $Na_2O$  are leached from the glass, at high pH the Si-O-Si structure of the glass begins to dissolve leaving an  $Al_2O_3$  enriched layer.

The heterogeneity of the surface composition of type 1 vials due to thermal gradients during production combined with degradation of the surface when in contact with low or high pH solutions can lead to stresses that can in some cases result in the shedding of lamellae from the glass vials, with a subsequent increased risk based on the end use of the solution in the vial.



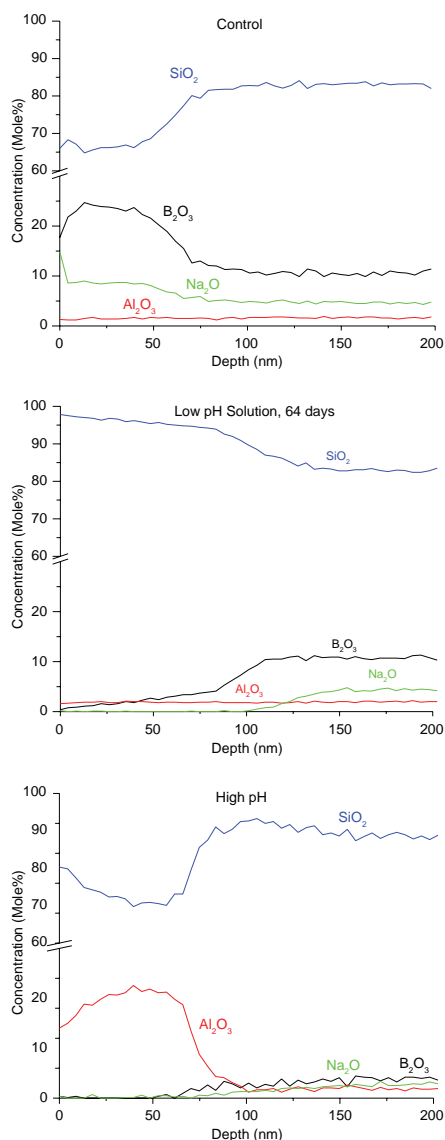


Figure 12. XPS depth profiles of an as-produced control vial and vials exposed to low and high pH solutions.

## Complementary Techniques

Other surface analysis tools with similar depths of analysis include Auger Electron Spectroscopy (AES) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). XPS provides short-range chemical bonding information that is not normally obtained from Auger. TOF-SIMS provides short range and long range molecular bonding information. Insulating materials, including organic compounds, are routinely examined by XPS and TOF-SIMS but are difficult with Auger. In terms of the analytical beam sizes, Auger has the smallest spot size (~10nm), followed by TOF-SIMS (~0.3µm), and finally XPS (~30µm). XPS and AES techniques are generally considered semi-quantitative at a minimum or quantitative in ideal cases. In contrast, TOF-SIMS results are very difficult to quantify absolutely, with the exception of surface metal contamination on silicon.

SEM/EDS and FTIR/Raman are not classical surface analysis methods but have some analytical similarities with XPS. SEM/EDS provides element identification/quantification but with a sampling depth of 10s of nm to a few µm and does not provide chemical bonding information. FTIR and Raman provide molecular bonding information but not element identification/quantification. Although the spatial resolution of FTIR and Raman are on the same order as XPS, the sampling depths are generally on the order of µm to mm in FTIR and Raman.

## XPS at EAG

EAG has many XPS instruments worldwide. Some of these instruments contain special capabilities such as an 8" sample stage for very large samples, a reaction chamber for custom-designed experiments, and a hot/cold stage for heating and cooling of samples in vacuum. Our XPS experience is unsurpassed with many of our XPS scientists having decades of experience. Contact us to learn how we can help you with your next project.