MICROSCOPY AND ANALYSIS

X-ray Photoelectron Spectroscopy

Essential Knowledge Briefings

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Front cover image: a sample in the ESCALAB Xi+ XPS microprobe.
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About Essential Knowledge Briefings

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INTRODUCTION

To a non-scientist, a surface is nothing special. It is merely a boundary – a thin volume at the extremity of an object that marks that object's transition to the surrounding medium. To many researchers, however, the surface of a solid object has a scientific importance that far exceeds its physical extent. Corrosion, wettability, catalytic activity, adhesiveness – all these chemical properties and many more derive not from an object's bulk, but from the few uppermost atoms at its surface.

X-ray photoelectron spectroscopy (XPS) is one of the foremost tools for studying this surface chemistry. In its simplest form, XPS involves shining X-rays onto a material to knock electrons from the surface atoms. By counting these ejected electrons and measuring their energy, it is possible to work out what elements are present on the surface and in what relative quantities. Indeed, it is even possible to work out the electronic state of those atoms and how they are bonded, thereby revealing a surface's precise chemical composition.

In the past 20 years or so that it has been a mature technique, XPS has been applied to the full breadth of surface chemistry, from problem-solving in engineering to cutting-edge scientific analysis. In this way, it has provided insights into a wide variety of subject matter, whether understanding the deterioration of a frying pan's non-stick coating or fine-tuning the design of a new semiconductor for solar cells. In recent years, XPS has also demonstrated its crucial relevance to nascent fields of materials science by helping researchers investigate new two-dimensional materials such as graphene.

XPS spectrometers are not especially cheap compared with, say, electron microscopes, and therefore tend to be found in specialist facilities that offer surface analysis. But these facilities are now commonplace, and inexperienced users can rest assured that experts are usually on hand to provide advice. Even so, it can help newcomers to have some prior understanding of the tool.

This Essential Knowledge Briefing (EKB) aims to give a simple introduction to XPS. It will explore the history of the technique, how it works, and what it can be used for. It will also detail some of the specific implementations of XPS, discuss what practical problems can arise, and explore what developments are likely to be seen in the future.

HISTORY AND BACKGROUND

The basis of XPS is the photoelectric effect, a phenomenon first reported by German physicist Heinrich Hertz in 1887. Hertz found that a metal electrode illuminated with ultraviolet light sometimes emitted a spark. This in itself was not a wholly mysterious observation, as classical physics stated that the light could simply be transferring its energy to the metal, generating an electric charge. But such classical reasoning predicted that the cut-off for the effect should depend on the intensity of the light. In fact, subsequent experiments – in particular those by German physicist Philipp Lenard – suggested a different cut-off criterion: the light's frequency. The explanation, courtesy of Albert Einstein 18 years later, was that light travels not in continuous waves but in discrete packets or 'quanta', each with energy proportional to frequency.

In the midst of these developments, German physicist Wilhelm Röntgen discovered X-rays and British physicist JJ Thomson and colleagues identified electrons as the particles of electric charge. In 1907, Thomson's student, PD Innes, wanted to know whether the photoelectric effect arose because light somehow disintegrated a metal's atoms or because light could directly knock electrons free. It was in his efforts to find out that Innes recorded the first primitive XPS spectra, by exposing a metal to X-rays and recording the numbers of electrons arriving at photographic plates as a function of velocity.

Innes concluded, incorrectly, that atomic disintegration was behind the photoelectric effect. He was ignorant of Einstein's work, and this was before British physicist Ernest Rutherford and Danish physicist Niels Bohr came up with the 'planetary' model of the atom as a dense nucleus orbited by electrons, which happened between 1911 and 1913. In time, however, a visual picture emerged of the photoelectric effect, with individual photons – provided they had sufficient energy – able to knock electrons from their atomic orbitals.

The Rutherford–Bohr model of the atom was still evolving by the 1920s, and XPS had the potential to play a practical role. 'An accurate knowledge of the energies associated with the different electronic orbits within the atoms is essential to the further development of the theory of atomic structure,' wrote H Robinson, a former colleague of Rutherford's and an XPS pioneer.

For XPS to become a refined analytical tool, however, science would have to wait three decades for the dedicated work of Swedish physicist Kai Siegbahn and colleagues. In 1954, Siegbahn's group built the first high-resolution system for XPS (which they preferred to call electron spectroscopy for chemical analysis, or ESCA) and used it to record the spectrum of cleaved sodium chloride. By 1967, they had published a comprehensive volume explaining the versatility of XPS for analyzing all sorts of organic and inorganic materials, paving the way for the first commercial system two years later. In 1981, Siegbahn won the Nobel Prize in Physics for his work on XPS.

One of the revelations of Siegbahn and colleagues' early work was their discovery that the sensitivity of XPS was limited to depths of less than 10 nanometers beneath an object's surface. A standalone layer of this depth would today be categorized as an 'ultra-thin film'. Such depth-sensitivity contributes to the uniqueness of XPS as an analytical tool, along with a few other characteristics.

The kinetic energy of an electron measured by an XPS system can determine the energy with which that electron was originally bound by its host atomic nucleus. That binding energy, in turn, depends on several factors: the atomic element, the orbital previously occupied by the electron, and that orbital's chemical environment. It is in this way that XPS can be used to measure elemental composition, empirical formula, chemical state and electronic state. Moreover, because the emitted electrons are counted by an XPS system, the analysis reveals 'how much of what', making it a quantitative technique.

XPS can be used to study just about anything, including metals, alloys, semiconductors, glasses, polymers, organics, ceramics, oils – the list goes on. The only elements it cannot detect are hydrogen and helium; everything else it can detect down to levels of parts per thousand.

The sophistication of XPS has improved since the early commercial systems of the 1970s, particularly with the parallel evolution of computing; since the 1990s, it has been considered a mature analytical technique. In that time, various specialist implementations of XPS have also been developed. These include: depth profiling, in which an ion beam etches away a sample between X-ray exposures to allow successive layers to be analyzed; XPS imaging, which reveals the distribution of chemistries across a surface; angle-resolved XPS, which can distinguish electrons from different depths in the surface of a sample; and charge compensation, which allows for the analysis of insulators. Some of these specialist implementations are discussed in forthcoming chapters.

Of course, many other tools for analyzing surface chemistry exist. Infra-red and Raman spectroscopy are widely used techniques that can reveal a surface's molecular, but not elemental, composition. One instrument that can supply quantified elemental information is the scanning electron microscope when fitted with an X-ray analyzer. However, this provides limited chemical information and, despite a good spatial resolution, probes well beyond the surface of a material into the bulk. Several techniques based on this approach have been developed, including energy dispersive spectroscopy and electron probe microanalysis, both of which are the subject of separate EKBs.

Much better surface sensitivity – with a depth limited to a couple of nanometers or so – is provided by secondary ion mass spectrometry (SIMS), a technique that has evolved in parallel with XPS for the past few decades. In SIMS, energetic ions, rather than X-rays, are directed at a surface, and it is ejected secondary ions, rather than electrons, that are analyzed. SIMS has even higher elemental sensitivity than XPS, but the data are harder to quantify. Another technique that employs ions for bombardment is ion scattering spectroscopy (ISS), which, as its name implies, measures the energy change as different ions are scattered off a surface. ISS is so surface-sensitive that sample contamination can be a serious problem; with careful use, however, ISS can be a useful companion technique to XPS, providing elemental information from just the outermost layer of atoms.

The main disadvantage of XPS is its spatial resolution, which is typically 1mm, but can be improved to 10µm or less in small-area XPS and XPS imaging. Nevertheless, no other analytical technique provides quite the same useful combination of surface sensitivity, quantifiable elemental and chemical information, and application to both organics and inorganics as XPS.

IN PRACTICE

Although XPS systems can be very sophisticated, their basic operation is fairly straightforward. From an external point of view, the most obvious feature of these systems is that the entire non-control apparatus is concealed inside a chamber: this is the vacuum system, which brings the internal pressure down to an ultra-high vacuum range of 10^{-6} to 10^{-8} pascals. Without this vacuum, gas would quickly adsorb onto and contaminate the sample surface, and any ejected electrons would be scattered en route to the detector.

One of the most important components inside the vacuum chamber (Figure 1) is the X-ray source: an anode (a neutral or positively-charged target) that is bombarded with high-energy electrons from a cathode, which is usually a thermal source such as a heated filament. The material that the anode is made from determines the energies of the X-rays that are generated: the most common material for lab-based

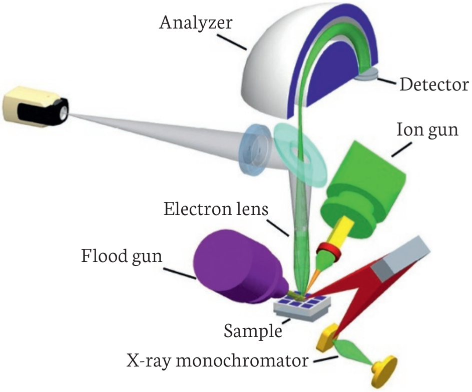

Figure 1. Components of an XPS system.
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instruments is aluminium. Although regarded as ‘soft’ X-rays, the Kα X-rays generated by aluminium are of sufficiently high energy to knock electrons from all elements in the periodic table, while at the same time being sufficiently narrow-band to avoid ‘blurring’ the spectrum too much. The energies of the X-rays can be further narrowed by a quartz monochromator, which has a suitable lattice spacing to pick out just the Kα radiation via crystal diffraction.

Spectroscopists have a standard notation for labeling the electrons knocked free from the atoms at the surface of a sample according to the energy levels from which they came; such knocked-free electrons are termed photoelectrons. This notation takes the form nl_j, where n is the orbital number (taking the integer values 1, 2, 3 and so on, and roughly charting the size of the orbital); l is the orbital angular momentum (taking the ‘values’ of s, p, d and f); and j is the magnetic quantum number (determined both by l and the electron’s up/down ‘spin’, and taking integer multiples of ½). Figure 2, for example, depicts the photoemission of an electron from the lowermost 1s energy level.

Once ejected, the photoelectrons are collected by a lens system and focused into a device that will count the number at each kinetic energy. This device, known as a hemispherical sector analyzer, consists of a pair of hemispherical electrodes across which a voltage is applied, deflecting the electrons into a circular path. The voltage specifies the kinetic energy of the electrons that will be able to circle cleanly through the electrodes to the detector: those electrons with a kinetic energy that is lower or higher will instead strike the inner or outer

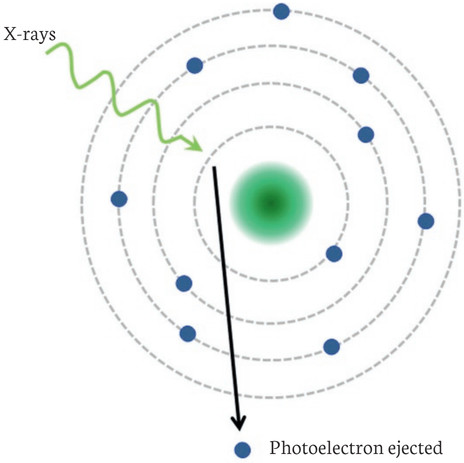

Figure 2. Depiction of the photoemission of an electron from the 1s energy level. Reproduced with permission from Thermo Fisher Scientific

electrode, respectively. In fact, the lens system initially slows all the electrons by a fixed amount to prevent their combined flux from affecting the applied voltage. The detector counts the numbers of electrons arriving; and by stepping up the voltage in increments, the analyzer can count the numbers of photoelectrons at each kinetic energy.

Of course, there is some leeway in the kinetic energies that make it through to the detector at each voltage, and this is known as the pass energy, which can range from narrow to broad. A broad pass energy produces quick, low-resolution 'survey' scans, while a narrow pass energy produces scans of high kinetic energy resolution, suitable for the study of particular spectral features.

The detector is a form of electron multiplier and counter, and measures the number of electrons arriving at a particular kinetic energy, E_K. What the analyst usually wants to know, however, is the electron's binding energy,

E_B, as this is specific to the atomic element and the energy level that the electron came from. E_B is calculated in an XPS system according to the simple equation:

$$E_B = h\nu - E_K - W$$

Where $h\nu$ (Planck's constant multiplied by the photon's wavelength) is the known energy of the incident X-ray, and W is the spectrometer work function – a value, again known, that corrects for the few electron volts of energy given up by a photoelectron as it is absorbed by the detector.

As can be seen, the binding energy is negatively related to the kinetic energy. This should make sense, as electrons that are only loosely bound by an atomic nucleus will carry away far more of an incident photon's energy than a strongly bound electron. In general, the greater the energy level (that is, the farther an electron is from the atomic nucleus), the less the binding energy.

The process of taking an initial survey scan of a sample will normally take just under a minute, and will produce a spectrum of the sort seen in Figure 3. An XPS spectrum shows the numbers of electrons arriving at the detector at each calculated binding energy; convention dictates that binding energy increases on the horizontal axis right to left. The most obvious features are the peaks, which correspond to the electron energy levels of the various elements present on the surface of the sample.

Printed tables of the binding energies for different elemental energy levels are available for identifying these

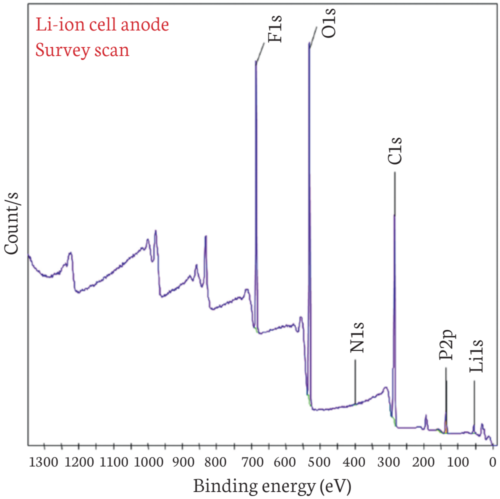

Figure 3. An example of a spectrum produced by XPS.
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peaks, such as those provided by the US National Institute of Standards and Technology. This is often unnecessary with modern XPS spectrometers, however, as the control system automatically identifies the most prominent peaks and only asks the user to check those that exhibit some degree of ambiguity. The control system also calculates the area underneath each peak, which is directly related to the amount of each element present at the surface and so crucial for determining the surface's composition. In Figure 3, photoelectron peaks can be identified for oxygen in the 1s and 2s energy levels, and carbon in the 1s energy level: these peaks reflect the electronic structure of polyethylene terephthalate (PET), the sample under analysis. The additional peaks are due to the so-called Auger process, which will be discussed in the next chapter.

If, as is usually the case, the analyst had no knowledge of the sample's exact composition beforehand, he or she would follow up this survey scan with higher resolution scans of the binding-energy regions of interest. Such scans would reveal any subtle shifts or distortions of the photoelectron peaks due to the precise electronic states of their parent atoms – that is, due to the way the parent atoms are bonded in the sample. Again, these shifts can be identified using online reference materials. Armed with this knowledge, and a general understanding of the context in which the sample was taken, it will finally be possible to work out the surface composition.

Electrons are strongly scattered by matter, and undergo more scattering if they originate from deeper in a sample. This means there is a limit to how deep within a sample the photoelectrons can come from, and is the reason why XPS is such a surface-sensitive technique. Basic physics shows that about 65% of photoelectrons emitted perpendicular to a sample's surface originate at a depth less than their 'attenuation length' (proportional to the square root of the electron energy), λ, which is typically a few nanometers. About 95% of photoelectrons originate within 3λ.

The characteristic rising shape of an XPS survey spectrum, as seen in Figure 3, is a consequence of this scattering process. Photoelectrons that lose kinetic energy become part of the inelastically scattered background signal, which explains why the rising steps occur at the high binding energy (low kinetic energy) side of each peak. The shape of the background signal can reveal information too, such as how close a particular element is to the surface.

The maximum depth of origin is even less for photoelectrons leaving at an angle to the surface because they have had to travel farther through the sample to cover the same vertical distance. The more acute the angle, the less the maximum depth of origin. This trait is exploited in angle-resolved XPS (ARXPS), one of XPS's specialist implementations, which involves collecting photoelectrons at different emission angles to see how their number varies, as the photoelectrons emitted by components at different depths will be attenuated to different degrees. It is particularly useful to perform ARXPS depth profiles of very thin films (up to the information depth of XPS), as the technique is non-destructive.

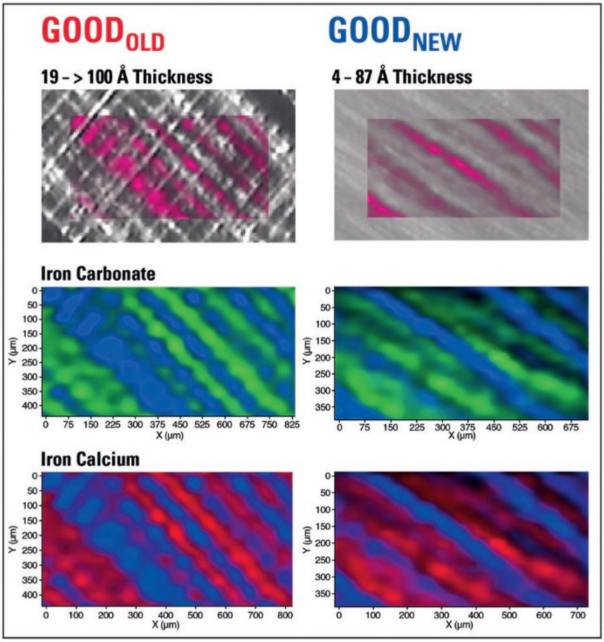
If sample destruction is not an issue, a depth profile can be obtained more conventionally by using the ion gun that is usually present alongside the sample stage in the vacuum chamber. Once an XPS spectrum of the surface of a sample has been taken, the ion gun scans a beam of (usually argon) ions across the sample in a raster pattern to etch away a few layers of atoms, after which another XPS spectrum is taken. Repeating the process again and again, the XPS system builds up a depth profile of the sample's composition – though obviously the sample is gradually destroyed in the process.

One other powerful implementation of XPS, and one that is gaining in popularity, is XPS imaging and mapping. In mapping, a two-dimensional series of XPS snapshots is taken across and down a sample, with each 'pixel' representing the size of the smallest analysis area. Depending on the surface being mapped and the feature size, this area can vary from a few hundred microns to less than 20µm.

XPS imaging requires more sophisticated instrumentation, such as the Thermo Scientific™ ESCALAB™ Xi$^+$, which contains additional lenses inside the spectrometer and a two-dimensional detector. The lenses acquire photoelectrons from an entire sample simultaneously and transmit them around the hemispherical sector analyzer in such a way that their original spatial distribution – that is, their two-dimensional position on the sample – is retained. Unlike XPS mapping, XPS imaging cannot acquire data for more than one energy level in each cycle, but it does have the advantage of being fast and high resolution – to less than 3µm.

CASE STUDY 1. The right layers to wear

Tribology is the area of science that explores friction between surfaces, so it is no surprise that it can make good use of XPS's surface specificity. Such was the case in a study of three steel samples that had been treated with a wear-resistant coating known as ZDDP (zinc dialkyldiphosphonate). One of the samples, 'GOOD_{OLD}*', had already been subject to much surface movement and was still performing well in friction tests; the second sample, '*GOOD_{NEW}*', was a new sample also performing well; while a third sample, '*BAD_{NEW}*', was a new sample performing poorly. Initial survey scans showed the*



XPS maps of the GOOD_{OLD} and GOOD_{NEW} samples showing the thickness of the calcium carbonate layer and its location.
Reproduced with permission from Thermo Fisher Scientific

presence of calcium in only the $GOOD_{OLD}$ *and* $GOOD_{NEW}$ *samples, and carbon in all three.*

The experimenters, from the Austrian Center of Competence for Tribology, decided to study the carbon in more detail with some high-resolution scans, and found that although photoelectron peaks indicative of C–C, C–O and C=0 bonds were present in all the samples, only the good samples contained carbonate (CO_3^{2-}) *peaks. Subsequent XPS imaging of these samples revealed alternating tracks of high and low carbonate concentrations correlated with high and low calcium concentrations, indicating that in these tracks a common compound – calcium carbonate – was forming. These tracks were slightly thicker in the* $GOOD_{NEW}$ *than the* $GOOD_{OLD}$ *sample.*

What was going on? The tribologists knew that ZDDP is mixed with detergents containing calcium. They concluded that these detergents, when mixed in the right quantities with ZDDP, produce calcium carbonate under tribological load – and that this calcium carbonate is actually the substance responsible for the friction stability in the two good samples. The answer for future steel coatings, then, was to make sure that the detergent-to-ZDDP ratio was correct.

PROBLEMS AND SOLUTIONS

The photoelectric effect is not the only process by which electrons can be emitted from a sample during an XPS analysis. Once an X-ray has knocked an electron free from an atom, an electron from a higher energy level may fall down into the newly vacated spot, releasing some potential energy that can be transferred to yet another electron, ejecting it from the atom. This process was discovered by Austrian physicist Lise Meitner in 1922, although it came to be known after a later investigator, French physicist Pierre Auger.

Auger peaks will often appear in XPS spectra, as is seen in Figure 3, and indeed they provide the basis for a complementary analysis technique, Auger electron spectroscopy (AES), which can be performed with XPS instrumentation. A detailed discussion of AES is beyond the scope of this EKB, but it is important with XPS to be able to distinguish peaks generated by the two emission processes.

Because Auger emission is a secondary emission process, it is not dependent on the energy of the incident X-ray photon. That is critical to its identification, because if the X-ray energy changes, the kinetic energy of only the photoelectrons will change. This means that on a binding-energy scale, which takes photon energy into account, the photoelectron peaks will stay put while the Auger peaks will shift left or right.

In order to differentiate between photoelectron and Auger peaks in this way, older XPS systems often had two X-ray anodes (usually aluminium and magnesium) built into the same source. In modern instruments, though, the standard use of monochromated sources makes it quite easy to isolate photoelectron and Auger peaks from each other. Auger peaks are more often helpful than troublesome, and can yield important additional chemical information that cannot be obtained from the photoelectron peaks alone.

One aspect of XPS that can sometimes be problematic is the nature of the sample itself. Samples that are porous, or samples that contain volatile components, such as solvents, often fare badly in a vacuum, and so may not be suitable for XPS analysis.

The electrical conductivity of samples is also an issue, albeit one that can be simply remedied. If a sample is insulating, then the sustained emission of photoelectrons will gradually leave a positive charge on its surface (in conducting materials, electrons will rise through the sample to replace the photoelectrons lost at the surface). This positive charge attracts the emitted photoelectrons, reducing their kinetic energy and distorting the shape of the spectrum, making analysis impossible. To combat this, an electron ‘flood gun’ situated next to the sample provides a source of low-energy (five electronvolts or less) electrons. The energy is sufficiently low to avoid damaging the surface and interfering with the XPS spectra, but enough to neutralize the positive charge.

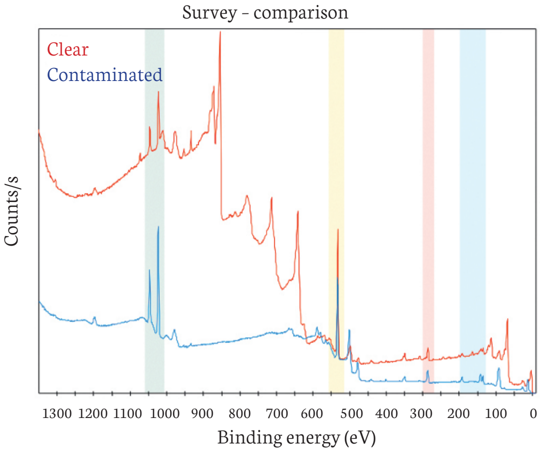
Finally, as XPS is by definition a surface analysis technique, it is inherently susceptible to contamination. Fortunately, this is another problem that can be easily solved: the same ion gun that is used to perform depth profiling can also remove the top (contaminated) layer of a sample prior to analysis, usually without affecting the sample’s composition.

CASE STUDY 2: A faulty heating sensor

The photo below shows a temperature sensor taken from a domestic water boiler. This was the last in a series of identical replacements that had proved faulty; on close inspection, the normal metallic surface had been buried under a white opaque substance. The heating engineer suggested that the substance could be calcium carbonate from hard water, but the boiler was situated in a very soft water area. What, then, was causing the white deposit?

To find out, the boiler company decided to investigate by performing XPS analyses of both the clear part of the temperature sensor and the white deposit. The initial survey spectrum contained an obfuscating amount of carbon, probably caused by the component's general uncleanliness from repeated handling, so the first step involved using the ion gun to gently remove this carbon layer. The subsequent survey spectra were then processed by the control system to identify the main peaks.

The main differences in the contaminated area (shown in the far right column of the accompanying table) compared with the clear area (second to right column) were the much greater presence of zinc and phosphorous photoelectrons, and to a lesser extent, carbon and oxygen photoelectrons. To find out more, the next step involved performing higher resolution scans of the binding-energy ranges for these elements. Online resources such as Thermo Fisher's XPS Knowledge Base helped to reveal that the zinc was present in a 2+ oxidation state



Name	Peak binding energy (eV)	Atomic %	Atomic %
S 2p	163.6	1.3	0.0
P 2p	134.8	-	8.1
P 2s	191.6	2.5	-
Cl 2p	200.5	0.3	0.0
Ar 2p	243.7	0.6	0.0
C 1s	285.4	12.3	19.7
K 2p	294.6	0.3	0.0
Ca 2p3	348.0	0.9	1.8
N 1s	399.7	0.7	1.9
O 1s	532.0	46.1	50.5
Ni 2p	854.3	27.8	0.0
Cu 2p	933.4	1.3	0.3
Zn 2p	1023.0	3.7	17.6
Na 1s	1073.2	1.2	0.0
Mg 1s	1305.0	0.9	0.0

XPS spectrum of temperature sensor (left) and analysis (right) of the elements

and the phosphorus was present in a 5+ oxidation state. This suggested that the culprit was $Zn_3(PO_4)_2$*, a type of corrosion inhibitor that is not stable under a boiler's normal operating conditions. The boiler manufacturer did not use this inhibitor, proving that the temperature sensor was produced by a third party and was not in fact suitable for use in the boiler. The answer, then, was to repair the boiler using the correct part.*

WHAT'S NEXT?

XPS systems are still gaining in sophistication. Perhaps the biggest overarching improvements are being delivered in computer control systems, with modern ones able to manipulate samples automatically, acquire and process data, and display reports, all in one package.

Indeed, modern spectrometers have made the process of performing XPS more straightforward than ever: energy levels are automatically identified; overlapping peaks are automatically resolved; reference materials are readily accessible; and depth profiles are easily built up.

XPS is seeing innovation in other aspects of instrumentation too. One recent improvement has been the development of the cluster ion source, which fires a heavy, weakly-bound cluster of gaseous ions at low velocity.

Unlike a regular monatomic ion source, which fires a stream of focused ions at a surface, the cluster ion source is able to spread the energy of the ions over the sample’s surface – still removing material, but in a much gentler manner. That is of huge benefit when conducting XPS analyses of softer materials, such as the polymers used in food packaging or organic electronics.

Perhaps the biggest recent development with XPS has not been in the tool itself, but in the subjects it is being used to study. A good example is graphene, a two-dimensional lattice of carbon atoms bonded in chicken-wire fashion that was first isolated in 2004 by physicists Andre Geim and Konstantin Novoselov at the University of Manchester in the UK. Graphene – along with other recently isolated two-dimensional materials such as borophene (which is based on boron) – is proving very attractive to scientists because of its superlative electrical and mechanical properties, while its atom-thick nature makes it an ideal candidate for XPS.

Using XPS, scientists have been able to check whether new methods to fabricate graphene and other two-dimensional materials are working properly, and how the materials bond to neighboring surfaces.

In 2014, for example, materials scientist Kian Ping Loh at the National University of Singapore and colleagues invented a new way to grow graphene on wafers made of silicon and silicon dioxide, which have the advantage of being compatible with existing microelectronics.

Normal growth of graphene on these wafers requires the silicon dioxide to be coated with a copper catalyst that stimulates the growth of graphene when a carbon-containing gas such as methane flows over the top, a process known as chemical vapor deposition. After graphene growth, the copper must be etched away, but this often leads the wafer to break free, leaving the graphene with defects.

Loh and colleagues had the idea of treating the wafer prior to graphene growth with a nitrogen plasma, which would form bubbles during the etching process. These bubbles would stick to the graphene while the copper was etched away, preventing the graphene and silicon/silicon dioxide wafer from separating – much like the air bubbles that allow beetles and amphibians to stick to leaves and other small objects underwater.

To test whether their method worked, Loh and colleagues performed XPS on the etched wafer and found that the nitrogen remained only in the silicon, and not the graphene. Furthermore, there was no evidence of any copper, suggesting their novel process didn't have any negative side-effects (Gao L, ***et al.*** 2014).

This kind of study shows that, even though XPS is now a mature analytical technique, its unique capabilities ensure that it remains at the forefront of scientific research.

CASE STUDY 3: Analyzing a single strand of hair

The potential of modern gas cluster sources is seen in an XPS depth profile of a single hair fiber, a biological sample that would easily be damaged by a regular monatomic ion source. Human hair is mostly made of keratin – a polymer chain of amino acids – and is coated with a layer of fatty acids that repel water and, ultimately, protect the hair fiber. The keratin bonds to the fatty acids via sulfur-containing cysteine groups.

An initial XPS survey scan showed that the hair sample comprised mainly carbon but also contained a substantial amount of silicon, an ingredient in silicone-based products designed to make hair appear sleek and shiny. A higher resolution scan of the carbon-1s region revealed that the carbon bonds were mostly C–C and O–C=O, which are found in keratin and fatty acids. A similar high-resolution scan of the silicon region pointed to organically bonded silicon, rather than SiO_2*.*

After the fatty layer was removed using the gas cluster source, the relative concentrations of the carbon bonds remained the same, indicating that the cleaning had not damaged the hair's composition. That meant it was safe to proceed further, so the gas cluster was used to remove successive layers of the sample to investigate how sulfonate (SO_3^-) *and sulfide* (S_2^-) *chemistry altered with depth. Sulfonate is associated with the cysteine link to the fatty acids, therefore it was no surprise to find more evidence of this species in the upper layers of the sample. Likewise, sulfide* *species form the links between keratin chains, therefore it was no surprise to find more evidence of these lower down.*

In sum, this analysis revealed nothing unexpected – but it did demonstrate that ion cluster sources are effective for the depth profiling of samples as delicate as a single human hair.

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MICROSCOPY AND ANALYSIS

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