



KeyWords

XPS, Polymers, Measurements,
PTFE, PET, Toy Brick, Charge Compensation

Investigation of Polymers and Plastics with EnviroESCA

This application note describes how EnviroESCA can be used to analyze the surface of polymers and bulk insulating material. EnviroESCA's ability to perform X-Ray Photoelectron Spectroscopy (XPS) at non vacuum conditions shows its main advantage when being applied to insulating material. Specimens that tend to charge up under vacuum conditions and need to be extensively charge compensated with expensive low energy electron and low energy ion sources can be measured with ease and without the problem of overcompensation.

Motivation

Polymers and plastics are used in many fields such as food grade packaging and medical technology. Their composition is especially important when the polymers get in direct contact with food, as a packaging material or humans, for example kids toys. Therefore it is essential to know the chemical composition at the surface of these materials, how they react to different atmospheres and chemicals in gaseous and liquid form.

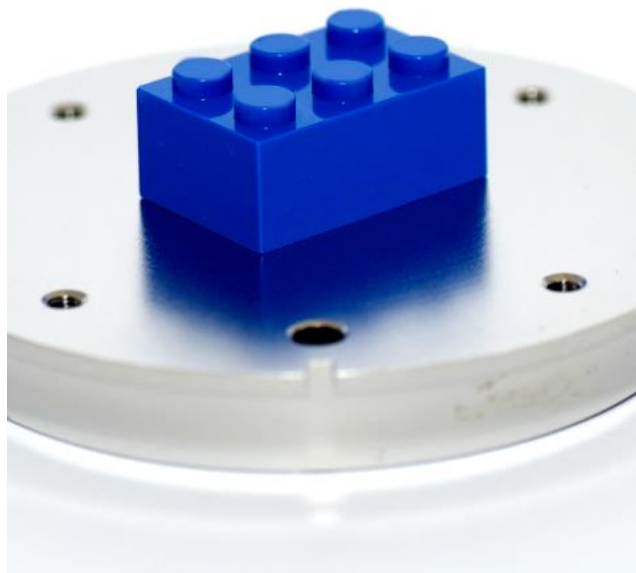


Fig. 1 A plastic toy brick, an example for a bulk polymer

Method

EnviroESCA utilizes X-Ray Photoelectron Spectroscopy (XPS) as its main analytical technique.

Hereby an electron beam is generated inside the X-Ray Source and focused onto an X-Ray Anode made of Aluminum. The deceleration of the electrons on the anode leads to the production of X-Rays. This X-Ray beam is monochromated and focused onto the Sample.

Due to the interaction between the photons and the atoms and molecules on the surface electrons with specific kinetic energy are released. Thereby only electrons from atoms up to a depth of approx. 10nm are able to leave the surface. These electrons travel through the lens system of the Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The electron paths end at an electron sensitive detector where the electrons are amplified and measured as an intensity in counts / second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum. From these spectra the amount of atomic material on the surface can be calculated.

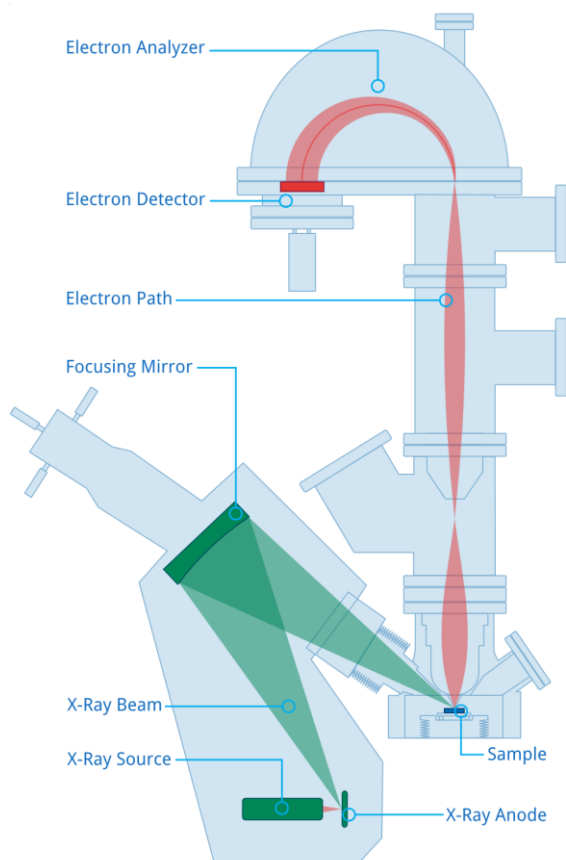


Fig. 2 XPS with EnviroESCA

Experimental Section

The three polymer samples used in this study are the two quasi standards to characterize the ability of any XPS system to measure useful data on polymer surfaces, Polytetrafluoroethylene (PTFE) and Polyethylene terephthalate (PET). For the third sample we have chosen a well known toy which can be found nearly in any household with children, a plastic toy brick.

The foils were cut in pieces and mounted to the sample plate with a carbon tape. The toy brick was loosely positioned to the plate without any means of gluing. All three samples were not shielded, coated or electrically contacted in any way.

After introducing the sample plates into the SampleEnvironment of EnviroESCA the automated pressure controlled pumping system was started with a setpoint below 1E-5 mbar. After taking spectra at these vacuum conditions the mass flow controlled gas inlet system

was used to introduce ambient air into the analysis region. The pressure controller was set to different setpoints between 0.5 and 5 mbar and spectra were recorded.

Results

In the following we are presenting unmodified raw data taken with EnviroESCA. The data was not smoothed or shifted on the energy scale.

1. Polytetrafluoroethylene (PTFE)

PTFE is a quasi-standard sample in benchmarking XPS systems as it charges up pretty quickly in vacuum conditions when it is illuminated with X-rays.

Figure 3 shows a survey scan taken with EnviroESCA right after pump down of the SampleEnvironment to a pressure lower than 1E-5 mbar. The survey clearly shows peaks of the Auger and the 1s and 2s core level Peaks of Fluor and the 1s peak of Carbon. Comparing the position of the F 1s peak (765 eV) to the literature value (689.67 eV [1]) leads to a charge up of the surface in vacuum of about 75 eV after about 10 min of illumination.

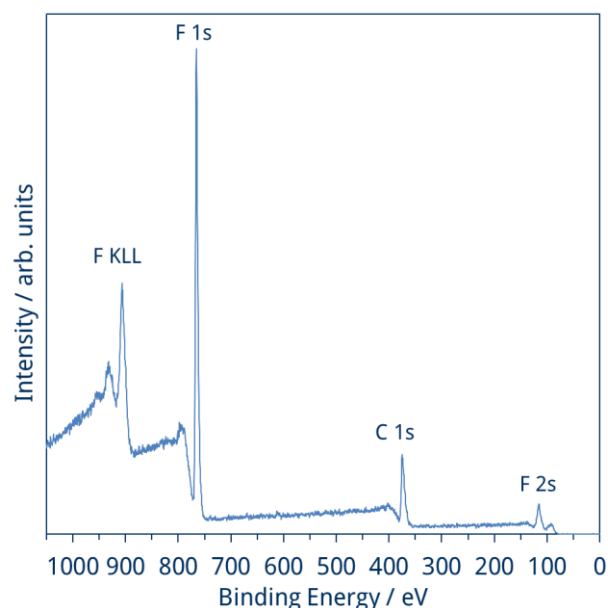


Fig. 3 Survey spectrum of PTFE ($p < 1E-5$ mbar)

Continuously measuring of the F 1s region leads to the spectra shown in figure 4. The Fluor peak continuously shifts to higher binding energies the longer the surface is illuminated with X-rays. The samples surfaces gets positively charged with every escaping electron.

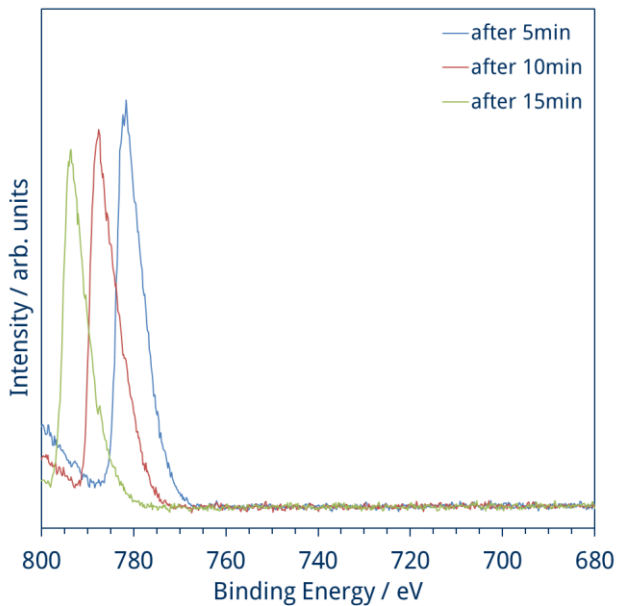


Fig. 4 Detail spectra of the F 1s region

As EnviroESCA is capable of performing XPS measurements in near ambient pressure conditions ambient air was dosed into the system until different pressures where stabilized around the sample.

Figure 5 shows the influence of the gas pressure onto the position and the shape of the F 1s peak.

The first thing that catches the eye is that the peak shifts significantly to lower binding energies with higher pressure. Also the peak shape changes dramatically as the pressure increases.

Figure 6 displays the pressure dependence of the intensity and the full width at half maximum (FWHM) of the F 1s peak.

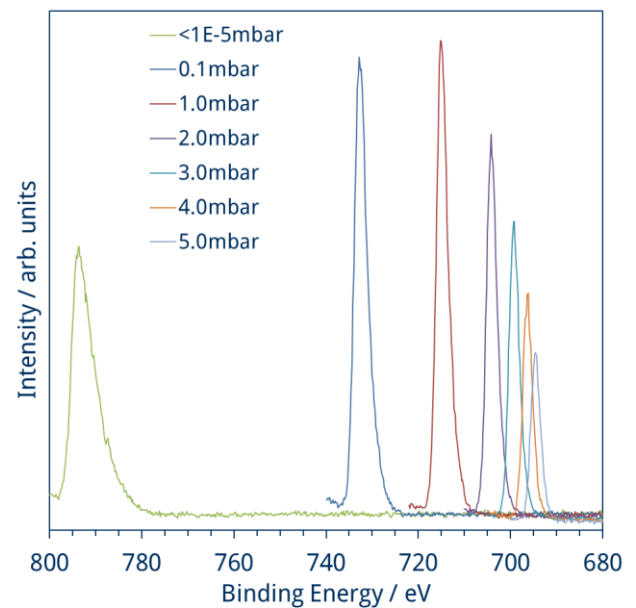


Fig. 5 Position and shape dependence of the F 1s peak on the surrounding pressure

The decrease of the signal intensity at pressures higher than 1 mbar is due to the absorption of the photoelectrons in the gas atmosphere between the sample surface and the analyzer entrance nozzle.

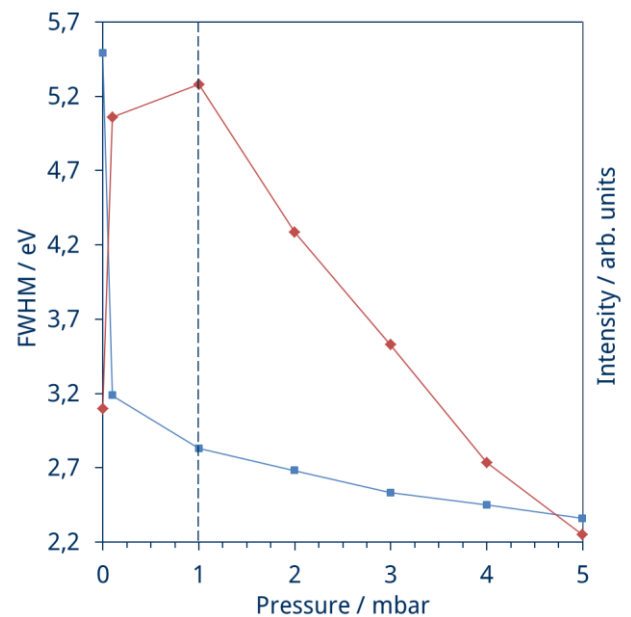


Fig. 6 Pressure dependence of the FWHM (blue line) and the intensity (red line) of the F 1s peak

2. Polyethylene terephthalate (PET)

The second sample under investigation is a piece of a PET foil. Another quasi-standard sample for XPS systems. The survey spectrum taken at a base pressure lower than $5E-5$ mbar of this sample is shown in figure 7.

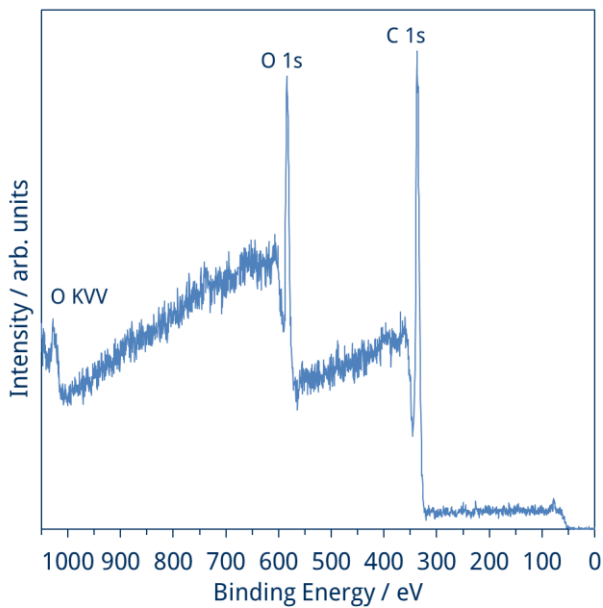


Fig. 7 Survey spectrum of PET ($p < 5E-5$ mbar)

The three most prominent features are the Oxygen KVV Auger, the Oxygen 1s core level and the Carbon 1s core level peaks. Like for the PTFE the shift of the whole spectrum to higher binding energies is evident when comparing the peak position of the C 1s (336 eV) to the literature value (284.70 eV [1]). The surface of the specimen gets positively charged by the escaping electrons.

When a gas atmosphere is surrounding the sample the peak position shifts to lower binding energies dependent on the pressure at the analysis region (See fig. 8 for details). A pressure of 1 mbar ambient air is enough to shift the C 1s by about 35 eV and reveals the different components corresponding to different bound Carbon atoms inside the molecule.

When having a closer look onto the C 1s a scan with higher resolution clearly reveals three different components in the C 1s as can be seen in the spectrum

displayed in figure 9. The spectrum of figure 9 was measured with a step width of 0.1eV in 4 minutes and 45 seconds.

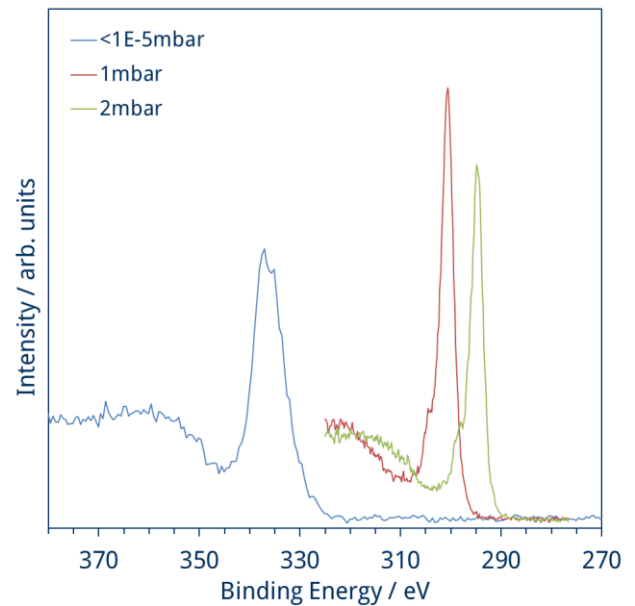


Fig. 8 Detail spectra of the C1s region

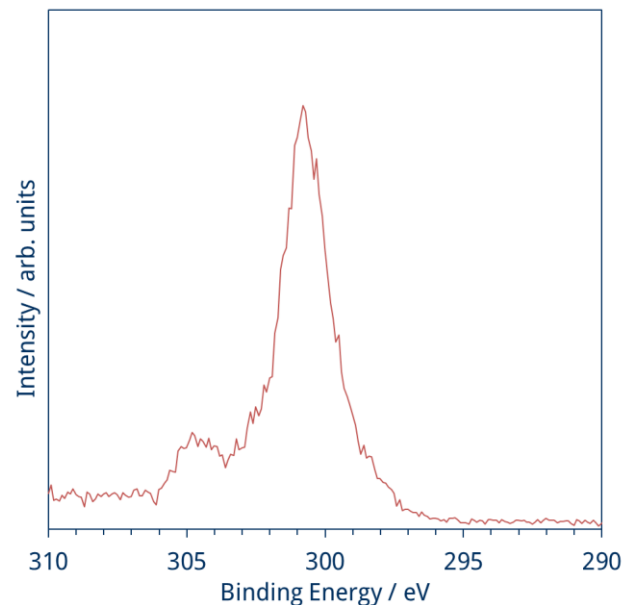


Fig. 9 Detail of the C1s region in higher resolution

3. Plastic toy brick

The plastic toy brick used in this analysis is an example for a real world polymer sample. With a dimension of about 16x24x11mm this specimens fits easily on the EnviroESCA sample plate which can accept samples up to 120mm diameter (60mm diameter addressable).

Figure 10 shows the XPS survey spectrum of this specimen. The spectrum has no clear structure and no peaks are visible.

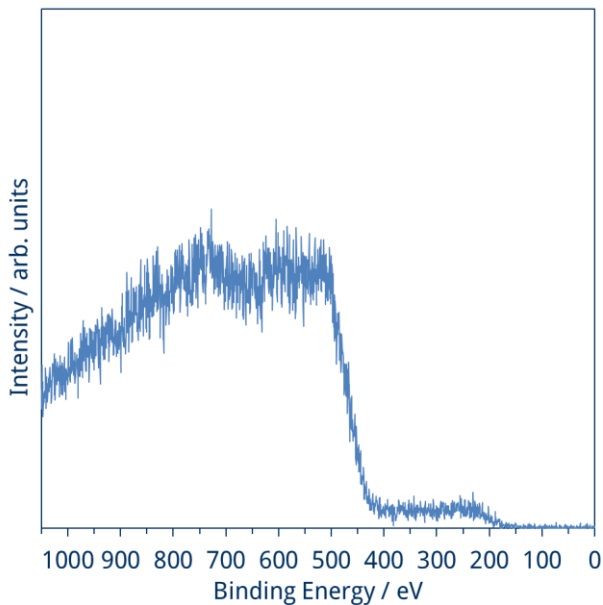


Fig. 10 Survey XPS spectrum recorded at $p < 1E-5$ mbar

When applying ambient air to the sample and measuring the Carbon 1s and Oxygen 1s region peaks become clearly visible. Figure 10 presents a rough scan over the O 1s region of the spectrum whereas figure 11 shows the more intense C 1s peak (measured with a step width of 0.1 eV in 4 minutes and 21 seconds).

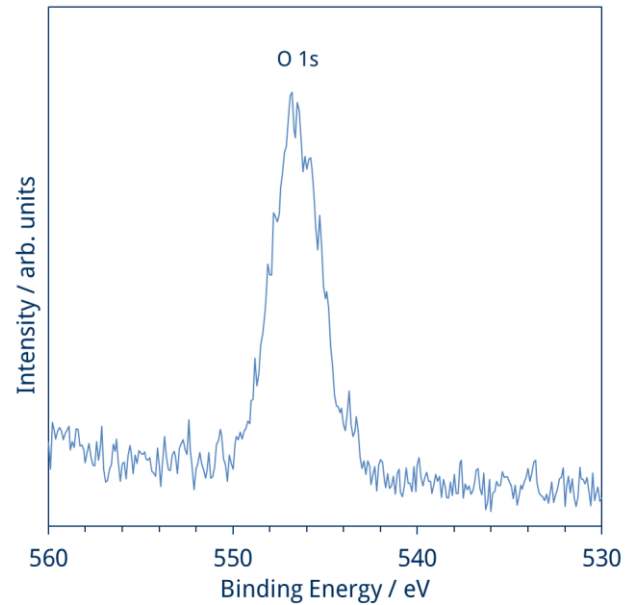


Fig. 11 Detail spectrum of the O 1s region ($p=1$ mbar)

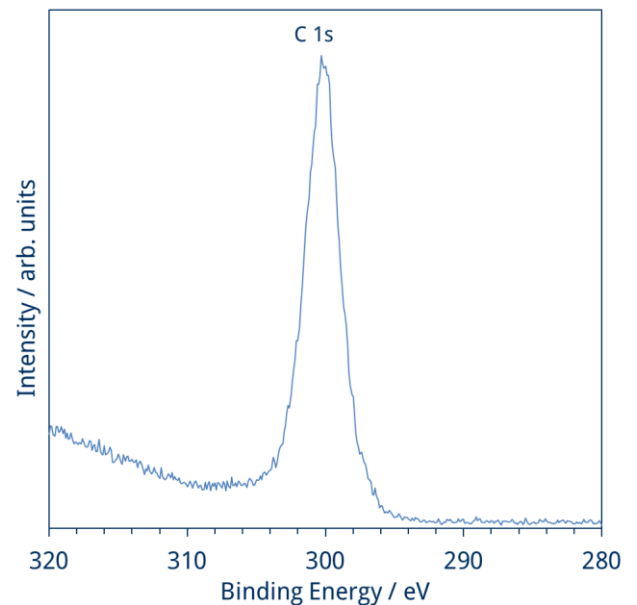


Fig. 12 Detail spectrum of the C 1s region ($p=1$ mbar)

Discussion

All three polymer samples show the well-known charge up effects when measured in low vacuum conditions. The complete spectrum gets shifted to higher binding energies. The peaks get broad and loose intensity (PTFE and PET) or vanish completely (toy brick).

When a sample atmosphere is applied, ambient air in this study, but also other gases like Nitrogen and Argon have the similar effect, the spectrum shifts towards lower binding energies and the peaks get narrower. This is due to a charge compensation effect that is related to the surrounding atmosphere of the specimens.

To use a soft or even hard X-ray radiation to reduce the surface charging or static of semi-finished parts is a new but rather common idea in manufacturing. Several manufacturers offer soft and hard X-ray sources to be used at production lines.

These static removers are based on the same working principle as the charge compensation in EnviroESCA, photoionization. The impinging X-rays pass a gas atmosphere on their way to the sample surface. The photons interact with the molecules of the gas atmosphere and ionize many of them generating free charges, like a cloud, around the sample, consisting of electrons and ions. If now an electron is escaping the specimens surface and being analyzed by EnviroESCA the hole can be filled by one of the electrons from the gas phase, thereby discharging the samples surface. An effect that could be named Environmental Charge Compensation in Near-Ambient Pressure XPS. Figure 13 shows an illustration of the effect.

A big advantage of this type of compensation is that it cannot overcompensate the sample as it could easily occur with classical compensation methods like low energy electron or low energy ion sources.

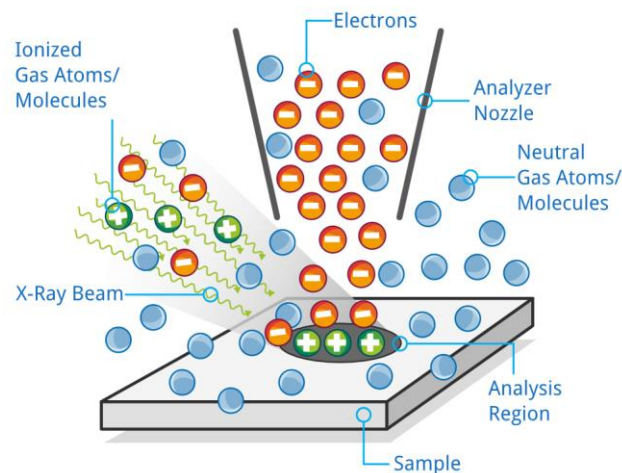


Fig. 13 Environmental Charge Compensation

The number of free charges depend on different parameters so an experimenter is able to tune and optimize the compensation effect. These parameters include the number of photons (the X-ray power), the density of the gas around the sample (gas pressure) and also the type of gas around the sample (Argon or Nitrogen could be added for that purpose).

Conclusion

EnviroESCA's ability to work in pressures much higher than ultra-high vacuum offers new possibilities to solve well known experimental challenges. Surface charging of specimens is a problem in all XPS systems but with EnviroESCA a new and much easier to use method of charge compensation is available for the user.

This, for UHV scientist, new approach but for the industrial users pretty common technique to handle static can now be applied to all XPS systems which are able to handle Near-Ambient Pressure sample environments.

[1] G. Beamson and D. Briggs, *High resolution XPS of organic polymers*, John Wiley & Sons Ltd, West Sussex, England, 1992, ISBN 0471935921

Related Applications

Here we present some related application of EnviroESCA you might be also interested in.

For more information about other fields of application feel free to visit www.EnviroESCA.com or contact us under info@specs.com.

Liquids



Water and aqueous reagents are essential in any biological process or system. But apart from a few special low vapor-pressure cases, liquids have not been accessible to any technique requiring UHV conditions. EnviroESCA opens up this exciting field of applications.

Gaseous and Liquid Environments



The interaction of gases and liquids with surfaces plays a key role in many different fields ranging from biological and catalytic systems to construction materials. EnviroESCA offers the possibility of investigating surfaces in contact with gases and liquids, such as salt water, acidic rain, wastewater, or gaseous atmospheres with high humidity.

Fabrics



The performance of highly sophisticated fabrics is governed by the interaction of the interface with the surrounding atmosphere. By studying the surface properties of the fibers in wet air, deeper insights into relevant processes under more realistic conditions can be gained.

Energy Materials and Devices



Batteries and fuel cells are devices that use chemical reactions to store and convert energy. Fuel cells for instance consume fuel and oxidants during operation so that their investigation is not

possible in traditional XPS spectrometers. With EnviroESCA the fundamental steps in such devices can be investigated in operando.

Medical and Biomaterials



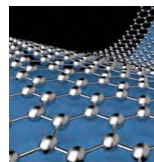
Medical implants are devices or tissues that are placed inside or on the surface of the body. A widely used material for surgical implants is Titanium. It is important to be able to analyze the Ti surface to achieve optimized interactions with the surrounding tissue.

Coatings and Thin Films



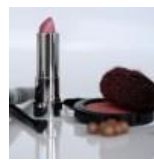
Coatings and platings are widely used in optics manufacturing and metal refinement as they optimize the surface properties of materials to make them harder, stronger and more durable. The coatings are thin films which interact with the substrate on one side and the gaseous or liquid environment on the other.

Nanomaterials



Nanomaterials have attracted a lot of attention from research and industry in the past decades. Questions about the influence of the surrounding atmosphere on the chemical composition and potential core-shell structure are ideally addressed by EnviroESCA.

Cosmetics



Cosmetics in contact with skin and hair interact on the molecular level. Therefore tuning and optimization of the interface plays a key role for the character of the interaction between the ingredients and the tissue.

Technical Specifications

EnviroESCA	
Electron Spectrometer	<ul style="list-style-type: none"> Hemispherical electron analyzer with 150 mm mean radius Differentially pumped lens system Delayline detector with up to 400 channels
X-ray Source	<ul style="list-style-type: none"> Al K_α micro-focused monochromator Rowland circle diameter of 600 mm Spot sizes of 200 μm-1 mm optimized to analysis area
Charge Neutralization	<ul style="list-style-type: none"> System immanent charge compensation by X-ray photoionization
Ion Source (optional)	<ul style="list-style-type: none"> Scannable small spot ion source (200 eV-5 keV) or gas cluster ion source
Pumping System	<ul style="list-style-type: none"> Turbomolecular pumps Oil-free backing pumps
Pressure Range	<ul style="list-style-type: none"> Defined by analyzer aperture (up to 100 mbar with an aperture of 300 μm; other aperture sizes on request)
Gas Dosing	<ul style="list-style-type: none"> Two separated mass flow controlled gas dosers at analysis position
Cameras	<ul style="list-style-type: none"> 3 digital microscopes for sample navigation and documentation
Automation and Software	<ul style="list-style-type: none"> Fully automated vacuum and gas dosing system Advanced software package



SampleEnvironment (standard, others on request)	
Samples Stage	<ul style="list-style-type: none"> High precision 3-axis stage
Sample Size	<ul style="list-style-type: none"> Up to 120 mm in diameter and 40 mm in height 50 mm inner diameter addressable
Gas Dosing	<ul style="list-style-type: none"> Mass flow controlled process and purge gas
Cleaning	<ul style="list-style-type: none"> Downstream RF plasma cleaner
Camera	<ul style="list-style-type: none"> Digital microscope for sample observation and documentation

