Application Note #000386

KeyWords
XPS, Human Hair, Cosmetic Science, Forensic Science, Measurements, Surface Analysis

EnviroESCA and NAP-XPS in the field of Cosmetic Science

This application note presents the application of EnviroESCA to the field of Cosmetic Sciences and Forensic Sciences. Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) measurements on human hair treated with different personal hair care products.

Motivation

The structure and composition of the outermost surfaces of human hair fibers is of major importance for the interaction with ingredients of hair care products. On the molecular level the surface termination can help to tune and optimize the shielding of the hair from harmful environmental conditions and to optimize the cuticular uptake of temporary color or other personal hair care products.

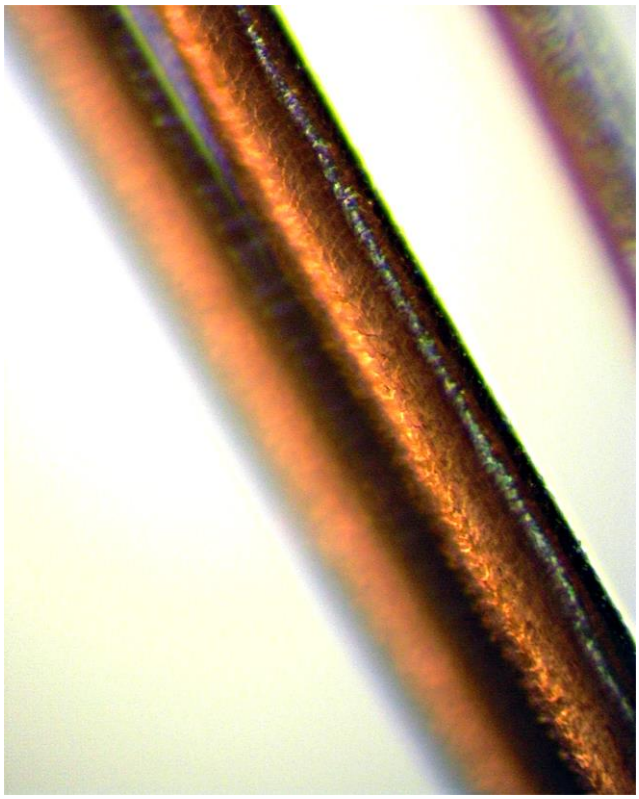


Fig. 1 Close up view of a hair fibre used in this study.

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.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with specific kinetic energy determined by their binding energy and the photon energy of the X-rays. Thereby only electrons from atoms up to a depth of approx. 10nm are able to leave the surface. These electrons propagate 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 a quantitative analysis of the atomic composition of the sample surface can be done.

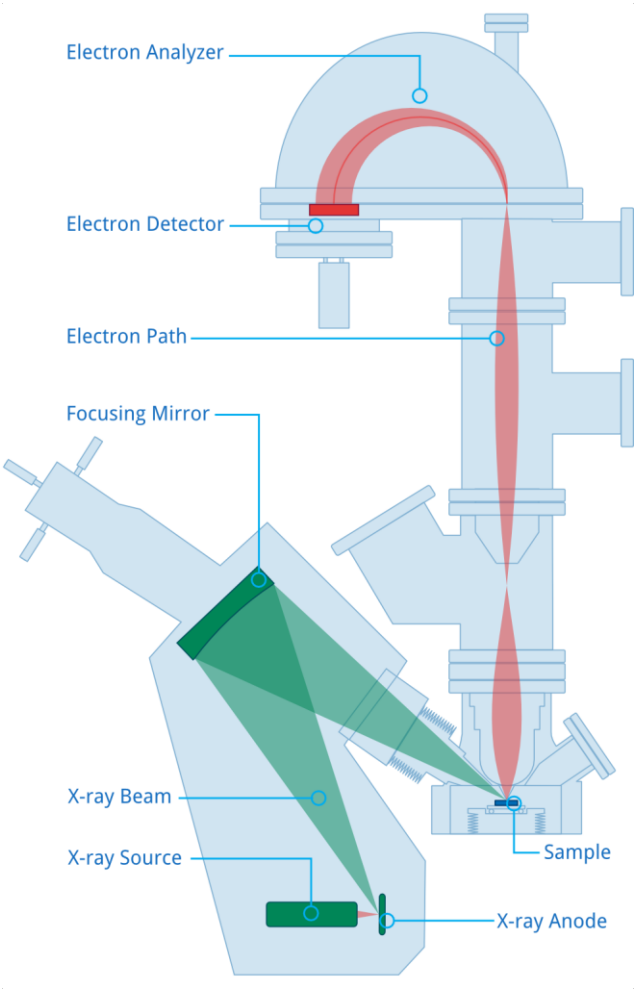


Fig. 2 XPS with EnviroESCA

Experimental Section

For this investigation we have chosen three different hair samples. The first one, named thereafter blank hair, was not treated with any hair care products and can therefore be seen as the reference sample. The second sample was treated with a temporary color and a commercial deep conditioner, thereafter named colored hair. The third sample was bleached and treated with a different deep conditioner, thereafter named bleached hair.

The samples were collected from the three subjects and mounted to the sample plate with carbon tape. This mounting technique leaves an area of about 5x5 mm accessible for the X-rays and the analyzer nozzle.

Dust and particles where removed by blowing gaseous nitrogen on the mounted samples.

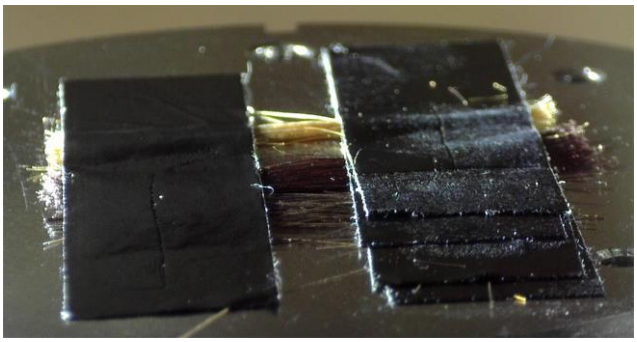


Fig. 3 The three test samples mounted on the sample plate

Figure 1 shows a closer look onto the colored sample with the EnviroESCA SampleExplorer. The visible area in the photograph is about 300x400 µm and the high resolution through-the-lens camera that mimics the view of the analyzer allows a view on the outer structure of the sample.

A human hair fiber consist of three different components the medulla as the inner core, surrounded by the cortex, a well-structured layer and the cuticle, the outermost part consisting of several layers of cells arranged like roofing shingles (compare fig. 4 and 5, both photos taken with the EnviroESCA SampleExplorer).

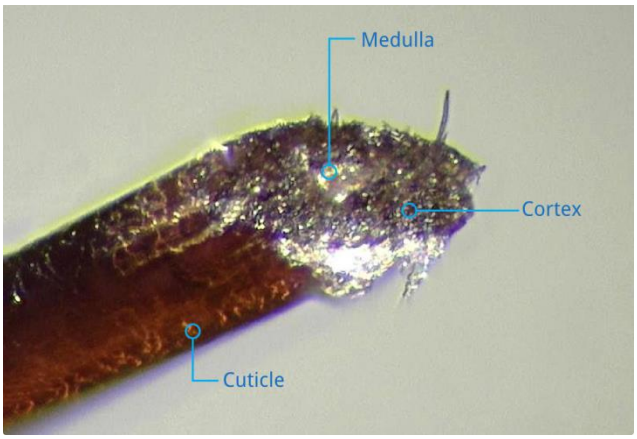


Fig. 4 Cross sectional view of a hair fiber (focus stacked image of hair sample 2)

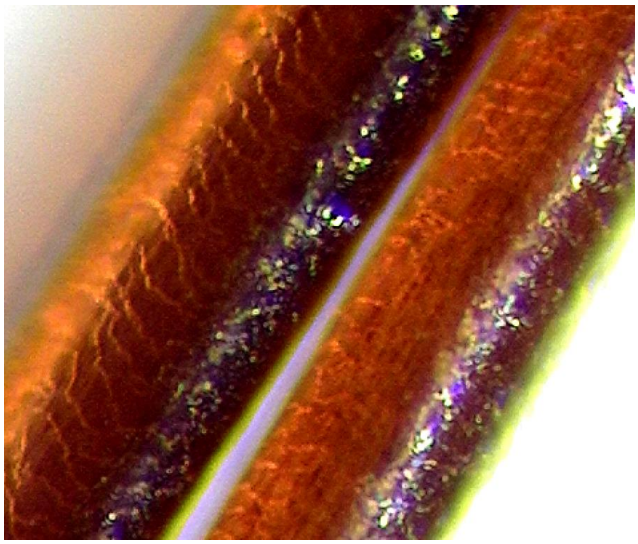


Fig. 5 High resolution close up view at the cuticle (hair sample 2)

On the molecular level the hair fiber is made up of proteins, therefore the XPS spectra should show a high amount of Oxygen, Nitrogen, Carbon and Sulfur as the ingredients of the amino acids.

The investigation of a whole bunch of hair fibers is pretty difficult in classical XPS systems as the specimens will outgas and tend to charge up under the illumination with X-ray photons due to their insulating nature.

With EnviroESCA experiments on hair fibers are not only possible but also easy to perform. EnviroESCA can work in pressures up to several dozens of mbar, also in water atmosphere, which would allow the investigation of in-situ changes of the surface when offering water or dissolved reagents.

An intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources for charge compensation as in classical XPS systems unnecessary. The gas atmosphere that is surrounding the fibers delivers all the free charges, when illuminated with the soft X-rays, that is needed to compensate for surface charging (see figure 6 for an illustration).

A working pressure of 1 mbar was chosen because the surface of most organic samples is known to charge up in vacuum conditions.

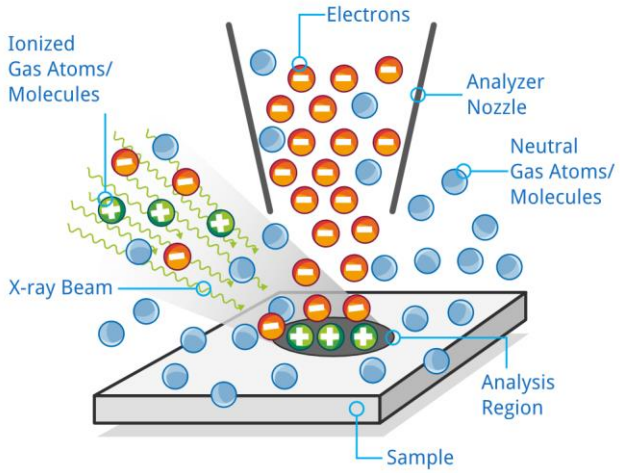


Fig. 6 Environmental Charge Compensation

Results

In the following we are presenting unmodified raw data taken with EnviroESCA. The data was not smoothened. For comparison the spectra where shifted on the energy scale so that the Carbon 1s peak overlap on all survey spectra at 284.5 eV.

1. Hair Sample 1 (blank hair)

Figure 7 shows a photo taken with one of the three digital microscopes at the analysis compartment. It shows the analyzer nozzle hovering above the blank hair fibers. The red dot that can be seen on some fibers originates from a pilot laser that shoots through the lens system of the analyzer and helps to navigate with the sample stage in selecting the analysis area.

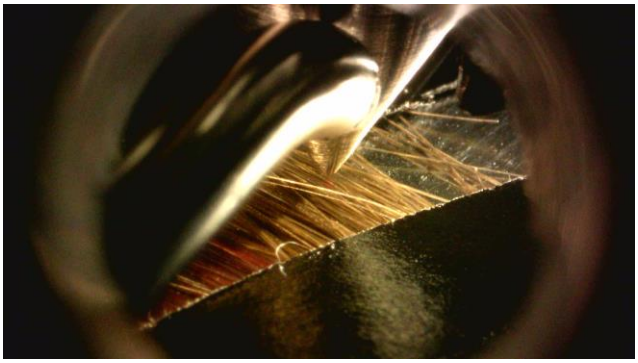


Fig. 7 The first hair sample underneath the analyzer nozzle

The first XPS spectrum that was measured right after pump down to 1 mbar is displayed in figure 8. It was measured with a step width of 1 eV in 21 minutes and 50 seconds. The main peaks can be identified as the KLL Auger and 1s of Oxygen, clearly visible are the Nitrogen 1s and the Carbon 1s but also the Calcium 2p and the 1s and 2p peaks of Sulfur.

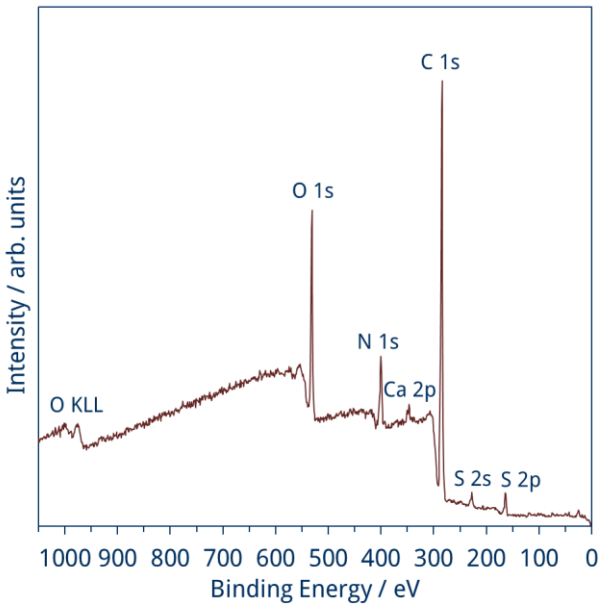


Fig. 8 Survey XPS spectrum measured on blank hair

As this hair sample was not treated in any way but just taken as it is it can be seen as a reference for the following two samples.

A closer look at the Sulfur 2p region (Fig. 9) reveals two separated peaks. The peak at 164 eV can be interpreted as electrons emitted from amino acid molecules containing sulfur like cystine. The peak at higher binding energy (168 eV) is due to oxidation of cystine resulting in the formation of sulfonate groups on the surface of the fibers. The detail spectrum was recorded in about 22 minutes with a step width of 0.1 eV.

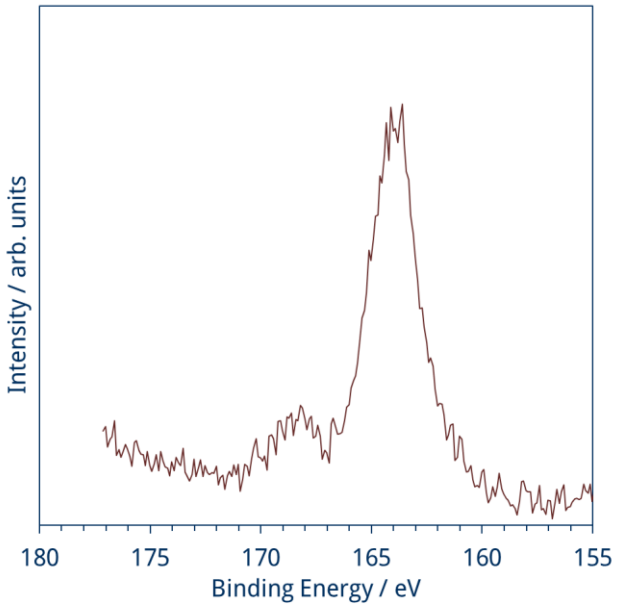


Fig. 9 Detail spectrum of the Sulfur 2p region of the blank hair (see text for interpretation)

2. Hair Sample 2 (colored hair)

Hair fibers that were temporally colored and treated with a deep conditioner have been chosen to become the second sample of this study.

Fig. 10 The analysis position on the second sample

Besides intense 1s peaks of Oxygen, Nitrogen and Carbon the 2s and 2p peaks of Silicon are visible in the spectrum. The peaks of Calcium and Sulfur are less visible and strongly reduced in intensity. The intense silicon peaks result from an organosilicon compound, Dimethicone, which is an ingredient of the deep conditioner the hair was treated with.

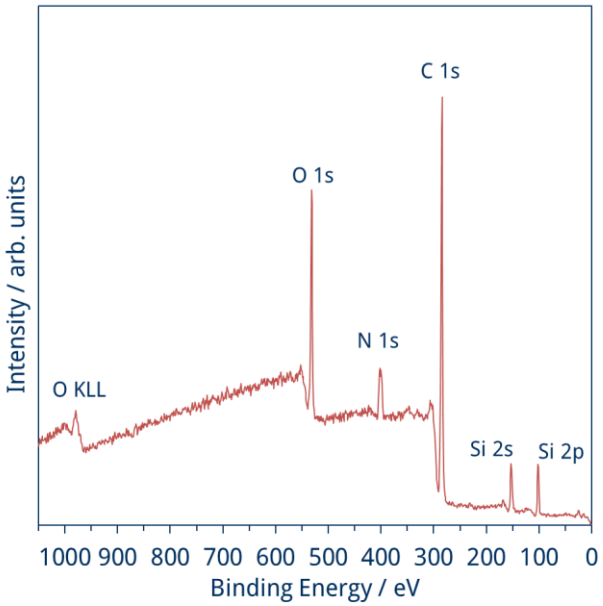


Fig. 11 Survey spectrum recorded on the colored hair sample

3. Hair Sample 3 (bleached hair)

The third hair sample that was investigated in this study is a bunch of bleached hair fibers that were treated with a different deep conditioner before analysis. The following image shows the fibers underneath the analyzer nozzle.

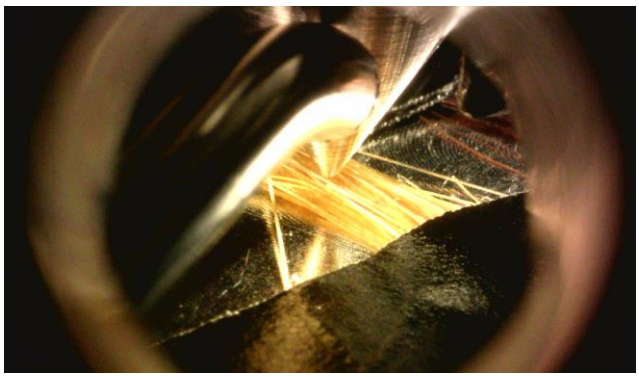


Fig. 12 The third sample underneath the analyzer nozzle

The survey XPS spectrum taken on the bleached hair sample shows higher Silicon and Nitrogen than the other two (please compare with figure 8 and 11). Furthermore the C / O ratio has changed showing less Carbon intensity than the colored hair.

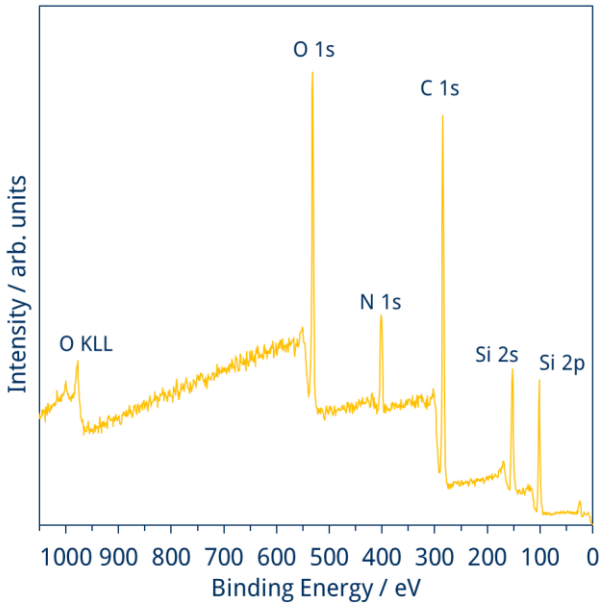


Fig. 13 Survey spectrum recorded on the bleached hair sample

Comparison

Organosilicon compounds are common ingredients of deep conditioners therefore the change in the spectra in the Silicon 1s and 2p region are the most prominent. Sample 3 shows a higher intensity when compared to sample 2 which is a clear sign that the used compounds differ (see fig.14).

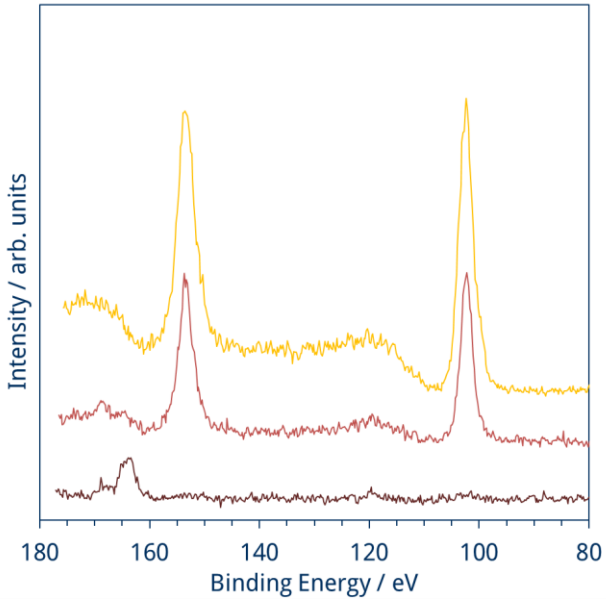


Fig. 14 Silicon 1s and 2p region of the blank hair (brown), the colored hair (red) and the bleached hair (yellow)

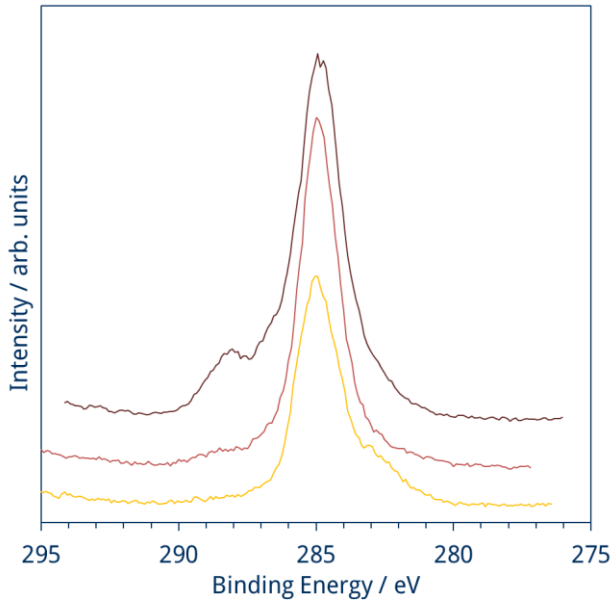


Fig. 15 Carbon 1s region of the blank hair (brown), the colored hair (red) and the bleached hair (yellow)

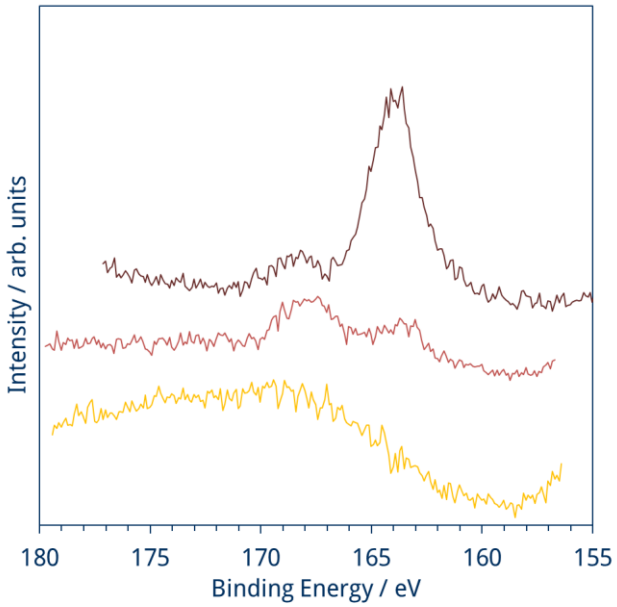


Fig. 16 Sulfur 2p region of the blank hair (brown), the colored hair (red) and the bleached hair (yellow)

This is also visible in the comparison of the Carbon 1s region of the spectra which are shown in figure 15. The spectrum of the bleached hair shows a shoulder in the 1s peak at the lower binding energy side. The high energy shoulder that can be clearly seen in the C 1s spectra of the blank hair is less visible on the spectra of the colored hair. This could be a screening effect due to the residues of the conditioner that remains on the surface of the hair fiber. This screening is also the cause for the less intense and the not noticeable Sulfur 2p peak structure on the colored and the bleached hair, respectively (see fig. 16 for details).

Conclusion

EnviroESCA has proven its ability when it comes to applications in the field of Cosmetic Sciences. The unique possibility to work at higher pressures in defined atmospheres will open up the field for new in-situ experiments that were not possible until now. The intrinsic charge compensation available only in systems that can work in pressures higher than 1 mbar makes additional electron or ion sources unnecessary and increases the usability and user friendliness of the machine.

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.

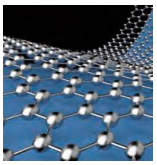
Biological Material

With the capability of operating in the near ambient pressure regime EnviroESCA offers an entirely new opportunity to investigate biological materials and processes, making ESCA more versatile than ever before.

Polymers and Plastics

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 or humans. With EnviroESCA the concentration of hazardous contaminations can be quantified regardless of their vacuum compatibility.

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.

Archaeology and Archaeometry

The analysis of priceless ancient artifacts with surface science techniques like XPS and NAP-XPS allows delivering results about the surface composition of metallic and non-metallic specimens without damaging or destroying them. EnviroESCA offers the possibility to load large and uneven samples and to perform the analysis in environmental conditions which will preserve the delicate relics.

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.

EnviroESCA™

Technical Specifications

EnviroESCA	
Electron Spectrometer	▪ Hemispherical electron analyzer with 150 mm mean radius ▪ Differentially pumped lens system ▪ Delayline detector with up to 400 channels
X-ray Source	▪ 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	▪ System immanent charge compensation by X-ray photoionization
Ion Source (optional)	▪ Scannable small spot ion source (200 eV-5 keV) or gas cluster ion source
Pumping System	▪ Turbomolecular pumps ▪ Oil-free backing pumps
Pressure Range	▪ Defined by analyzer aperture (up to 100 mbar with an aperture of 300 µm; other aperture sizes on request)
Gas Dosing	▪ Two separated mass flow controlled gas dosers at analysis position
Cameras	▪ 3 digital microscopes for sample navigation and documentation
Automation and Software	▪ Fully automated vacuum and gas dosing system ▪ Advanced software package

SampleEnvironment (standard, others on request)	
Samples Stage	▪ High precision 3-axis stage
Sample Size	▪ Up to 120 mm in diameter and 40 mm in height ▪ 50 mm inner diameter addressable
Gas Dosing	▪ Mass flow controlled process and purge gas
Cleaning	▪ Downstream RF plasma cleaner
Camera	▪ Digital microscope for sample observation and documentation