Application Note #000391

**KeyWords**
XPS, Paper, Polymers, Natural Products, Measurements, Surface Analysis, Charge Compensation

# XPS surface analysis of printed paper samples with EnviroESCA

**Results of the surface analysis of four paper samples obtained in EnviroESCA are presented. Neutralization of this insulating biopolymer is accomplished by Environmental Charge Compensation enabling X-ray Photoelectron Spectroscopy (XPS) on such important natural material with ease.**

## Motivation

Paper is one of the oldest and most often used materials in our daily life, e.g., in books, magazines, notepads, newspaper, money, packaging, arts, handkerchiefs, paper towels, filter paper or wallpaper. For printing the individual chemical composition and surface properties of a paper are very important factors as they can alter significantly the quality of the final print as result of adhesion and durability of the ink.

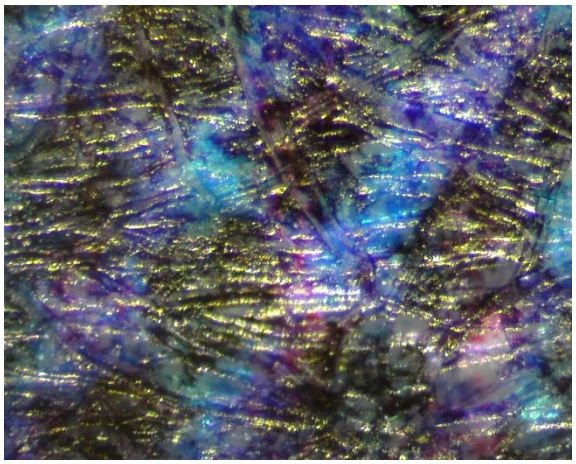



Fig. 1 Full size and microscopic image of the printed paper surface under investigation (visible area: 400x300µm).

## 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.

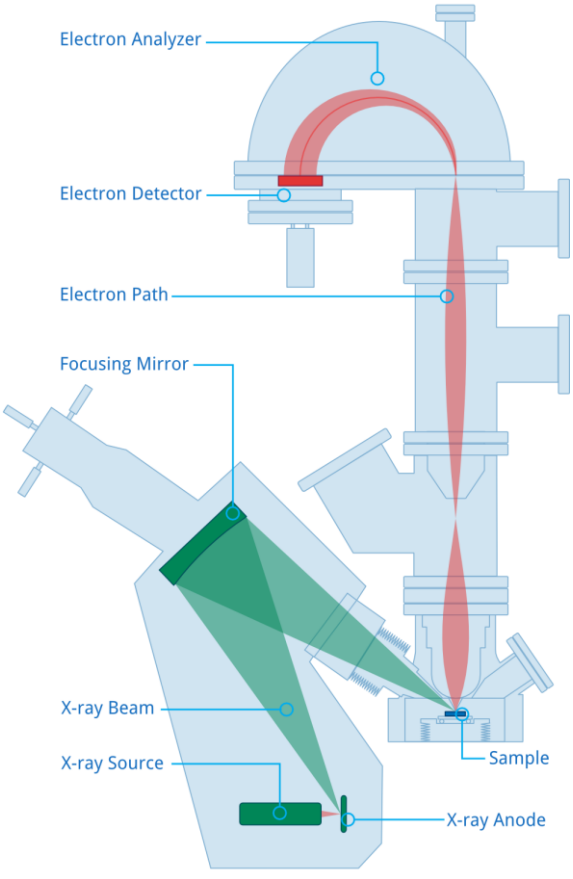



Fig. 2 XPS with EnviroESCA

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 intensity in counts per 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.

## Experimental Section

Paper is made of cellulose the most abundant organic polymer on Earth. Cellulose is a linear biopolymer of repeating cellobiose units as shown in Figure 3.

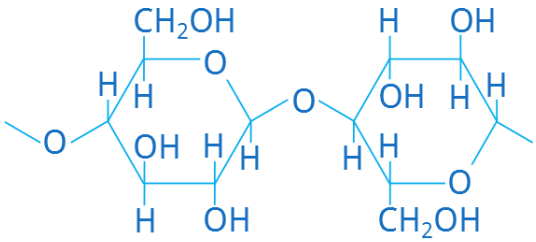



**Fig. 3 The chemical structure of cellulose which is composed of repeating units of cellobiose ($C_{12}H_{20}O_{10}$).**

EnviroESCA can work in pressures up to several dozens of mbar and therefore does not necessarily require vacuum conditions which overcome the problems of outgassing, drying or special treatment of natural samples.
In classical XPS systems non-conducting (bio) organic polymers tend to charge up quickly under X-ray illumination which makes charge compensation inevitable. In classical XPS low energy electron and ion sources are being used in addition to the X-ray source to compensate the surface charge of the surface.

In EnviroESCA an intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources unnecessary. The gas atmosphere that is surrounding the sample delivers all the free charges, when illuminated with the soft X-rays, that is needed to compensate for surface charging (cf. fig. 4 for an illustration).

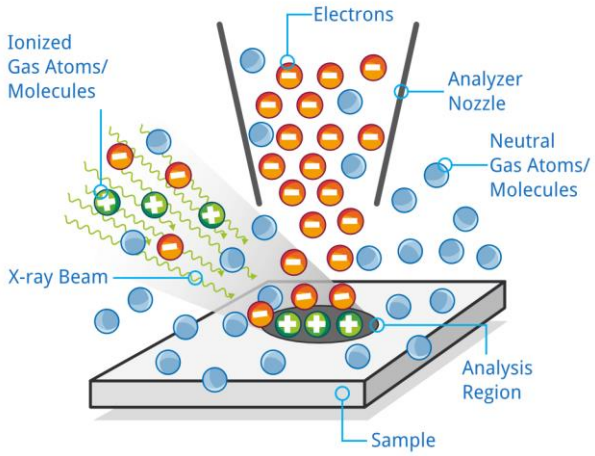



**Fig. 4 Environmental Charge Compensation**

The investigated paper samples were taken from a sticky note and a notepad sheet with a printed SPECS logo. From these samples one white non-printed, two blue printed and one yellow colored surface area were investigated with the EnviroESCA (cf. insets of Fig. 5).
A working pressure of 1 mbar of ambient air was chosen for this study to compensate for potential surface charging.

## Results

In the following we are presenting unmodified raw data taken with EnviroESCA.
The paper samples under investigation were placed on the sample plate, fixed with carbon tape, and analyzed directly without any additional treatment.
First of all survey scans were acquired on each sample in less than three minutes after starting the pump down of the Sample Environment to 1 mbar.
The main elements found are carbon and oxygen as expected. Additionally calcium and nitrogen can be found for all of the paper samples. A significant amount of silicon was present exclusively on the sticky note.

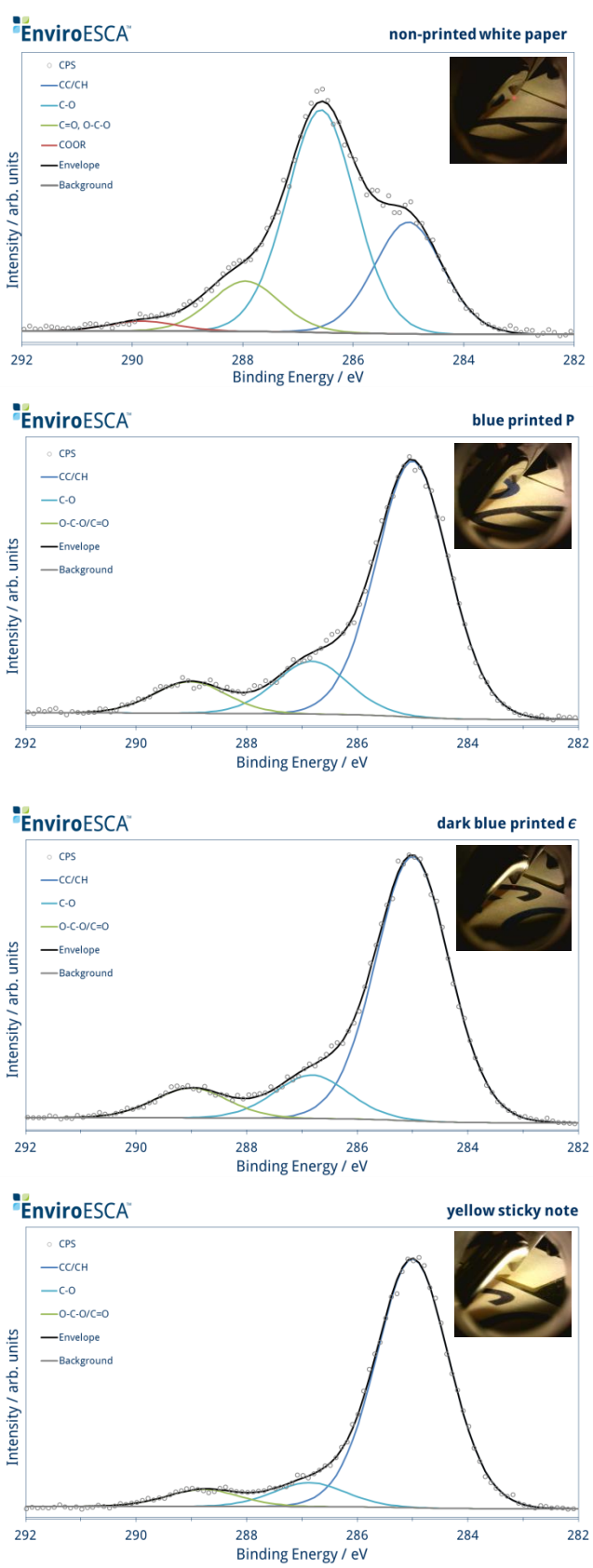



**Fig. 5 (four panels) High-resolution C 1s XP spectra of different paper samples measured at 1 mbar of ambient air. Open circles represent experimental data and black lines show fitted curves. Colored lines corre-spond to carbon atoms located in *C*C/*C*H, *C*-O, O-*C*-O / *C*=O, and *C*OO moieties.**

The studied paper samples show very different carbon core-level spectra as shown in Figure 5. A clear separation of non-printed, printed and colored paper is possible using the different C 1s peak components of the fitted spectra. In the white unprinted paper region the cellulose related *C*-O carbon species is dominating the C 1s core-level spectrum whereas the aliphatic *C*C/*C*H component originating from the ink is the major one on the printed and colored paper samples.

Another kind of discrimination of different paper samples is obtained by plotting the total *C*C/*C*H amount of each sample versus the O/C elemental ratio from survey scan spectra as shown in Fig. 6.

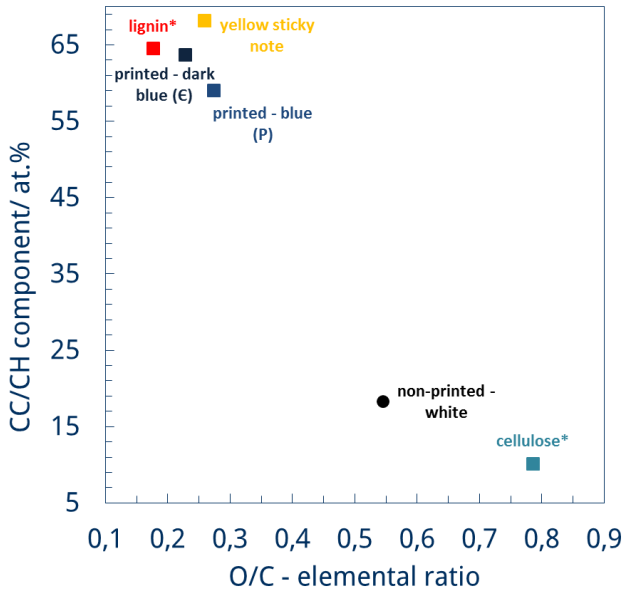
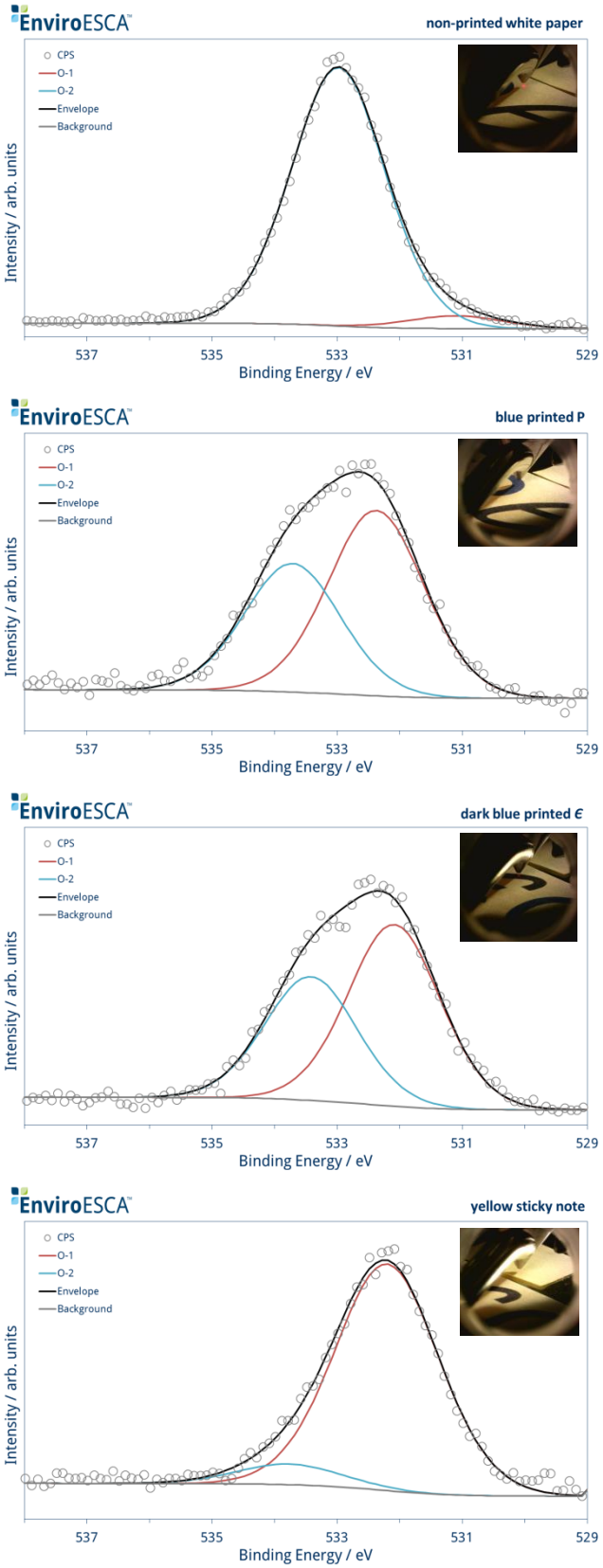



**Fig. 6 Correlation of *C*C/*C*H component in atomic percentage and O/C atomic ratio for the different paper samples. *Data taken from ref.[1]**

The printed and colored papers differ significantly from the non-printed samples. Similar findings were reported earlier.[2] For comparison data (taken from ref.[1]) from cellulose and lignin as the main wood components are also included.

**Fig. 7 (four panels) High-resolution O 1s XP spectra of different paper samples measured at 1 mbar of ambient air. Open circles represent exper-imental data and black lines show fitted curves. Colored lines correspond to different oxygen peak components O-1 and O-2.**




Additionally O 1s core-level spectra were acquired and fitted with two components but their interpretation is much more difficult compared to the C 1s spectra due to the less pronounced chemical shifts in the O 1s region.

But also here a clear differentiation between printed or colored papers and a non-printed, white paper region is possible. The O 1s peak component located at higher binding energies (≥ 533 eV) can be assigned to oxygen atoms in C-*O*H and *O*-C-*O* moieties from cellulose. [1-3] The second peak component in the O 1s core-level spectra at lower binding energies around 532 eV seems to be characteristic of the colored and/or printed paper areas originating most probably from *O*=C and/or C-*O*-C contributions from the applied ink and/or color.

## Conclusion

EnviroESCA has proven to be a powerful tool to investigate with XPS the surface of organic polymers such as paper. High resolution and high quality spectra are recordable with ease using the Environmental Charge Compensation. For EnviroESCA outgassing, wet and/or natural samples are no problem under the applied near ambient pressure conditions, here at 1 mbar of ambient air.

[1] J. Bañuls-Ciscar, M.-L. Abel, J. F. Watts *Surface Science Spectra* 23, 1 (**2016**); doi: 10.1116/1.4943099.

[2] D. Lützenkirchen-Hecht, K. Rohrmann, T. Stöcker, W. Thiel *Surf. Interface Anal.* **2007**; 39, 845.

[3] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers; Wiley: Chichester, UK, 1992