Photoelectron attenuation correction for quantitative NAP XPS

In this note we present quantitative NAP XPS results from a polytetrafluoroethylene (PTFE) sample using the EnviroESCA. A PTFE sample was analyzed in oxygen and water vapor atmospheres at pressures ranging from 1 mbar to 15 mbar. This study demonstrates the ability of NAP XPS to deliver reliable quantification results after correcting the photoelectron attenuation in the ambient gas atmosphere.

Motivation

X-ray Photoelectron Spectroscopy (XPS) is a powerful and non-destructive technique for material and surface analysis, which provides quantitative elemental and chemical information. Near ambient pressure NAP XPS has been developed to enable routine analysis of real-world samples. The transformation of XPS from a UHV-based method towards environmental conditions has dramatically revolutionized XPS and opens completely new application areas. NAP XPS is used extensively for *in situ* and *operando* studies of industrially relevant (electro) chemical reactions and catalytic processes, especially at gas-liquid, gas-solid, and liquid-solid interfaces but quantitative NAP XPS studies are still rare.

In NAP-conditions, the gas surrounding the sample surface may interact with the emitted photoelectrons by (in)elastic scattering. The extent of scattering depends amongst others on the photoelectrons, the density, and the type of gas. As a result of scattering the photoelectron peak intensity in a spectrum is reduced and the background signal at lower kinetic energies is increased.

The photoelectron attenuation in a gas environment is defined as

$$\frac{I_P}{I_0}(KE, p) = e^{-z\sigma(KE)p/kt}$$

with I_p the signal at pressure p, I_0 the signal in vacuum, $\sigma(KE)$ the electron scattering cross-section, and z the travel distance of the electrons.

Thus, the attenuation is a function of the ambient gas (type, p, T), the kinetic energy of photoelectrons (E_{kin}), the travel distance from surface to analyzer nozzle, and the cross section (σ_{KE}) of scattering of a photoelectron of E_{kin} at the ambient gas molecules. [1,2]

Fig. 1 Teflon (PTFE) sample used in this study.

An obstacle of quantitative NAP XPS is the decrease of XPS peak intensities with increasing working pressure due to an exponential increase of inelastic scattering events of photoelectrons emitted from the sample's surface in the gas volume when travelling to the analyzer entrance nozzle, cf. Fig. 1. [1] This attenuation of the photoelectron signal must be considered if a quantitative analysis to obtain a surface chemical composition, is needed.
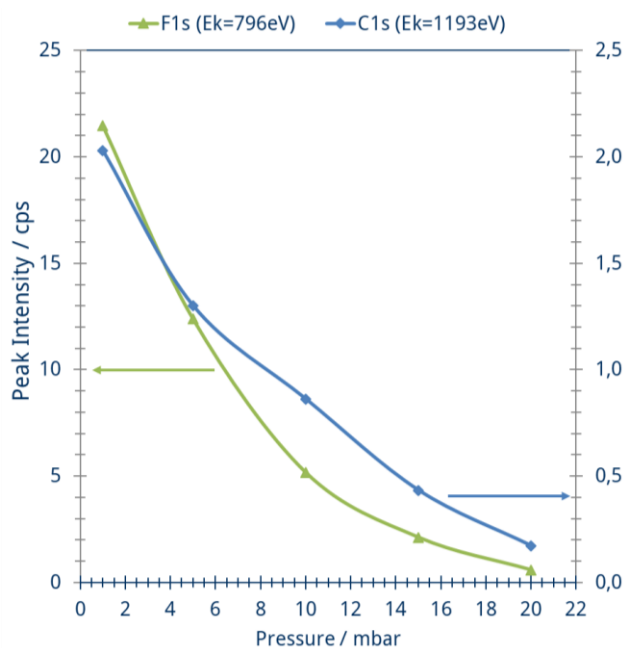
Fig. 2 C 1s and F 1s XPS intensities measured on PTFE in water vapor atmosphere with pressures from 1 mbar to 20 mbar.

An experimental solution to this problem is the characterization of the photoelectron attenuation observed with a well-defined sample in relevant gas atmospheres at different pressures. Such a characterization allows then a calculation of so-called attenuation factors for photoelectrons with a specific kinetic energy. Thus, quantitative NAP XPS data can be obtained using these experimental attenuation factors.

Method

The EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as analytical technique, cf. Fig. 2. Here an electron beam is generated inside the X-ray source and focused on an aluminum X-ray anode. The deceleration of electrons on the anode generates X-rays. This X-ray beam is monochromatic and focused on the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with a specific kinetic energy that is determined by their binding energy and the photon energy of the X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm can leave the surface.

These electrons propagate through the electron analyzer's lens system into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy.

The path of photoelectrons ends at an electron sensitive detector where the electrons are amplified and measured as intensity in counts per second.

A photoelectron spectrum is recorded by sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector. Then a quantitative analysis of the sample surface - giving the elemental composition - can be extracted from these spectra.
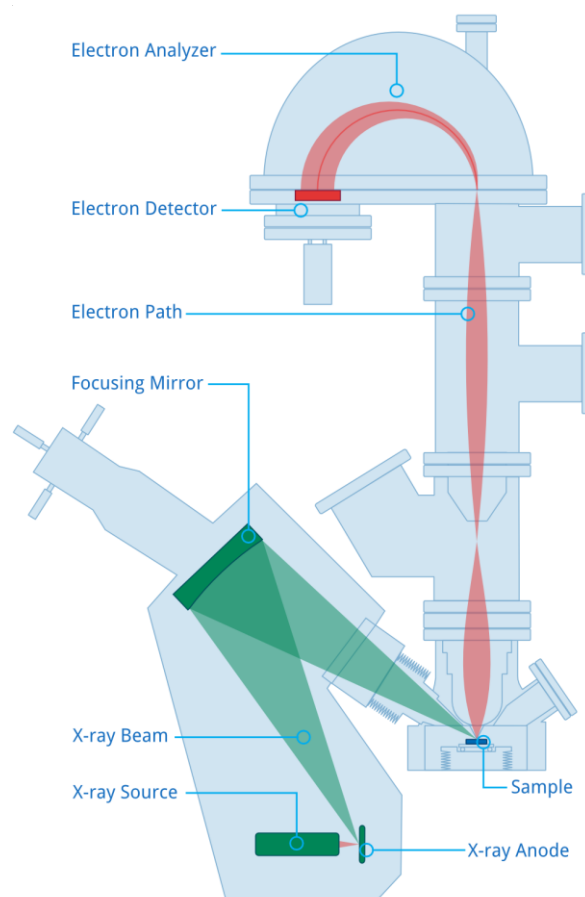

Fig. 3 XPS with EnviroESCA

Experimental Section

The EnviroESCA can work under vacuum as well as near ambient pressure (NAP) conditions up to several dozens of mbar. This NAP XPS capability of EnviroESCA allows *in situ* and *operando* surface studies on a multitude of different samples in various environments.

The EnviroESCA comes with an intrinsic charge compensation which we call *Environmental Charge Compensation* that makes additional low energy electron or ion sources unnecessary. As shown schematically in Fig.3 the illumination of the surrounding gas atmosphere with soft X-rays generates free charges, which compensate potential surface charging on the sample.
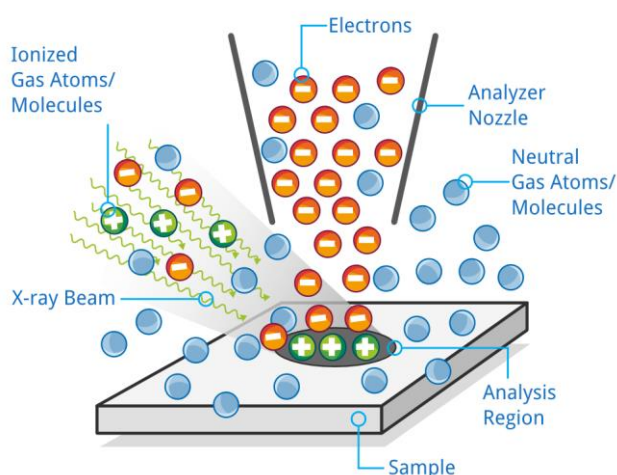

Fig. 4 Environmental Charge Compensation

Here we present first results of a proof-of-principle study about quantitative NAP XPS analysis of a PTFE sample in the presence of air and water vapor at different pressures ranging from 1 mbar to 15 mbar.

Results

The photoelectron signal in NAP-conditions is attenuated due to the inelastic scattering of photoelectrons in the ambient gas phase. As discussed earlier by *Tao et al.* [2] and *Kjærvik* [3], knowledge of the attenuation factor is the prerequisite for a quantitative analysis in NAP XPS experiments.

The attenuation factor is defined as I_p/I_0, where I_0 is the peak intensity of a given element and orbital in UHV XPS, and I_p is the intensity of the same peak at a pressure p.

Attenuation factors for the F 1s and C 1s core-level peaks were obtained experimentally by UHV XPS and NAP XPS measurements in different gases using a well-defined and characterized reference sample, the homogeneous and isotropic ionic liquid EMIM NTf$_2$. [3-5]

Polytetrafluoroethylene (PTFE) is a major industrial polymer with a well-defined composition, and it is often used as a reference insulator material to control the performance of XPS systems.

As a proof of principle, the attenuation factors for fluorine and carbon, calculated from the ionic liquid measurements, were used to quantify a PTFE sample in NAP conditions using air at 1, 5, and 10 mbar and water vapor at 5, 10, and 15 mbar. PTFE contains only fluorine and carbon in a 2/1 atomic ratio. The atomic F 1s/C 1s ratio was then corrected using the following formula:

$$\left(\frac{F\ 1s}{C\ 1s}\right)_{corrected} = \frac{F\ 1s}{C\ 1s} \times \frac{(I_p/I_0)_{C1s}}{(I_p/I_0)_{F1s}}$$

A similar approach was reported earlier by Tao *et al.* [2], who used experimental attenuation factors to correct the Rh/Ce atomic ratio of a catalyst nanoparticle system under nitrogen atmosphere.

Figure 4 shows the F 1s/C 1s atomic ratios in the various ambient atmospheres at pressures ranging from 1 mbar to 15 mbar before and after correction. Before correction, the F 1s/C 1s atomic ratios vary from 0.7 to 1.8 and are below the expected value for PTFE. At higher pressures above 1 mbar, the F 1s/C 1s atomic ratios are significantly smaller due to stronger inelastic scattering of the electrons. After correction for attenuation of the photoelectrons in the ambient gas phase the F 1s/C 1s atomic ratios range between 1.7 and 2.0 and are all very close to the expected atomic ratio of 2/1.
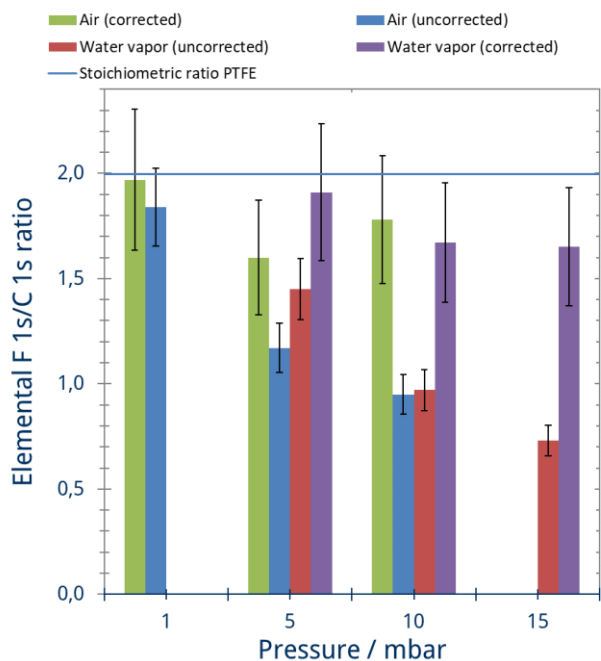
Fig. 5 Elemental ratio (F 1s/C 1s) of PTFE in water vapor and air. Blue and red columns represent the elemental ratio without correction for electron attenuation, green and violet columns were corrected with experimental photoelectron attenuation factors. [3] Error bars show ±10%. for uncorrected values and ±17% for corrected values.

Conclusion

In this application note we present a straightforward procedure to correct for the effect of photoelectron attenuation and by that enable quantitative NAP XPS experiments.

The experimental attenuation factors for fluorine and carbon were used to correct the F 1s/C 1s ratio of the Teflon sample for different NAP conditions (1–15 mbar). After attenuation correction the atomic F 1s/C 1s ratios were for all pressures very close to the expected atomic ratio (2/1).

As reported recently the same method can also be used for biological samples. [3]

For the near future a more sophisticated and user-friendly approach could be a software-based expert system correcting the photoemission peak intensity as a function of pressure and gas, using a well-defined reference material, giving an attenuation correction function for each measurement at NAP XPS systems comparable to a spectrometer transmission function for intensity correction in UHV XPS.

[1] H. Bluhm, Photoelectron spectroscopy of surfaces under humid conditions. *Journal of Electron Spectroscopy and Related Phenomena*, 177(2):71–84, **2010**. doi: https://doi.org/10.1016/j.elspec.2009.08.006

[2] F. Tao et al. Interactions of gaseous molecules with X-ray photons and photoelectrons in AP-XPS study of solid surface in gas phase. *Physical Chemistry Chemical Physics*, 20(15):9812–9823, **2018**. doi: 10.1039/C7CP08429C

[3] M. Kjærvik Applications of near-ambient pressure X-ray photoelectron spectroscopy in life science and materials research. PhD thesis TU Berlin, **2021**. https://doi.org/10.14279/depositonce-12360

[4] M. Holzweber et al. The use of ionic liquids for the determination of the spectrometer transmission function in X-ray photoelectron spectroscopy (XPS). *Journal of Electron Spectroscopy and Related Phenomena*, 233:51–56, **2019**. doi: 10.1016/J.ELSPEC.2019.03.008

[5] Y. Khalifa et al. Water vapor electron scattering cross-section measurements using a hydrophobic ionic liquid. *Journal of Electron Spectroscopy and Related Phenomena*, 222:162–166, **2018**. doi: 10.1016/J.ELSPEC.2017.06.002