



KeyWords

NAP XPS, Liquids, Aqueous Solutions, Measurements, Surface Analysis, Liquid (Solute)-Gas Interface

XPS surface chemical analysis of aqueous solutions with EnviroESCA

This application note presents how EnviroESCA can be used to analyze the surface of various aqueous solutions under near ambient pressure conditions. Such investigations of aqueous solutions are of paramount importance due to the vast number of essential water based processes in nature and industry.

Motivation

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.

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. 1 Watch glass filled with liquid water positioned on an EnviroESCA sample plate using an O-ring for stabilization.

In this paper first results from water based samples are presented as a proof of concept to demonstrate the special capabilities of EnviroESCA analyzing liquid samples. The following solutions were investigated under near ambient pressure conditions: i.) water, ii.) brine, iii.) an oil in water dispersion, iv.) aqueous iron(II) sulfate heptahydrate, and v.) a suspension of nano silver particles in water.

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 down to a depth of approx. 10nm are able to leave the surface in case of solid samples. 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 path of photoelectrons ends at an electron sensitive detector where the electrons are amplified and measured as an 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.

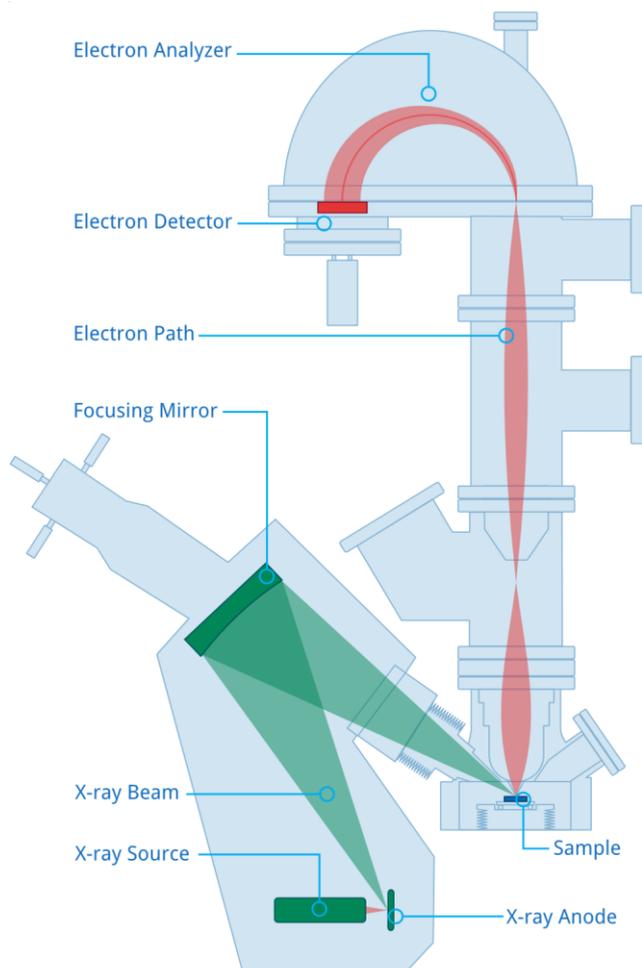


Fig. 2 XPS with EnviroESCA

Experimental Section

In a typical experimental setup a liquid volume of 2-4 ml was transferred with a pipette to a watch glass which was placed, together with an O-ring for mechanical stabilization, on a sample plate (cf. Fig. 1) directly in the Sample Environment of the EnviroESCA.

The different aqueous solutions were analyzed in the EnviroESCA without any further treatments after pumping down the Sample Environment to a pressure of about 20 mbar. During the analysis the valve to the backing pump was closed and the analysis section was pumped only through the nozzle.

Results

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

1. Water

First, pure water was studied acting as a reference for the following aqueous solutions.



Fig. 3 The water filled watch glass underneath the analyzer nozzle at a working distance of 0.3 mm. The reflection of the analyzer nozzle is clearly visible on the water surface.

The image shown in Fig. 3 was recorded with one of the three digital microscopes located at the EnviroESCA Analysis Module. The metal pipe coming from the lower left corner allows for dosing of gases directly onto the analyzed region of the sample.

Fig. 4 shows the difference in the O 1s signal at different nozzle to liquid surface distances. At first (green spectrum) the water surface is out of focus, thus all the analyzed electrons are generated in the water vapor in front of the nozzle yielding a single O 1s peak component O 1s_{gas}. With a decreasing nozzle to surface distance the intensity of the liquid water related component (O 1s_{liquid}) of the O1s peak around 534 eV increases significantly. For a working distance of 0.3 mm both O 1s components of water show similar intensities.

In the high resolution O 1s spectrum taken with a pass energy of 30 eV (presented in Fig. 5) these two peak components, O 1s_{gas} at ~536 eV and O 1s_{liquid} at ~534 eV, of the O 1s peak are clearly separated.

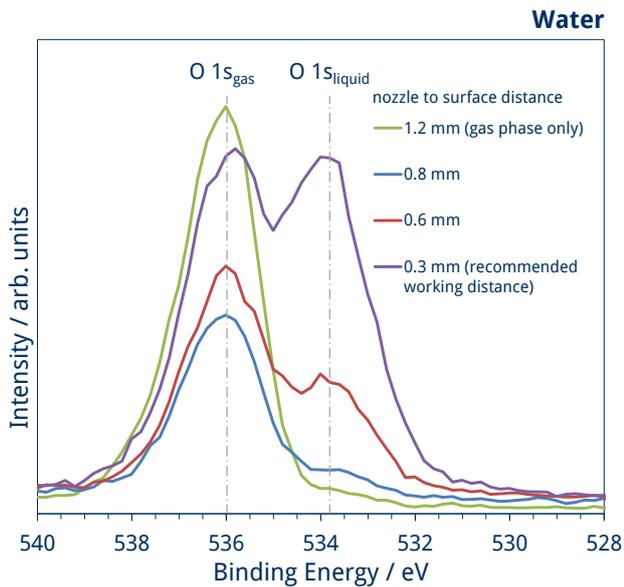


Fig. 4 XPS O 1s detail spectra of liquid water at different nozzle to liquid surface distances and at a working pressure of 18 mbar.

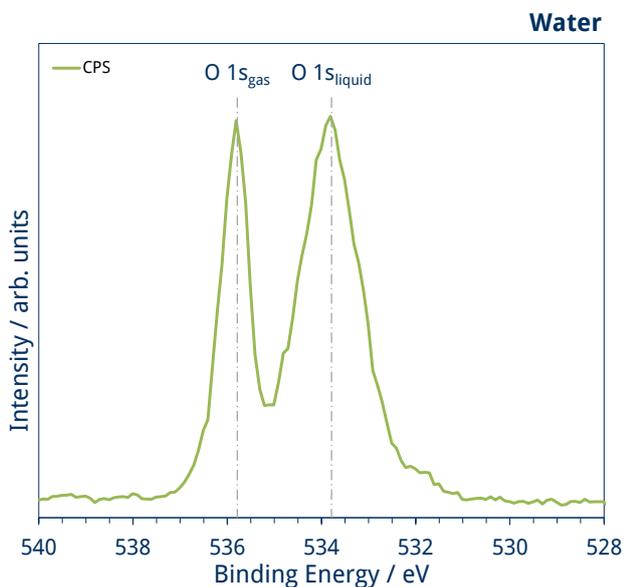


Fig. 5 XPS O 1s detail spectrum of liquid water at a working pressure of 13 mbar and a working distance of 0.3 mm.

In the survey spectrum of water (not shown) only oxygen and residual nitrogen from the ambient air and/or nitrogen used as venting gas were found.

2. Sodium Chloride Solution

The next liquid to be investigated was a saline solution (NaCl_{aq}) with an initial molar concentration of 2.5 mol/L.

The solution was measured starting with a pressure of 14 mbar which decreases due to pumping to a final pressure of 4 mbar. In the same time the solution is gradually concentrated during the analysis. Exemplarily the spectra of the aqueous NaCl solution taken at 12 mbar and 4 mbar are shown in Figs. 6 and 7.

Fig. 6 exhibits a detail scan of the chlorine related photoemission lines together with the C 1s line. Here the Cl 2p and Cl 2s peaks become clearly visible with the ongoing analysis (starting at approx. 5 mol/L).

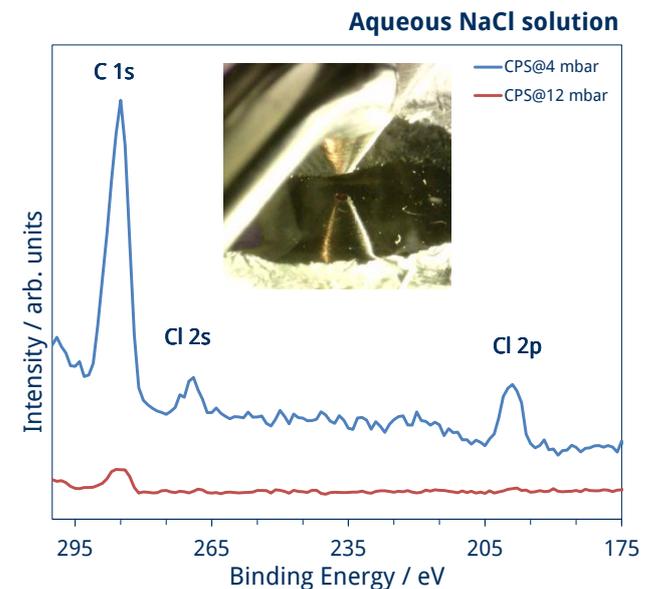


Fig. 6 Detail view at the C 1s, Cl 2s and 2p photoemission lines. the inset shows the analyzed region under the nozzle at a working distance of 0.3 mm.

Similarly peaks assigned to sodium chloride (Na 2s, Na 2p, Cl 3s, and Cl 3p) appear in the valence band spectra of the concentrated NaCl_{aq} solution as illustrated in Fig. 7. The effect of evaporating water from the solution can be seen also in the inset of Fig. 6, here crystals of solid NaCl can be seen at the edge of the solution.

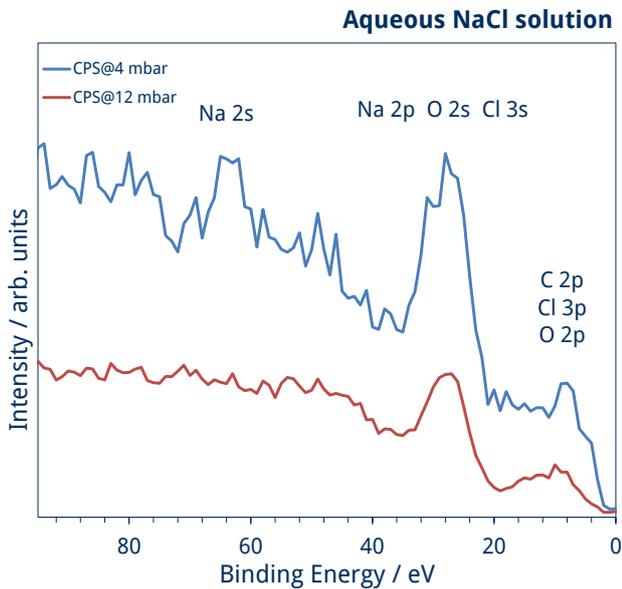


Fig. 7 Valence band spectrum of an aqueous NaCl solution.

Encouraged by these findings from aqueous NaCl solution further water based solutions were investigated.

3. Oil in Water Emulsion

In order to evaluate if a surface layer of oil on water can be investigated using the EnviroESCA under ambient conditions a small volume (0.2 µL) of native olive oil was deposited on the surface of liquid water.



Fig. 8 The images show the studied oil on water film (left) and oil in water suspension stabilized by a detergent (right) during analysis under the nozzle at a distance of 0.3 mm.

The resulting oil on water film (cf. Fig. 8) could be measured without any problems. The survey spectrum (not shown) exhibits oxygen and carbon as main elements together with a nitrogen contribution originating from a mixture of ambient air and pure nitrogen gas used for venting.

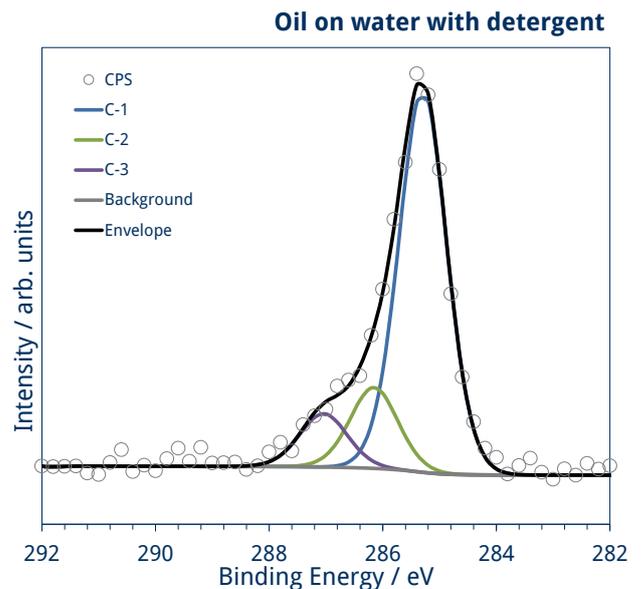
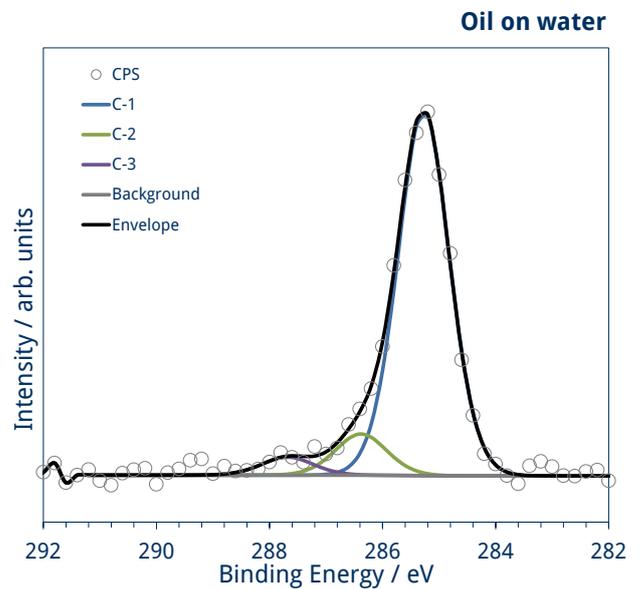


Fig. 9 C 1s core-level spectra of an oil layer on water (top) and of an oil-water-detergent emulsion @18 mbar. Open circles represent experimental data and black lines show fitted curves. Colored lines correspond to C 1s peak components C-1, C-2, and C-3.

The quantitative (surface) composition of the olive oil is unknown but the C 1s core-level spectrum reveals typical oil (fat) related components as hydrocarbons (C-1, 285.3 eV), carbon atoms bound to oxygen by a single C-O (C-2, 286.4 eV) or a double C=O bond (cf. Fig. 9, top).

After the analysis of the oil film on water a stabilized oil in water emulsion was prepared from that sample by adding a drop of dish washing detergent and homogenizing by sonication (5 min). The appearance of the sample changed completely and the stabilized emulsion appears turbidly white see Fig. 8.

Compared to the oil film the analysis of that emulsion gave a C 1s core-level spectrum with similar intensities but with very different peak component areas due to the presence of the detergent (cf. Fig. 9).

From that very simple experiment it is obvious that the EnviroESCA can be used to perform much more sophisticated studies on surfaces of various liquid samples with an ease which was till now not possible to such an extent with existent XPS system.

4. Aqueous Iron(II) Sulfate Heptahydrate

Besides the other tested solutions also an iron(II) sulfate solution in water was studied using the EnviroESCA. Exemplarily the Fe 2p_{3/2} photoemission line obtained at 25 mbar is presented in Figure 10.

This spectrum shows how dissolved metal salts, e.g., FeSO₄ can be studied in aqueous solutions.

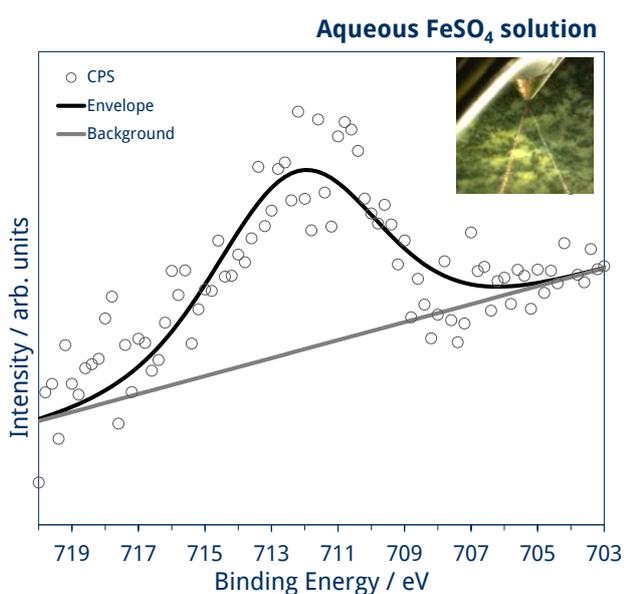


Fig. 10 Fe 2p_{3/2} photoemission line of an aqueous solution of FeSO₄ × 7H₂O at 25 mbar.

5. Nano Silver Particles

Finally, in collaboration with the Federal Institute for Materials Research and Testing (BAM), Division 6.1, a suspension of metallic nano particles was studied to demonstrate that these samples can be analyzed directly in their native environment of synthesis and application.

For that purpose *Nano Silver*, a certified reference material (BAM-N001), was chosen.[1] *Nano Silver* is an aqueous solution of silver particles with an average size of 20 nm and a silver concentration of 100 µg/ml. The aqueous suspension of nano silver particles was taken from the original container and placed directly in the watch glass before analysis. In that case the initial Ag concentration was sufficient to detect an Ag 3d photoemission line. The high resolution Ag 3d XPS core-level spectrum obtained at 12 mbar is shown in Figure 11.

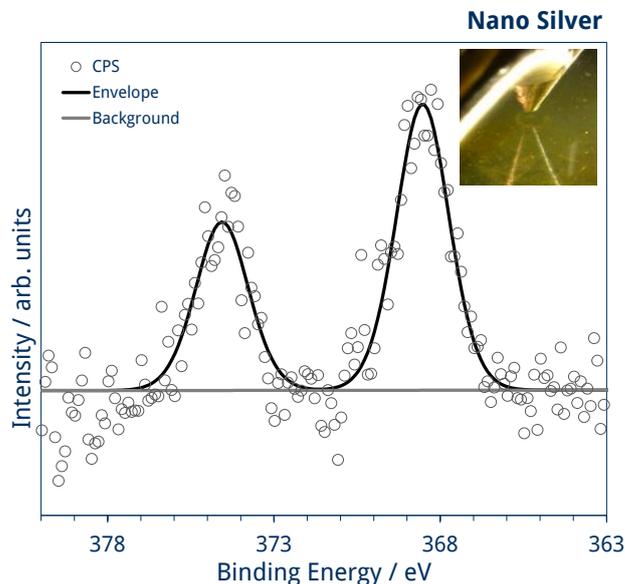


Fig. 11 Ag 3d core-level region obtained at 12 mbar from an aqueous solution of nano silver particles (BAM-N001).[1] Open circles represent experimental data and the black line shows the fitted curve. Inset shows the nano silver solution underneath the analyzer nozzle at a working distance of 0.3 mm.

Additional elemental contributions from carbon and nitrogen originating from the used stabilizing agents could be detected (not shown).[1]

Conclusion

The EnviroESCA is an extremely powerful tool when it comes to investigations of liquid samples under ambient conditions as demonstrated here with the presented examples of surface chemical analyses of different aqueous solutions.

These very basic experiments illustrate nicely what is possible already and what other work could be done in the (near) future on surfaces of liquids using the EnviroESCA.

[1] Nano Silver [BAM N-001](#). Aqueous solution with nano silver concentration of 100 µg/ml. The silver particles have an average size of 20 nm. The silver particle suspension has been stabilized by polyoxyethylene glycerol trioleate and polyoxyethylene (20) sorbitan mono-laurate. It contains also ammonium nitrate. For more details see the official [certificate](#) and [certification report](#).

We gratefully acknowledge Prof. Dr. Nora Kulak (Free University Berlin), MSc Marit Kjærvik, and Dr. Wolfgang Unger (BAM Division 6.1, "Surface Analysis and Interfacial Chemistry") for providing FeSO₄, Nano Silver ([BAM N-001](#)), and a very fruitful collaboration.