Application Note #000404

KeyWords
Food, Vegetables, Fruit
NAP-XPS, Bio-organic Surface Analysis

EnviroESCA™

Near ambient pressure photoelectron spectroscopy of fruit and vegetables

In this note we present first NAP-XPS results from a fresh tomato and apple using the EnviroESCA. Portions of tomato and apple were introduced into the system and the pressure was stabilized at 10 mbar. Different regions on the surface were studied and the photoelectron spectra show significant chemical differences between these regions. This study demonstrates the unique NAP XPS capabilities of the EnviroESCA and extends the field of applications to (processed) food samples and other natural or biological samples that could not be studied by XPS up to now.

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 NAP XPS studies of biological samples are still rare.[1-2]

Fig. 1 Tomato sample inside the EnviroESCA.

Method

The EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as an 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 monochromated 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 solid samples, only electrons from atoms down to a depth of about 10 nm can 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 path of the 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.

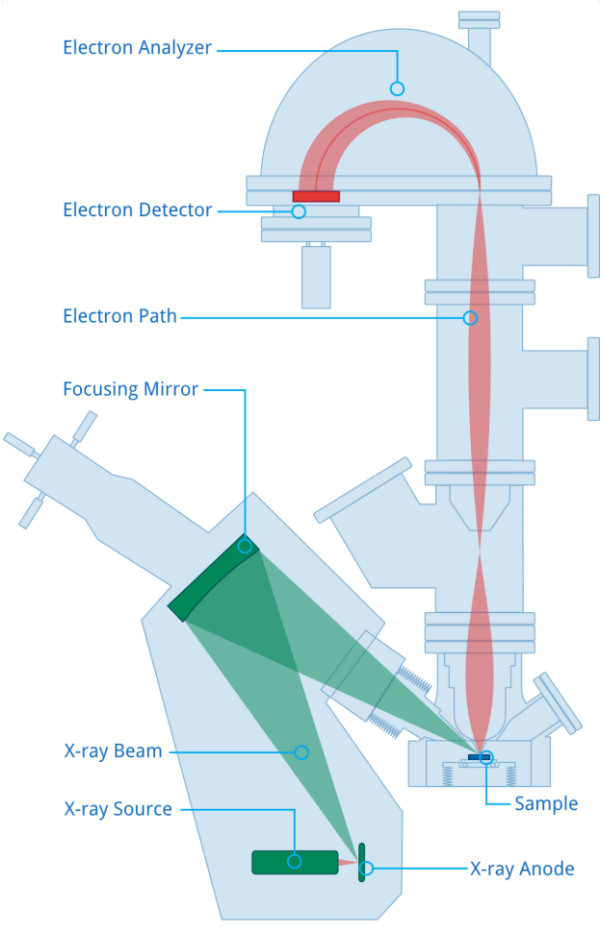

Fig. 2 XPS with the EnviroESCA

Experimental Section

The EnviroESCA can work under vacuum as well as ambient pressure (NAP) conditions up to several dozens of mbar. This AP XPS capability of EnviroESCA allows in-situ surface studies of a multitude of biological samples, e.g., cells, bacteria, biofilms, viruses, or foods in very different 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 illumination of the surrounding gas atmosphere with soft X-rays generates free charges, which compensate potential surface charging on the sample.

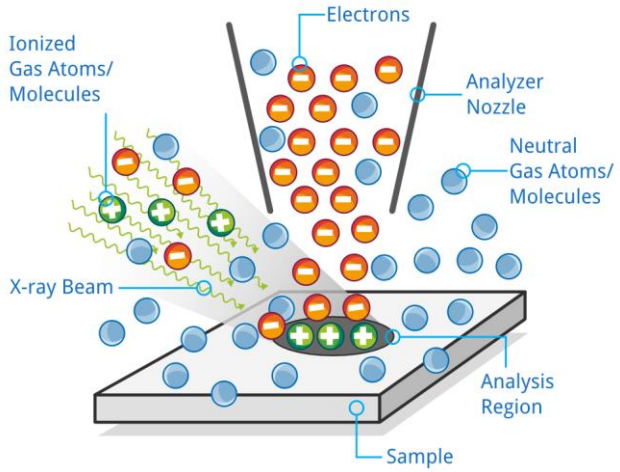

Fig. 3 Environmental Charge Compensation

Here we present results of a surface chemical analysis of a salad tomato and apple at a pressure of 10 mbar. One salad tomato, grown commercially in the UK, was cut in half and one half was put on a standard sample holder without any fixation. The apple, grown in a home garden, was sliced and slices were mechanically fixed onto the sample stage with either the peel or flesh side facing up.

Results

Tomato

After evacuation and pressure stabilization to 10 mbar a survey spectrum was recorded in the middle of the tomato half in a region where the white flesh is located, see Fig. 4. This survey shows carbon (49.5 at.-%,), nitrogen (3.8 at.-%), and oxygen (46.7 at.-%) as the main components in the analyzed surface region.

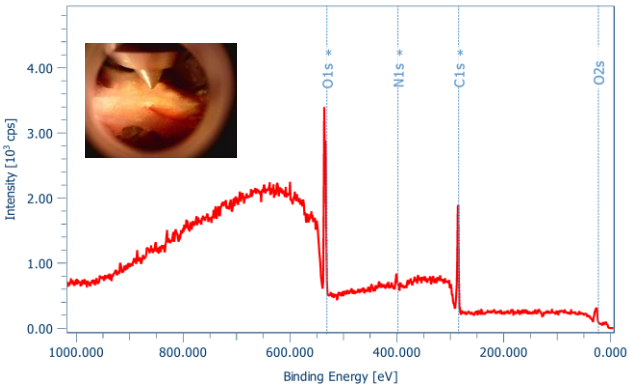

Fig. 4 Survey spectrum of a tomato's white flesh at 10 mbar

After that C 1s, N 1s, and O 1s detail spectra were recorded on different regions of an encapsulated tomato seed in the middle of flesh. The spectra and curve fits are shown in Fig. 5 and show a clear chemical difference between the two analyzed surface regions.

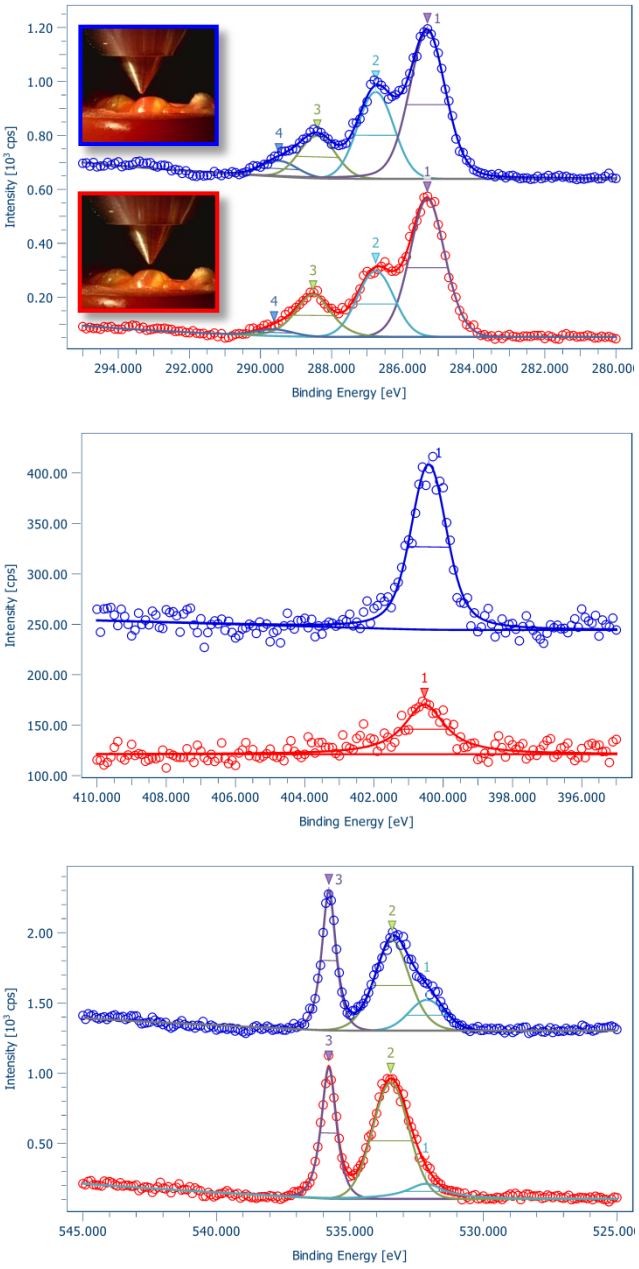

Fig. 5 C 1s (top), N 1s (middle), and O 1s (bottom) core-level spectra of two different regions on an encapsulated seed in a tomato's flesh at 10 mbar. Insets show the different analyzed regions (color coded).

Table 1. Assigned peaks component positions and areas of C 1s, N 1s and O 1s curve fits as shown in Fig. 5.

Peak	Component	Position /eV	Peak area* /%	
C 1s	CC/CH (1)	285.3	54	53
	C-O (2)	286.7	26	28
	N-C=O /C=O O-C-O (3)	288.4	17	14
	COOR (4)	289.5	3	5
N 1s	N-C=O (1)	400.5	100	100
O1s	O=C (1)	532.1	11	16
	O-C (2)	533.5	58	50
	H_2O (3)	535.8	31	34

*color code corresponds to the regions shown in Fig. 5 (top)

Apple

After evacuation and pressure stabilization to 10 mbar survey spectra of a reddish section of the apple peel and a white region of apple flesh were recorded. The survey spectra of the apple peel and flesh (Fig. 6) show carbon (90.0 at.-%) and oxygen (10.0 at.-%), and carbon (63.0 at.-%), oxygen (17.0 at.-%) and nitrogen (19.0 at.-%), respectively, as the main components in the analyzed surface region.

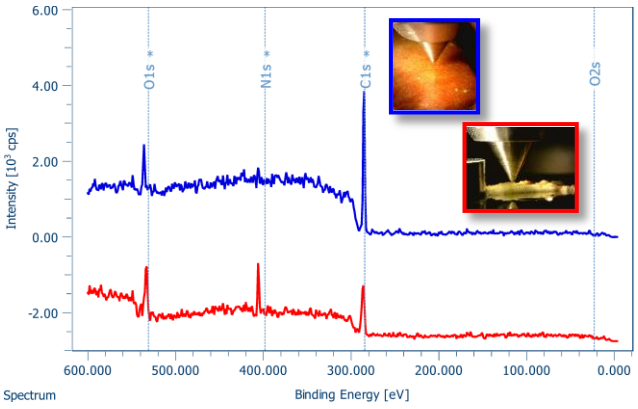

Fig. 6 Survey spectra of apple peel (blue) and flesh (red).

The C 1s and O 1s detail spectra highlight differences in surface chemical composition of the apple peel and flesh which are summarized in Table 2.

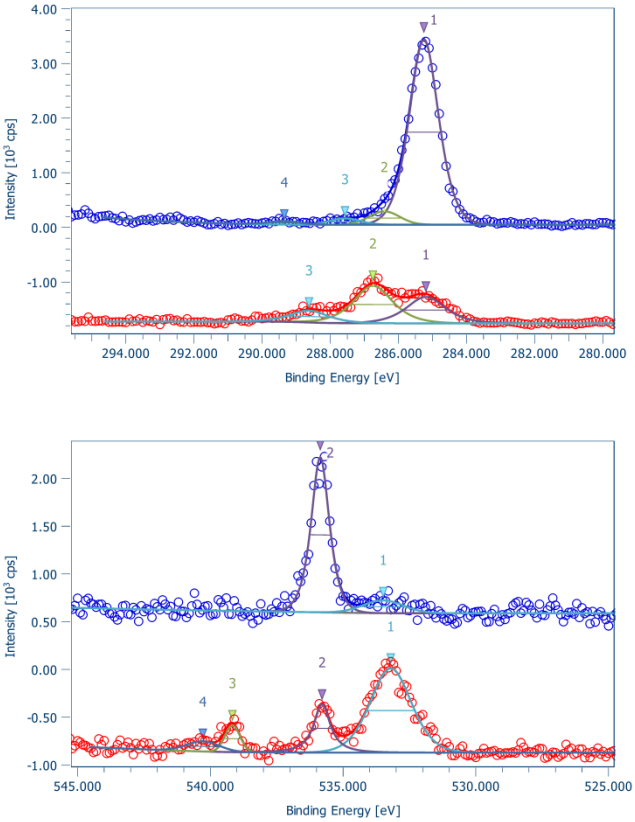

Fig. 7 C 1s (top) and O 1s (bottom) core-level spectra of apple peel (blue) and a white flesh (red) at 10 mbar.

Table 2. Assigned peaks component positions and areas of C 1s and O 1s curve fits as shown in Fig. 7.

Peak	Component	Position /eV	Peak area* /%	
C 1s	CC/CH (1)	285.2	**84.8**	**34.6**
	C-O (2)	286.1 286.7	**10.2**	**49.0**
	N-C=O /C=O O-C-O (3)	287.3 288.6	**3.5**	**16.4**
	COOR (4)	289.4	**1.5**	**0**
O1s	O-C (1)	533.2	**13.5**	**74.2**
	H_2O (2)	535.6	**86.5**	**16.7**
	O_2 (3/4)	539.2	**0**	**9.1**

*color code corresponds to the regions shown in Fig. 6

Conclusion

Investigations of a tomato and apple at elevated pressures have demonstrated EnviroESCA's unique NAP XPS capabilities on various natural samples like fruits and vegetables. Chemical differences were found when analyzing different surface regions of an encapsulated seed in tomato pulp and of an apple peel vs flesh.

This study extends the field of applications to (processed) food samples and other hydrated natural or biological samples that could not be studied by XPS up to now.

[1] M. Kjærvik *et al. Surf Interface Anal.* **2018**, 1–5.
[2] V. Jain *et al. Surface Science Spectra* **2019**, 26, 014027.

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