Application Note #000395

KeyWords
XPS, Human Biomaterial, Minerals, Measurements, Surface Analysis

EnviroESCA™

XPS surface analysis of a human urolith with EnviroESCA

A single human urinary stone (urolith) was characterized using EnviroESCA. The result of surface chemical analysis of the as received samples is presented. Charge neutralization on this insulating material is accomplished by Environmental Charge Compensation.

Motivation

Urinary (kidney) stone disease (urolithiasis) constitutes a major health problem and is affecting an increasing number of people. Calcium oxalate, calcium phosphate, uric acid, ammonium hydrogen urate and magnesium ammonium phosphate are the main components of stones. Dramatic changes in dietary habits including high consumptions of proteins, salt, and fructose rich carbonated beverages represent main causes of an increased incidence of calcium oxalate stones.[1]

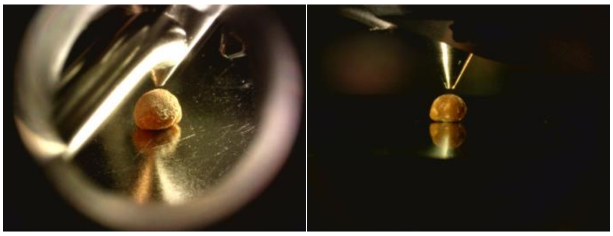

Fig. 1 Urinary stone underneath the analyzer nozzle at a working distance of 0.3mm

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 monochromatic and focused onto the sample.

Thereby only electrons from atoms down to a depth of approx. 10 nm are able to leave the surface in case of solid samples.

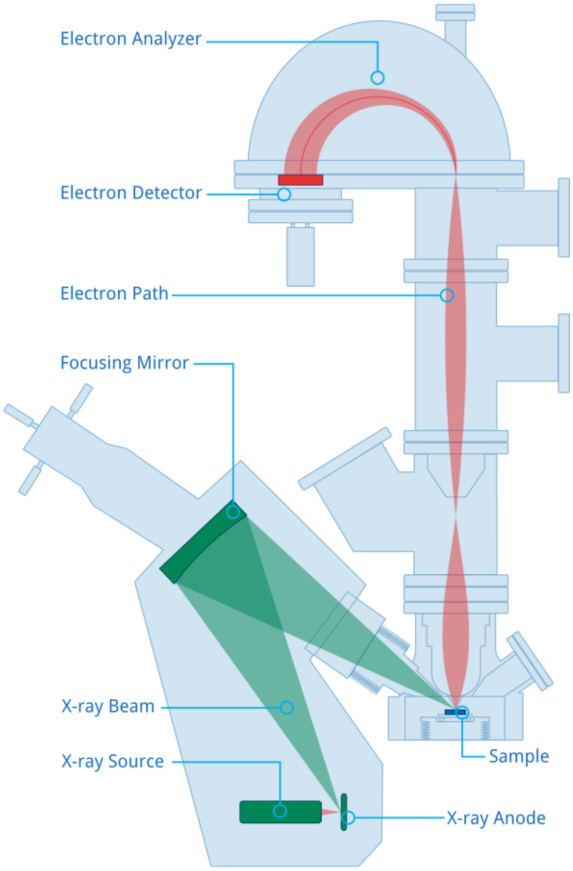

Fig. 2 XPS with EnviroESCA

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 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

Calcium oxalate is the major component of over 70% of all urinary stones in Western countries. Together with further (in)organic components calcium phosphate is another common chemical compound of urinary stones.

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 or biological samples.

In classical XPS systems biomaterial tend to charge up quickly under X-ray illumination due to their insulating nature 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.

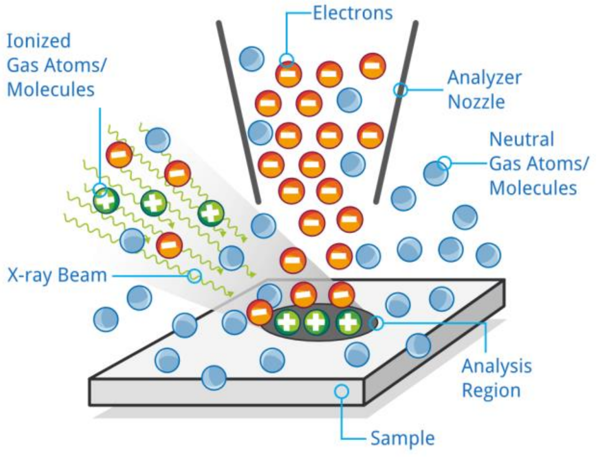

Fig. 3 Environmental Charge Compensation

The gas atmosphere that is surrounding the sample delivers all the free charges, when illuminated with the soft X-rays, that are needed to compensate for surface charging (cf. fig. 3 for an illustration).

The urinary stone sample was obtained from a male adult and was investigated with the EnviroESCA as received without any further pretreatments. A working pressure of 1 mbar of ambient air was chosen for this study to compensate for potential surface charging.

Results

In the following section we are presenting unmodified raw data taken with EnviroESCA which was not smoothened. All detail spectra were referenced using the maximum of the C 1s core-level region at 285 eV.

A whole urinary (kidney) stone, with a diameter of about 3 mm, obtained from an adult male human was investigated at 1 mbar using EnviroESCA. According to the survey spectrum shown in Fig. 4 the urinary stone consists of oxygen, carbon, nitrogen, calcium, and phosphor as the major elements.

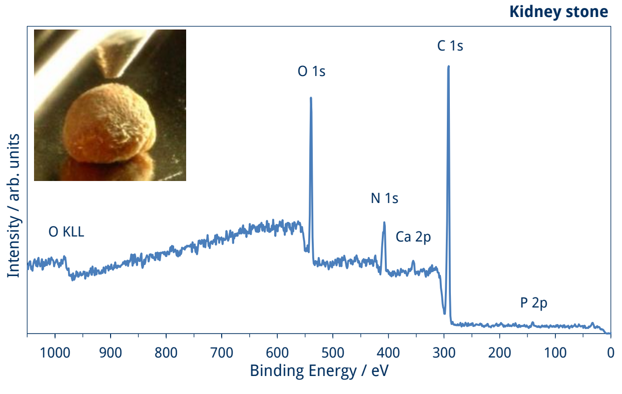

Fig. 4 Survey spectrum of a kidney stone

These findings are in accordance with other XPS studies of calcium oxalate and urinary (kidney) stones.[2,3]

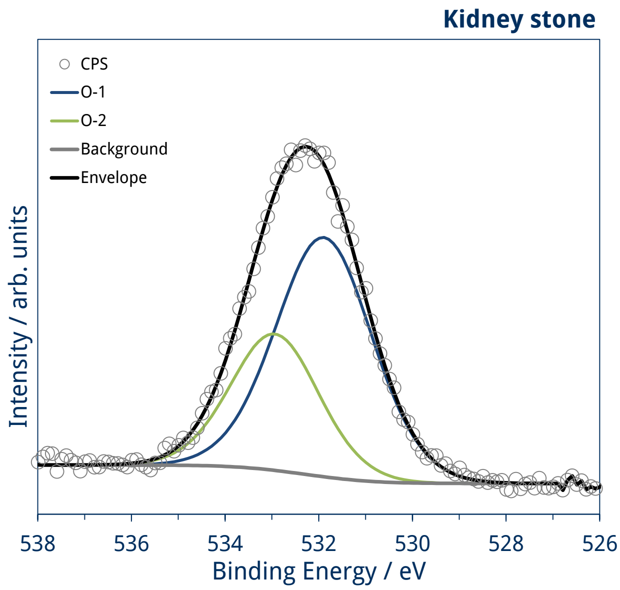

Fig. 5 O 1s core-level spectrum of a urinary (kidney) stone

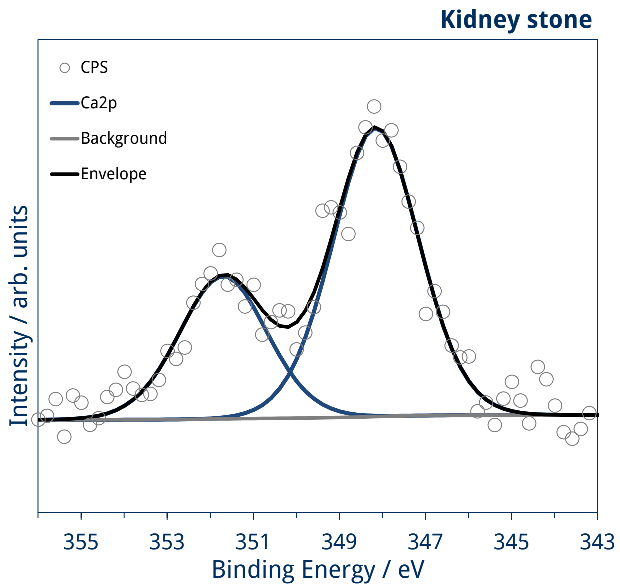

Fig. 6 Ca 2p core-level spectrum of a urinary (kidney) stone

Additional details about the chemical composition are obtained from high-resolution XP spectra of the main elements. O 1s, Ca 2p, and the C 1s core-level spectra (cf. Figs. 5–7) indicate that calcium oxalate (CaC_2O_4) is the main component of the investigated urinary stone. The presence of phosphor suggests also a minimal amount of calcium phosphate, which is usually present in the core.

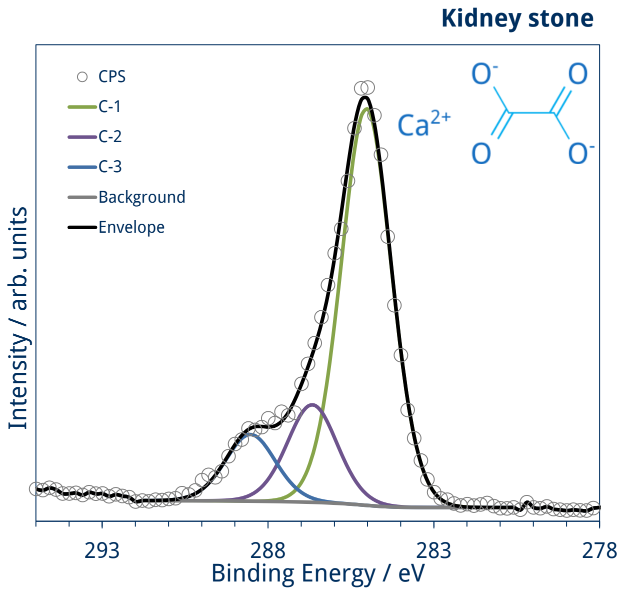

Fig. 7 C 1s core-level spectrum of a urinary (kidney) stone with the chemical structure of calcium oxalate (inset)

Conclusion

EnviroESCA is able to work with samples of human origin in near-ambient pressures conditions and opens new routes to study biological materials, e.g., tissue or bone under native conditions.

The new and much easier to use method of Environmental Charge Compensation prevents surface charging of otherwise challenging specimens.

Here we demonstrated with a urinary stone the possibility to study biological (human) samples without special (pre)treatment or sample preparation. The urinary (kidney) stone analysis yielded calcium oxalate as main component together with some phosphate.

[1] J. Cloutier, L. Villa, O. Traxer, M. Daudon "Kidney stone analysis: 'Give me your stone, I will tell you who you are!'" *World Journal of Urology* **2015**, *33*, 157.

[2] J.-M. Ouyang "Identification of Urinary Stone Components by X-Ray Photoelectron Spectroscopy" *Spectroscopy Letters* **2004**, *37* (6), 633.

[3] A. M. Salvi, F. Langerame, A. E. Pace, M. E. E. Carbone, R. Ciriello "Comparative Spectra Illustrating Degradation of $CaC_2O_4{\cdot}H_2O$ During XPS Analysis" *Surface Science Spectra* **2015**, 22, 21.