



KeyWords

XPS, Roman Coin, Archaeology, Ancient artifacts, Measurements, Surface Analysis

EnviroESCA applications in Scientific Archaeology

This application note presents the application of EnviroESCA to the field of Archaeometry. Besides the ability of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) to analyze the surface composition of metallic and nonmetallic specimens, EnviroESCA allows for a nondestructive analysis of artifacts without special pretreatment procedures.

Motivation

When it comes to the analysis of ancient artifacts the first methods that come to mind are based on photo-optical techniques. First of all because they can mostly be applied to artifacts of all sizes and do not harm or destroy the specimens. Surface Science techniques that require vacuum in machines that can only handle relatively small portions of the relics are powerful methods that allow determining the surface composition of the specimen. But these techniques require the samples to be vacuum compatible, to not outgas, to be cut in pieces or small chunks. Until now.

EnviroESCA is the next generation tool for Photoelectron Spectroscopy with X-rays (XPS) in Archaeometry and Scientific Archaeology as it accepts samples with a maximum diameter of 120 mm whereas the inner 28 cm² (circle of 60mm dia.) of the specimen can be analyzed. EnviroESCA does not require high vacuum or ultra-high vacuum to operate as it can also operate in pressures up to 100 mbar, it does not require the specimen to be cleaned with divergent or other chemicals, blowing of loose particles with dry nitrogen gas or dry air is sufficient. Due to an intrinsic charge compensation effect the operator does not bother with charge compensation equipment for almost all samples independent of their type, metallic, non-metallic, ceramic, organic, organometallic or even liquid. The samples can be laid flat without gluing or mechanical fixing (dependent on the weight of the sample) onto the sample stage.

For very sensitive samples humidified air can be supplied during the analysis along with other inert gases if needed. After the non-destructive analysis with XPS the sample can be directly brought back to the collection in the exhibition hall or handed over to the collector.



Fig. 1 Roman coin showing the face of Licinius (308-324 A.D)

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.

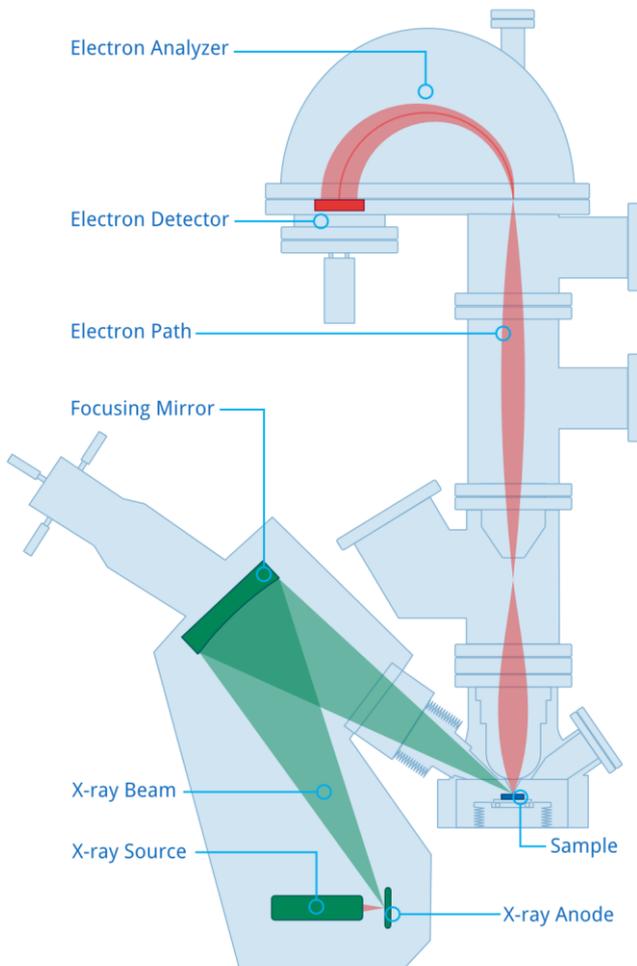


Fig. 2 XPS with EnviroESCA

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 an intensity in counts / 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.

An intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources for charge compensation as in classical XPS systems unnecessary. The gas atmosphere that is surrounding the specimen delivers all the free charges, when illuminated with the soft X-rays, that is needed to compensate for surface charging (see figure 3 for an illustration).

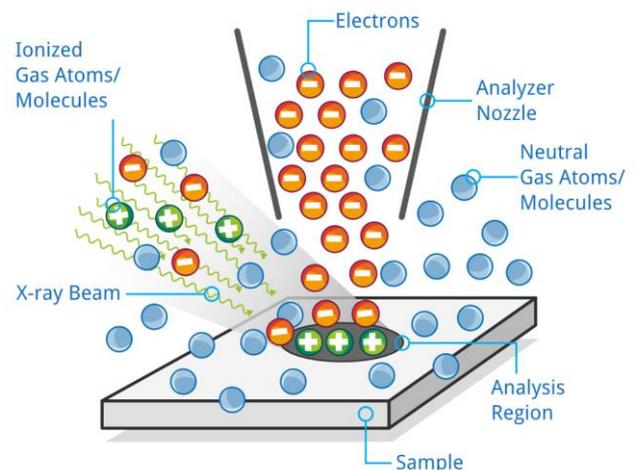


Fig. 3 Environmental Charge Compensation

Experimental Section

For this investigation we have been offered an ancient roman coin from a local collector. The coin is dated 313-314 A.D. and is currently more than 1700 years old. The coin itself has a grey and partly green patina with small orange spots and exposes blank metal at several positions.

Loose dust and particles were removed by blowing gaseous nitrogen across the surface of the coin before it was put on the sample plate. No gluing or mechanical fixing in any way and also no electrical contacting or masking were applied.

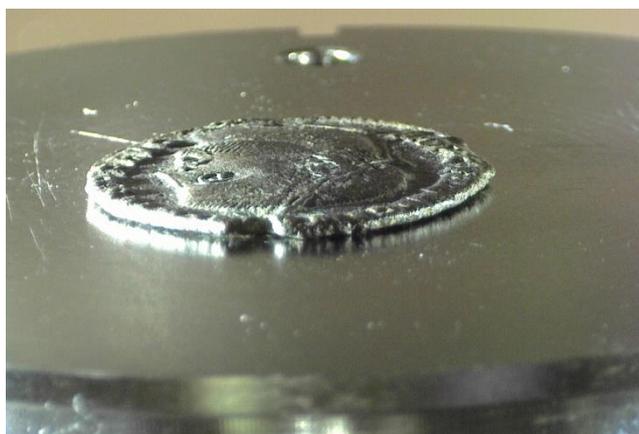


Fig. 4 The coin loosely positioned on the sample plate in the SampleEnvironment

Measurement positions were selected on both sides of the coin for what it took two venting cycles of the SampleEnvironment (approx. 3 minutes each).

Figure 5 shows the three positions where the surface analysis took place.

For the first measurements the exposed surface close to the hand of the displayed person was chosen. The second position is close to the edge of the coin at an orange spot. The third measurement position was placed on the front side of the coin at the end of the nose of the image of Licinivus.

Because the electrical contact to the sample plate differs depending on which side of the coin is establishing the contact we have shifted all following spectra for

comparison in a way that Carbon 1s peaks in different spectra are located at 284.5eV.



Fig. 5 The three measurement positions

Because of the thick patina charging up of the specimen under the illumination with X-rays was expected. To address this circumstance a working pressure of 1 mbar ambient air was chosen so that the binding energy shift in the spectra due to charging effects were negligible (only 2.45 eV).

As these coins are known to be made of alloys of metals that were available at this time survey spectra with longer acquisition time were measured on each position before regions in the energy spectrum were selected for the recording of detail spectra.

Results

In the following unmodified raw data taken with EnviroESCA will be presented. The data was not smoothed. For comparison the spectra were shifted on the energy scale so that the Carbon 1s peak on all survey spectra is located at 284.5 eV, as mentioned above.

1. Position

Figure 6 shows a photograph of the analysis area that was selected for the first spectra.



Fig. 6 First measurement position

After pumping down of the SampleEnvironment to about 1 mbar the data acquisition was started which delivered the survey spectrum of figure 7.

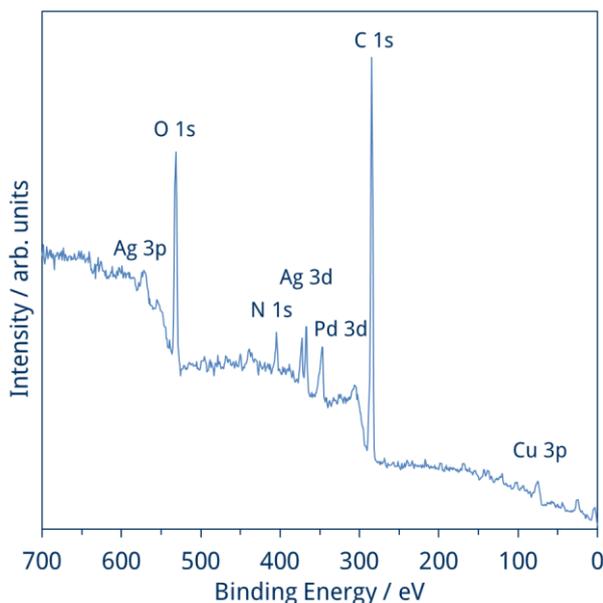


Fig. 7 Survey XPS spectrum recorded at position 1

This spectrum was recorded in 12 minutes and 25 seconds with a step width of 1 eV. The spectrum shows clear evidence of Silver and Copper besides large Oxygen, Nitrogen and Carbon 1s core level peaks. Peaks resulting from electrons escaping Palladium atoms are also visible.

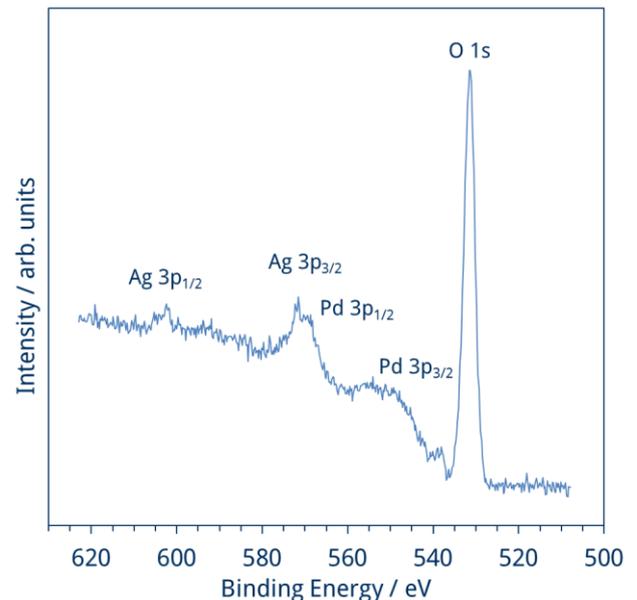


Fig. 8 A closer look at the Oxygen 1s region

A closer look at the Oxygen 1s region (see fig 8) shows a light oxidation of the silver as the Ag 3p peaks exhibiting shoulders on the higher binding energy side. The low energy shoulder of the Ag 3p_{3/2} peak results from the Palladium 3p_{1/2} core level excitation.

The spectrum displayed in figure 9 is a detail view at the Carbon 1s region on the spectra where besides the intense Carbon 1s the split 3d peaks of Silver and Palladium can be seen. The sharp Nitrogen 1s core level emission is due to the ambient air gas phase surrounding the specimen in this experiment. The spectra is the result of 5 scans of this region with a step width of 0.2 eV and a total measurement time of 17 minutes and 13 seconds.

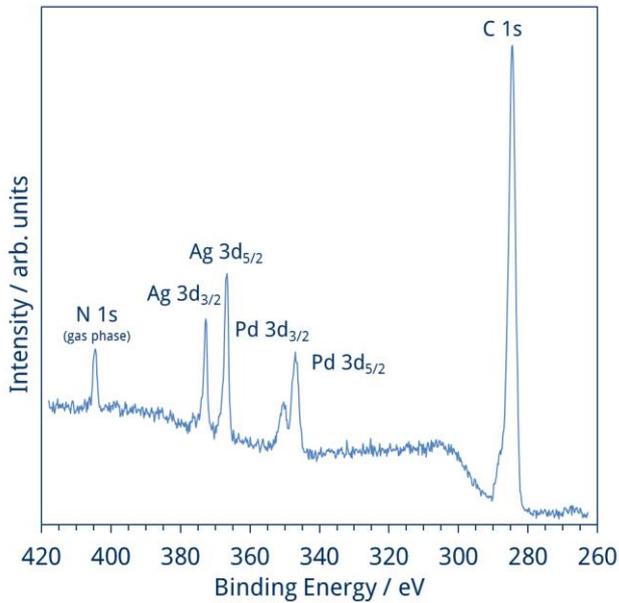


Fig. 9 Detail view at the Carbon 1s region

The valence band spectrum recorded at this position shows peak structures related to Copper, Lead, Palladium and Sulfur (see figure 10 for details)

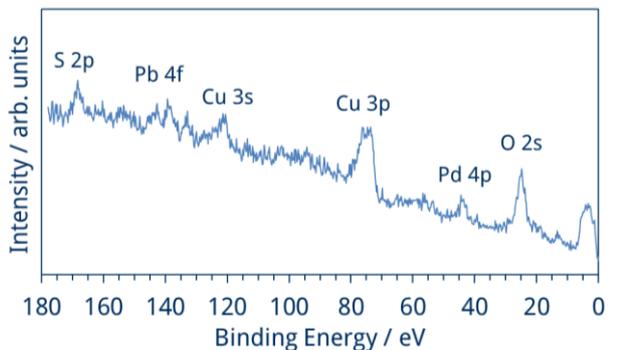


Fig. 10 Valence band spectrum recorded at position 1

2. Position

The survey spectrum recorded at the second position at the edge of the coin reveals Silicon core level peaks (2s and 2p) in addition to the peaks of the metals also found at position 1.

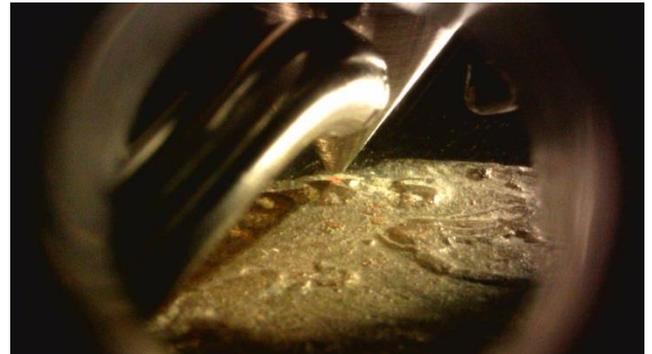


Fig. 11 Measurement position 2 underneath the analyzer nozzle

The detection of signals belonging to Silicon can be due to sand that was not removed by the cleaning with dry nitrogen. Nevertheless the valence band spectrum shown in figure 12 shows a nicely split Lead 4f peak in between the Silicon 2s and 2p core level peaks.

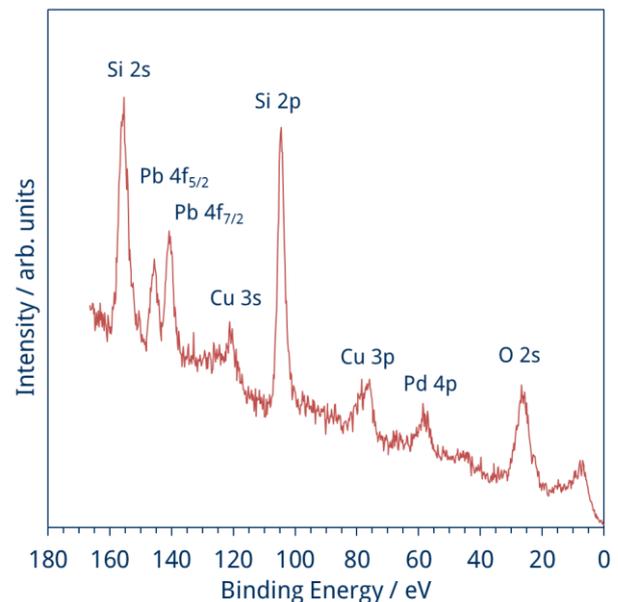


Fig. 12 Valence band spectrum recorded in about 20 minutes

3. Position

For the third measurement position a site on the front side was chosen. Because a position at the tip of the nose caught the eye with a metallic luster the position shown in figure 13 was selected.

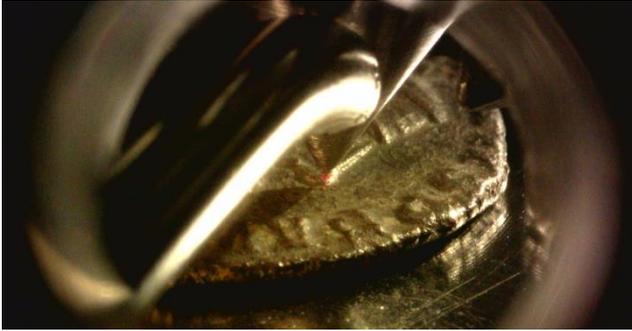


Fig. 13 The third measurement position on the front side of the coin

The survey spectrum measured at this position shows more pronounced Silver peaks than in the other survey spectra (figure 14). In addition a peak resulting from Tin on the surface is visible (Sn 3d).

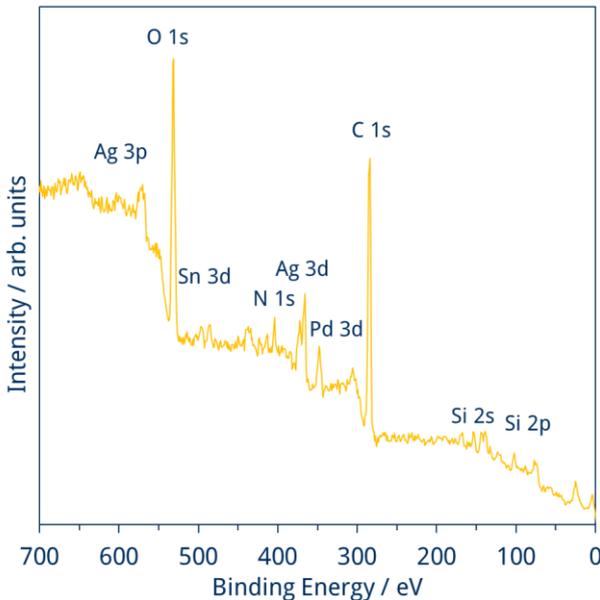


Fig. 14 Survey spectrum measured at position 3

A closer look at this region presents signals from metallic Silver and oxidized Silver on the surface resulting in the shift of the split Silver 3d peak towards higher binding energies.

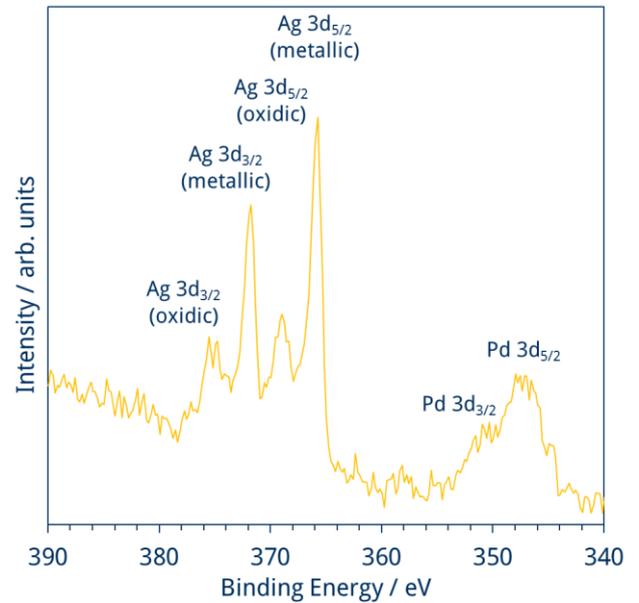


Fig. 15 Silver 3d region of the spectrum

Conclusion

EnviroESCA using Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) or Ambient Pressure-XPS (AP-XPS) as it is also called has shown its ability in the analysis and characterization of the surface composition of artifacts without the need to damage or destroy them for data acquisition.

Even on a sample with a thick patina it was easy to find sites on the faces of the coin for analyzing the metal surface. The small spot size of the X-ray source of the EnviroESCA comes in handy to suppress the signal of the surrounding patina and organic residues.

We were able to provide evidence that the coin was made up of a bronze consisting of the following metals: Silver, Lead, Copper, Tin and Palladium.