

# Parameter study of self-absorption effects in TXRF-XANES analysis of arsenic

F. Meirer<sup>a</sup>, G. Pepponi<sup>b</sup>, C. Strel<sup>a</sup>, P. Wobrauschek<sup>a</sup>, P. Kregsamer<sup>a</sup>, N. Zoeger<sup>a</sup>, and G. Falkenberg<sup>c</sup>

<sup>a</sup> *Atominstytut, Vienna University of Technology, 1020 Wien, Austria.*

<sup>b</sup> *ITC-irst, via Sommarive 18, 38050 Povo (Trento) Italy*

<sup>c</sup> *Hamburger Synchrotronstrahlungslabor at DESY, 22607 Hamburg, Germany*

Total reflection X-Ray Fluorescence (TXRF) analysis in combination with X-ray Absorption Near Edge Structures (XANES) analysis is a powerful method to perform chemical speciation studies at trace element levels [1-4]. However, when measuring samples with higher concentrations and in particular standards, damping of the oscillations is observed. In this study the influence of self absorption effects on TXRF-XANES measurements was investigated by comparing measurements with theoretical calculations. Preliminary investigations showed a significant damping of the XANES spectra of standard samples [3, 4]. This effect could be correlated to self absorption effects. It is therefore of interest to investigate the absorption effect depending on the total mass deposited. As(V) standard solutions were prepared at various concentrations and dried on flat substrates. TXRF-XANES measurements of these samples confirmed a correlation between the damping of the oscillations and the As mass deposited. A Monte-Carlo simulation was developed using data of the samples shapes obtained from confocal white light microscopy. The results showed good agreement with the measurements; they confirmed that the key parameters are the density of the investigated atom in the dried residues and the shape of the residue, parameters that combined define the total mass crossed by a certain portion of the incident beam.

The arsenic K-Edge XANES measurements in fluorescence mode and grazing incidence geometry were carried out using the setup at the beamline L at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY [1, 5]. All measurements were performed in vacuum. A sample series consisting of dried droplets on quartz reflectors with masses of 4, 9, 20, 72, 100 ng and 500 ng of arsenic was additionally analyzed with a confocal optical microscope to gain information about the 3-dimensional shape of the dried residues.

The results of the TXRF-XANES measurements showed a linear correlation of the damping of the oscillations of the scans with the total mass of the samples (Figure 1a). It was assumed that this attenuation originates from self absorption effects caused by the extreme grazing incidence geometry. To verify this hypothesis a simple Monte-Carlo algorithm was developed to simulate these effects. The data about the geometry of the samples required for the simulations was received by measurements with a confocal microscope (Figure 2). The simulations performed with this data showed good agreement with the measurements confirming the influence of sample mass and geometry on the damping of the oscillations above the edge (Figure 1b). The sharp edge-step of the simulations derives from the devolution of the theoretical  $\tau_K$  used for the simulation. However, for the investigation of the damping of the oscillations above the edge this region is of little interest.

With these results we show that performing an Extended X-ray Absorption Fine Structure (EXAFS) analysis under grazing incidence conditions for higher concentrated samples is very difficult. The damping of the oscillations would make a study of the EXAFS signal almost impossible. A direct correction of the measured scan is not possible because of the loss of information that the phenomenon brings about. For dilute samples on the other hand the measurement time has to be increased drastically to get reasonable counting statistics. With TXRF acquisition for XANES used as a fingerprint method the investigated self-absorption effect is not dramatic. The energy position of the absorption edge is slightly affected for very high concentrations. This effect does not hinder quantitative evaluations, especially if analysis is carried out by fit of the XANES spectra with analytical functions [6, 7]. However, for a quantitative analysis performed by fitting of scans of unknown samples with those of known reference samples (linear combination method) it would be desirable to have undamped references. Therefore a compromise between counting statistics, measurement time and absorption effects has to be found for the measurement of (higher concentrated) standard samples. The presented work proposes a rather simple way to study *a priori*

the absorption effects that will show up in TXRF-XANES and allow the scientist to prepare the sample according to needs (measuring time, acceptable self absorption) for the actual experiment. Moreover the method could be extended to allow the *a posteriori* correction for the self absorption of higher concentration standards.

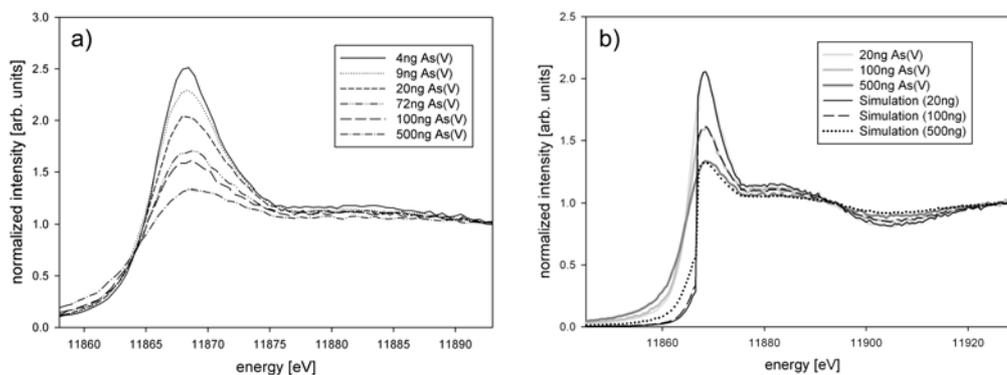


Figure 1: a) XANES scans of sample series 2 (4 - 500ng of As(V) on quartz reflectors) showing the damping of the oscillations. b) Measurements and simulations for three samples of this series.

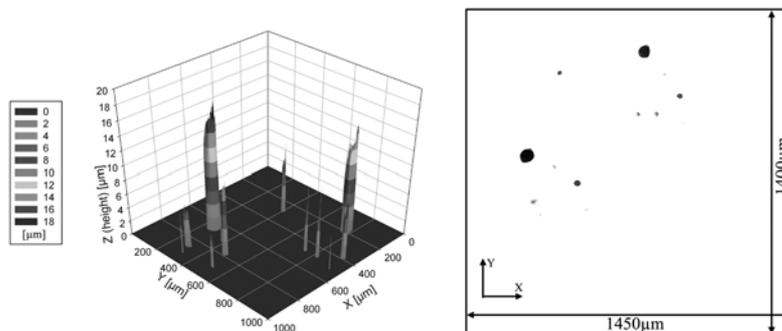


Figure 2: Corrected three dimensional and corresponding lateral distribution of the "100ng As(V)" sample obtained by confocal optical microscopy.

This work was presented at the TXRF conference 2007 in Trento, Italy and supported by the Austrian Science Fund (FWF), Proj.Nr.: P18299 and the EC, Proj.Nr.: II-20042060.

## References

- [1] C. Strelj, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Zaray, X-Ray Spectrometry 34 (2005) 451-455.
- [2] A. Singh, K. Baur, S. Brennan, T. Homma, N. Kubo and P. Pianetta, MRS Proceedings 716 (2002).
- [3] G. Falkenberg, G. Pepponi, C. Strelj, P. Wobrauschek, Spectrochimica Acta Part B: Atomic Spectroscopy 58 (2003) 2239-2244.
- [4] F. Meirer, G. Pepponi, C. Strelj, P. Wobrauschek, V.G. Mihucz, G. Záray, V. Czech, J.A.C. Broekaert, U.E.A. Fittschen, G. Falkenberg, X-Ray Spectrometry 36 (2007) 408-412.
- [5] C. Strelj, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Zaray, J. Broekaert, U. Fittschen, B. Peschel, Spectrochimica Acta Part B: Atomic Spectroscopy 61 (2006) 1129-1134.
- [6] J. Osán, B. Török, S. Török, K.W. Jones, X-Ray Spectrometry 26 (1997) 37-44.
- [7] F. Goodarzi, F.E. Huggins, Energy Fuels 19 (2005) 905-915.