

Arsenic speciation in cucumber (*Cucumis sativus* L.) xylem sap by K-edge TXRF-XANES

F. Meirer, G. Pepponi¹, C. Strelti, P. Wobrauschek, V. G. Mihucz², G. Záray², V. Czech³, J. A. C. Broekaert⁴, U. E. A. Fittschen⁴ and G. Falkenberg⁵

Atominstytut, Vienna University of Technology, 1020 Wien, Austria

¹ITC-irst, via Sommarive 18, 38050 Povo (Trento) Italy

²Joint Research Group of Environmental Chemistry of Hungarian Academy of Sciences and L. Eötvös University, P. O. Box 32, H-1518 Budapest, Hungary

³Department of Plant Physiology, L. Eötvös University, P.O. Box 120, H-1518, Budapest, Hungary

⁴Department of Chemistry, University of Hamburg, 20146 Hamburg, Germany

⁵Hamburger Synchrotronstrahlungslabor at DESY, 22607 Hamburg, Germany

X-Ray Absorption Near Edge Structure (XANES) analysis in combination with Synchrotron Radiation induced Total reflection X-Ray Fluorescence (SR-TXRF) acquisition was utilized for the speciation of arsenic in cucumber (*Cucumis sativus* L.) xylem sap.

Different arsenic species have different toxicity - consequently information on the oxidation state is necessary to assess health risks caused by arsenic entering the food chain. Inorganic species, like arsenite and arsenate, are more toxic than the organic ones, e.g. monomethyl arsonic (MMA) and dimethyl arsinic (DMA) acids, and arsenite (As(III)) is generally more toxic than arsenate (As(V)). It is assumed that plants have the capability to change the oxidation state of arsenic and therefore, this issue was investigated.

XANES measurements deliver information on the oxidation state of the element of interest. By utilizing X-ray Fluorescence Analysis in the TXRF geometry for XANES measurements, an analysis of trace absolute amounts (pg) of most medium Z elements is possible. For the case of arsenic, speciation down to 30 ng/mL level in these samples was found possible.

A major challenge in elemental speciation is to avoid chemical transformation during analyses. In this work the big advantage of SR-TXRF is utilized that the xylem sap can be directly measured after collecting it with micropipettes in argon atmosphere. It could be shown that the oxidation state was not altered during analysis by repetition of measurements. All measurements were performed in vacuum.

Experiments were performed by growing cucumber plants in hydroponics containing As(III) or As(V) in order to identify the arsenic species of the collected xylem saps. Arsenate and arsenite standard solutions diluted to 10 ng/mL, as well as nutrient solutions containing arsenic in the two above-mentioned species in concentrations of 150 and 750 ng/mL, and xylem sap containing arsenic in concentrations in the 30-50 ng/mL range have been analyzed and compared.

The vacuum chamber for SR-TXRF analysis with a new sample changer, now available at the bending magnet Beamline L of HASYLAB [1-2], was utilized to carry out K-Edge XANES measurements for arsenic in the fluorescence mode. The exciting energy was tuned with a Si(111) double crystal monochromator and the fluorescence spectra were recorded using a Silicon Drift Detector (SDD) with an active area of 50mm².

The As(III) contained in the nutrient solutions was found to be partially oxidized to As(V) after a certain time period (48h). It was possible to quantify the phenomenon by performing a linear fitting of the XANES spectra of the nutrient solutions with the XANES spectra of the standards.

Analysis of the xylem saps showed that the As(V) taken up from the nutrient solution was reduced to As(III). Although the signal to noise ratio of these spectra here was worse quantitative

results could also be obtained. These findings are consistent with the result obtained in Reference [3].

It is assumed that the reduction of As(V) to As(III) is an essential process for arsenic detoxification (e.g., by depositing As(III) in the senescent leaves fronds [4]), although As(III) is generally more toxic than As(V). However, as arsenate acts as an analogue of phosphate, and therefore can alter the energy metabolism of the plants, the reduction of As(V) to As(III) seems to be crucial.

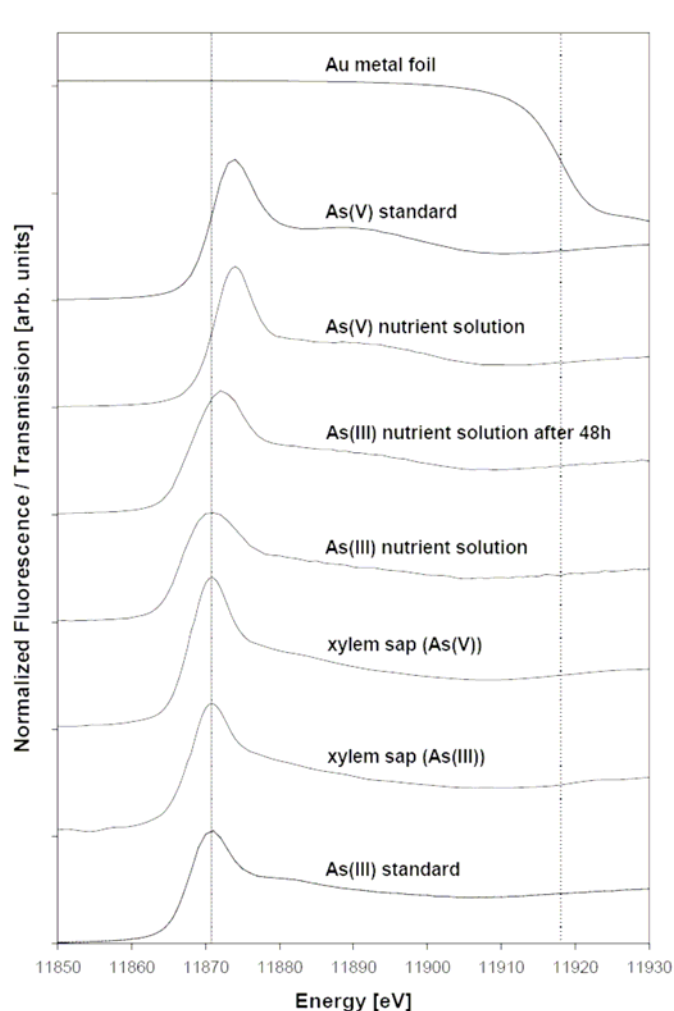


Figure 1: Normalized arsenic K-Edge XANES spectra for xylem sap, nutrient solution and As standard solution. The spectra are displaced vertically for clarity. The energy scale was corrected to the Au-L3 edge (11918 eV), which is indicated by the vertical dotted line. To illustrate the edge shifts, the vertical solid line marks the peak position above the edge in the spectra of the As(III) standard solutions.

References

- [1] C. Strelí, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Záray, *X-Ray Spectrometry*, 2005. **34**(5): p. 451-455.
- [2] C. Strelí, G. Pepponi, P. Wobrauschek, C. Jokubonis, G. Falkenberg, G. Záray, J. A. C. Broekaert, U. E. A. Fittschen, and B. Peschel, *Spectrochimica Acta Part B: Atomic Spectroscopy*. **In Press, Corrected Proof**.
- [3] V. Mihucz, E. Tatár, I. Virág, E. Cseh, F. Fodor, and G. Záray, *Analytical and Bioanalytical Chemistry*, 2005. **383**(3): p. 461-466.
- [4] W. Zhang, Y. Cai, C. Tu, and L. Q. Ma, *The Science of The Total Environment*, 2002. **300**(1-3): p. 167-177.