

μ -SR-XRF Imaging of heavy metals in the cells of hyper-accumulator plants used in phytoremediation technology

Akiko Hokura^a (8701), Ryoko Onuma^a (13356), Kyoko Shirai^a (8687),
Izumi Nakai^{a*} (3077), Yasuko Terada^b (4099)

^a Faculty of Science, Tokyo University of Science, ^b JASRI, SPring-8

Phytoremediation is the use of plants to remove, destroy or sequester hazardous substances from the environment. It is an emerging technology for environmental remediation that offers promise as a low-cost, versatile technique suitable for use against a number of different types of contaminants in a variety of media. Some specific kinds of plants are known as the hyperaccumulator for heavy metals; for example, it was reported that brake fern accumulated high level of arsenic (As: ca. 22,000 p.p.m.) when they were grown on the contaminated soils.¹ It is quite interesting to know how they efficiently extract such a toxic heavy element from the contaminated soil into its fronds. In the present study, X-ray fluorescence (XRF) spectroscopy using a synchrotron radiation (SR) microbeam was applied to the hyperaccumulator plants for As or Pb in order to reveal the distribution of toxic heavy elements in these tissues and cells and investigate their physiology and accumulation mechanism for heavy elements.

The plant samples, e.g. tobacco and

mustard, cultivated with MS medium containing As or Pb were subjected to the analysis. The samples were prepared as a slice of tissues by microtome. The μ -SR-XRF imaging was carried out at BL37XU of SPring-8. Monochromatic X-ray microbeam (beam size $0.7 \times 1.2 \mu\text{m}^2$) was produced by Fresnel zone plates.² X-rays with energy of 13.04 and 14.6 keV were used for the XRF imaging of As and Pb, respectively.

The two-dimensional distributions of the trace elements in the plant tissues and cells were clarified. It was found that As and Pb were accumulated in the vascular tissue and the cell wall seemed to play some role. The present study has demonstrated that the SR-XRF microprobe is a powerful tool for ultra-sensitive analysis of the hyperaccumulator plant to reveal the distribution of trace heavy elements with a cell-level resolution.

References.

- 1) L.Q. Ma, K.M. Komar, C. Tu, W. Zhang, and Y. Cai, *Nature*, **409**, 579 (2001)
- 2) Y. Suzuki *et al.*, *Jpn. J. Appl. Phys.* **40**, 1508 (2001).

Design of a high resolution x-ray fluorescence spectrometer for chemical state analysis of light elements

*Shinjiro Hayakawa (1240)^a, Taku Esumi (13059)^a, Hideaki Matsuo (7062)^a, Kazuma Yamane (8438)^a, Yasuhiro Nagai(8439)^a, Susumu Tohno (6032)^b, Chang-Jin Ma (7495)^b, Atsushi Morikawa(9904)^b and Takeshi Hirokawa (3151)^a

^a Department of Applied Chemistry, Hiroshima University, Hiroshima 739-8527, Japan

^b Department of Socio-Environmental Energy Science, Kyoto University, Kyoto 611-0011, Japan

Trace elemental analysis using an x-ray microprobe is a powerful tool for many research subjects in materials science, life science and environmental science[1]. Though the information on chemical state or local structure of 3d transition metals can be easily discussed using XAFS spectra or high resolution x-ray fluorescence (XRF) spectra[2], chemical state analysis of counter light elements has intrinsic difficulties because the tunable energy range cannot cover the absorption edge of the element of interest. As the lowest limit of the tunable energy range is around Ti K edge for the BL37XU, we have been exploring the possibilities of chemical state analysis using high resolution XRF spectroscopy. In this period experimental layout for high resolution XRF analysis of Si, P, S and Cl has been examined.

Fig. 1 shows Fe K β spectra of SUS304 thin film and FeO dispersed onto adhesive tapes. A spectrometer composed of a flat Ge 111 analyzer crystal and a PSPC was used[2]. The peak energies of spectra were not calibrated, and the unexpected peak shift was observed between two spectra owing to the misalignment of the sample surface.

As the Bragg angle of Ge 111 reflection for S K α line is similar to that of the 333 reflection for Fe K β line, the similar experimental layout is applicable for S K α line except that the attenuation of the XRF with the windows and the air path should be considered. The PSPC is usually operated with the gas pressure of 3 atm, and the chamber is covered with the thick Be window to maintain the spatial resolution of the detector. For the light element analysis the detector window is changed to that of the Al coated organic thin film, and the chamber should be used under atmospheric pressure. The degradation of the spatial resolution is approximately 30 %.

Expected count rate for S K α was estimated from the count rate for Cu K α with the 10 keV

incident x-rays of 150 $\mu\text{m} \times 500 \mu\text{m}$ (V). Considering the sensitivity for S is smaller than that for Cu by the factor of 1/40, the expected count rate for S is approximately 40 cps without the attenuation through the path. Owing to the delay in fabrication of He filled chamber for analyzer crystal the high resolution XRF measurements of S were gave up in this experiment.

Rest of the beam time was utilized for XAFS measurements of dissolved Cu into the silicon lattice. The Cu film of 6 nm in thickness was deposited onto the Si wafer using an electron beam evaporation technique, and the sample was annealed at 400 °C. The obtained Cu XAFS spectra indicate that Cu atoms are in the substitutional site in the Si lattice.

References

- 1) S. Hayakawa *et al.*, *Anal. Sci.* **17s**, i115 (2001).
- 2) S. Hayakawa *et al.*, Experimental report 2003A 6029
- 3) S. Hayakawa *et al.*, *Spectrochim. Acta. B*, **54B**, 171-178(1999).

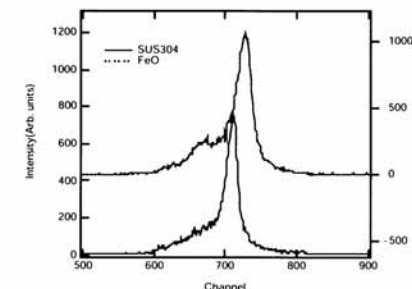


Fig. 1 High resolution XRF spectra of Fe K β region obtained with a flat Ge analyzer crystal and a PSPC. Ge 333 reflection was used for measurements.