

SRXRF and XAS spectroscopy for detection of contaminants in fruits

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Purpose.

The purpose of this experiment was to characterize the chemical environment of *lead* by means of EXAFS/XANES techniques. On another hand, the detection of trace elements present in the different prepared samples by XRF (X-Ray fluorescence) was also carried out.

The samples.

Two kinds of samples were prepared: *phaseolus vulgaris* naturally doped and *pineapple juice* diluted with an aqueous lead solution.

The samples of *Phaseolus vulgaris* were prepared in the CNDRI laboratory, according to the methodology of [Sarret G. et al. 2001]. In our case, we contaminated the plants with nutritive solutions with 37.5, 75 and 125 $\mu\text{mol l}^{-1}$ of lead like $\text{Pb}(\text{NO}_3)_2\text{-EDTA}$. After growth, the samples were dried in cool, grinded and compressed in form of a tablet (13 mm of diameter and 2 mm of thickness).

The pineapple juice samples were obtained by pressing either pulp, skin or heart of the fruit. In order to be able to visualize the capacities of detection, we chose 7 lead concentrations in the pineapple juice (using a $\text{Pb}(\text{NO}_3)_2$ doping solution) and a control sample. The selected concentrations were 1000, 100, 10, 5, 1, 0.1 and 0.05 mg.kg^{-1} . The samples were remained in freezing state until the experiment and quartz capillaries were used for the measurement.

The setup.

The XRF experiment was performed using a monochromatic beam set at 14 keV. We used a 30 multi-elements Germanium detector to collect fluorescence photons. The position of detector was set at 90° and the counting time at 600 s. Depending on the experiment, the detector was moved forwards or backwards or filtered by aluminium foil to avoid the detector saturation.

The X-Ray Absorption Spectrometry experiment was performed using the same experimental device, i.e. using the “fluorescence mode”. Each spectrum was obtained for energies varying in the range from 12,8 to 13,8 keV. The fluorescence signal was recorded counting 2 s in the zone before element absorption, 5 s in XANES zone and up to 10 s in the EXAFS zone.

The experiment.

41 XRF measurements were performed and 122 EXAFS/XANES spectra acquisitions.

The XRF experiments are used to study the relative quantity of the different elements present in the sample. The figure 1 shows a example of spectra obtained with pineapple juice samples with and without doping with Pb. The reference doping solution is also shown for comparison. Apart from Pb, other elements such as Fe (6,4 keV), Ni (7,48 keV), and Zn (8,6 keV) are detected. The spectra are normalised for incident intensity of the beam, and the spectrum of the capillary alone was subtracted.

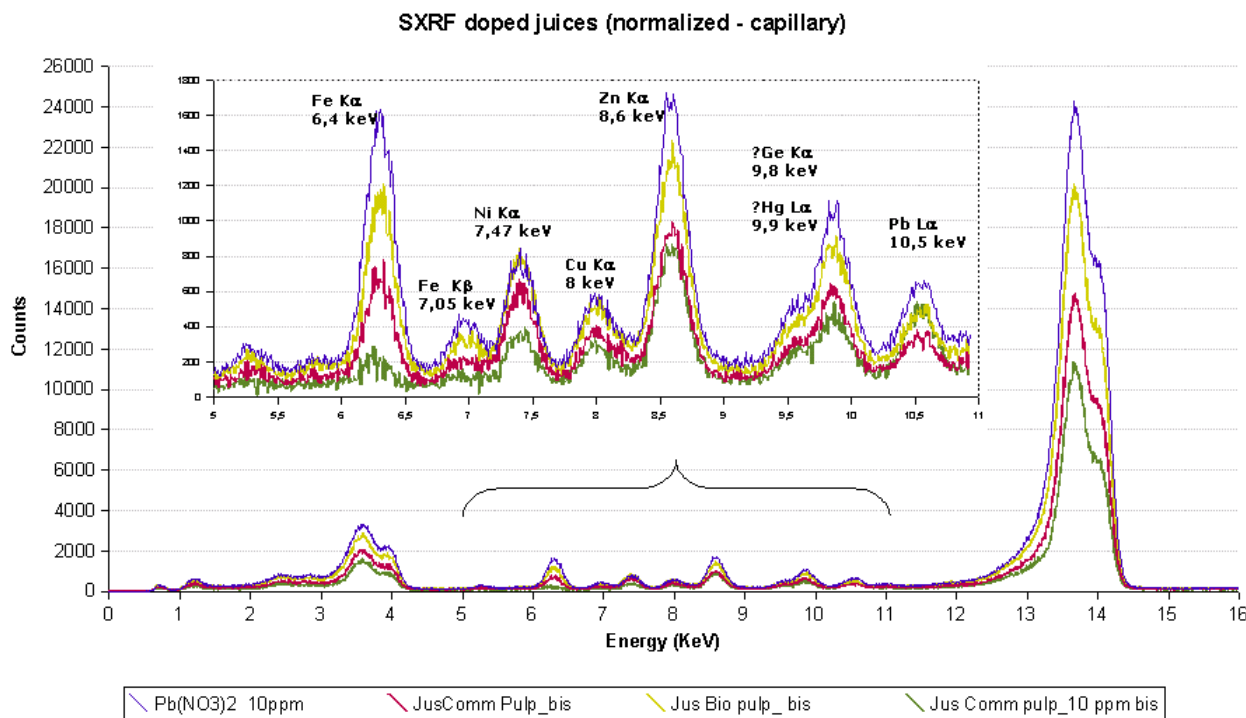


Figure 1: Normalized spectrum obtained for two different pineapple juices, “Jus Comm pulp_10ppm” means juice doped with 10ppm of lead as $Pb(NO_3)_2$.

On the other hand, reference chemical measurements have been carried out, and are shown in the table below. The amount of Pb measured in the doped sample shows that the doping procedure is not perfect. It was identified to be a precipitation problem of Pb.

No Labo	Identification	Cu ppm	Fe ppm	Zn ppm	Ni ppm	Pb ppm
05-06161	1 JUS ANANAS BIO NON DOPE	0,3	1,8	0,7	0,22	0,03
05-06162	2 JUS ANANAS TRAD NON DOPE	0,6	2,2	1,2	0,06	0,04
05-06163	3 JUS ANANAS TRAD DOPE 10 ppm	0,5	1,7	1,0	0,03	4,94

The complete quantitative analysis was not carried out for all the samples, as the geometrical conditions were sometimes modified to avoid saturation. Another problem was the capillary, whose spectrum contains some of the elements present in the samples. Although the capillary spectrum was subtracted, it is expected that changes from one capillary to another could mask the real quantity of an element in the sample.

The only conclusion is that the Pb peak was detected in the 10ppm-doped juice, although the calibration is not accurate enough to relate the peak intensity on the XRF spectrum to the exact value (measured to be about 5 ppm).

Concerning the XANES/EXAFS spectroscopy, the spectra presented on figure 2a) and 2b) have been obtained on *Phaseolus vulgaris* samples. The first interesting result is that the chemical environment of the lead contained inside the doped plants is different from the $\text{Pb}(\text{NO}_3)_2$ reference solution, and from Pb^{2+} and Pb-metallic standards. On another hand, on the EXAFS graph, the peak positions obtained by [Sarret 2001] for Pb-EDTA are reported on the x axis. The values obtained for the plant samples are slightly different, as shown also by [Sarret2001]. The Pb-EDTA is known to be the first complex to appear from the mother solution ($\text{Pb}(\text{NO}_3)_2$ -EDTA), but the values indicate that the speciation changes in the plant itself. Spectra coming from different regions of the plant (root, leaf or stem) only present slight variations.

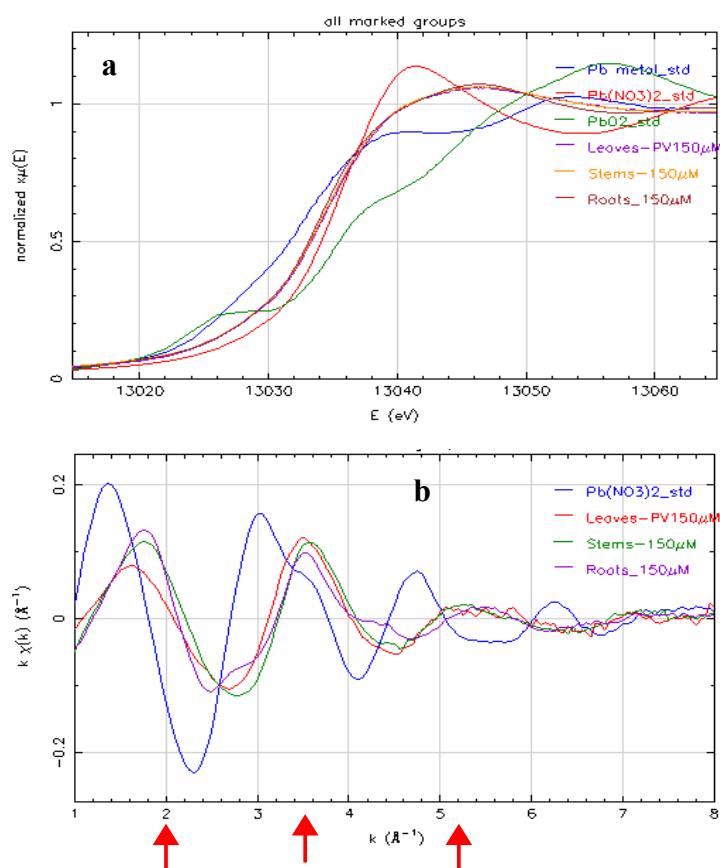


Figure 2: Spectra a)XANES et b)EXAFS obtained on *Phaseolus vulgaris* samples. On the x axis, the arrows indicate the k values reported by [Sarret2001] for Pb-EDTA.

Conclusions.

The characteristics of the beamline allowed to detect concentrations down to 10 mg l^{-1} in pineapple juice (detection without vacuum), however uncertainties due to the capillaries prevent from a quantitative analysis of the results.

More lead organic standards samples are necessary to determine the exact chemical speciation of Pb in the samples of *Phaseolus vulgaris* and therefore, the simulation is not possible. These experiments show the feasibility of XRF, EXAFS and XANES for the study of transport and absorption of trace elements in plants.

References

[Sarret2001] SARRET G., VANGRONVELD J.; MANCEAU A. et al. 2001, "Accumulation forms of Zn and Pb in *Phaseolus vulgaris* in the presence and absence of EDTA". Environ. Sci. Technol. 35,2854-2859.