EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:**	**Experiment number**: HS-2790
Beamline: ID22	**Date of experiment**: from: 15/06/2006 to: 19/06/2006	**Date of report**: 20/07/2006
Shifts: 12	**Local contact(s)**: Isabelle Letard	*Received at ESRF:*

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Report:

During the allocated beam time, we have tested a new experimental geometry to improve the limits of detection of elements down to the ppm level in a fluid sealed in a Diamond Anvil Cell (DAC). Measurements were conducted at room temperature and low pressure on standard solutions. They validate our experimental protocol for lowering the detection limit, and demonstrate the feasibility of *in situ* determination of element as low as 5ppm. This was a necessary step to comfort our set-up and to carry out further experiments in order to determine elemental partitioning between fluid and mineral at high pressure-temperature.

Since the cell designed for the purpose of the LTP on ID22 was not yet machined, we borrowed for this experiment a panoramic DAC from J.C.Chervin and A.San Miguel. However this cell does not allow Hight Temperature measurements. We also tested the gaskets, which are developed in the frame of the current LTP. The most appropriate gasket at the time is a 600 microns ring of titanium with a hole of 200 microns lined in a Teflon® supporting ring. The rather light weight of titanium allows detecting elements which exhibit higher X-Ray fluorescence lines. To fulfill the goal and achieve a very low detection limit, it is of prior importance to lower the signal to noise ratio. The main contribution to the background intensity arises from the Compton scattering due the interaction of the incoming beam and the diamond anvil. This phenomenon produces huge quantities of parasitic radiations from the DAC's body. To reduce these effects, we have placed an indium shielding on the diamonds and their seats, and finally, a collimator of indium was focused on a small area around the sample. On figure 1, one can see the effect of these slights modifications on the X-Ray Fluorescence signal, and show the importance of a shielding on parts submitted to scattering radiation in the DAC.

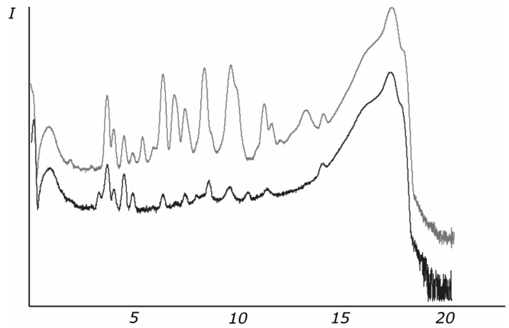

Figure1. X-Ray fluorescence acquisition of the empty gasket. The line in grey is the spectra with no indium shielding. The black one was taken with the indium shielding. The two spectrum are offset in intensity to fully appreciate the peaks arising from the cell and their reductions.

Further improvements are still conceivable in order to reduce the scattering arising from the diamonds. One solution is to use partly drilled diamonds, to reduce the pathway of the X-Ray beam through the diamond anvil.

The monochromatic beam intensity was set to an energy of 18 kev and a spot size of 1.5 x 4.3 square micrometers using a KB mirror focusing device. A 13th Si(Li) elements GRSHAM® detector was placed at 90 degrees, the summation of first row containing six elements and the central element were used to obtained the spectrum, the seven outer elements of the second row were not taken in the sum as too many scattered photons impinged their surface.
Samples were prepared from commercial standard solution for ICP-Mass Spectrometer calibrations. Two single element solutions have been used, and a multi elementary one composed of 24 different species. Dilutions were made to obtain a set of solutions with concentrations ranging from 5ppm to 500ppm. Using this set-up, we were able to achieve a detection down to 5 ppm of Arsenic and Rubidium. In the multi-elementary solution, we were able to detect six different elements down to 10 ppm (Rb, Bi, Tl, Pb, Ga, Mn), the others remained hide by the background arising from the cell's body. Figure 2 illustrates the results obtained with Arsenic in a single element solution. Detection limits have been calculated from these series of spectrum and values of 1.7ppm have been obtained from the 5ppm solution. It is the first time that so low detection limits are obtained in a fluid using SR-XRF in a DAC device.

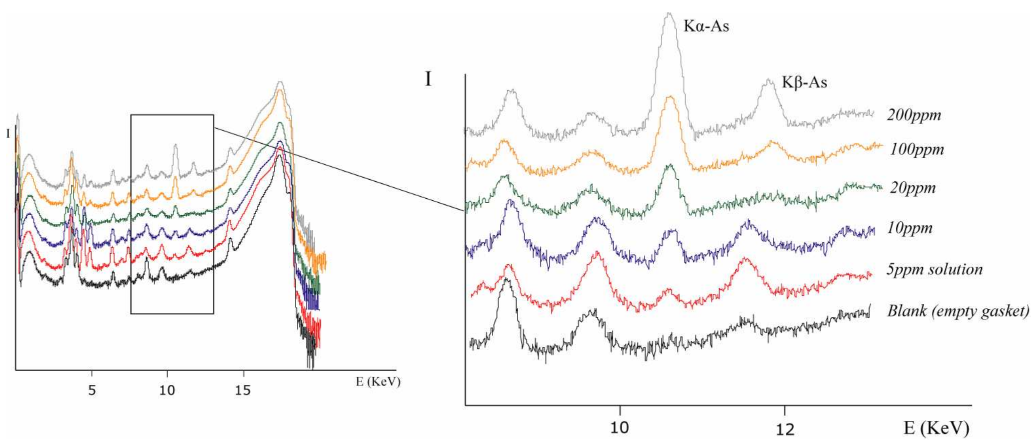

Figure2. X-Ray fluorescence spectra of Arsenic solutions with different concentrations ranging from 5ppm to 200ppm. The first spectrum (lowest) corresponds to the empty gasket for a comparison.

This experiment allows us to validate our protocol and is consistent concerning the capability of detecting element down to the ppm level. The next step will be done with a natural sample in equilibrium with a fluid at extreme conditions. This work will presented at the "Forum de Technologie des Hautes Préssions" in

November 2006. A manuscript is in preparation, that describes the improvements made to lower the detection limit in a DAC.

Hence, during the allocated beam time, we have been able to:

- measure element at the 5ppm level (corresponding to a DL of 1.7ppm), which is one order of magnitude better to precedent studies.
- improve multi element measurements
- secure the High pressure set up at ID22, including motors, detectors…

This first experiment of the LTP was also very helpful to identify the required improvements needed for the definitive HP set up on ID22 such as:

- Shielding the DAC
- using a collimator
- knowing the chemical composition of the diamond glue, but also the gasket composition. We find out that Boron epoxy gasket could not be used for this kind of experiments due to their composition.