



## 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.

	<b>Experiment title: Spectroscopic approach of aqueous chemistry of Protactinium (V)</b>	<b>Experiment number:</b> IH-20-01-645
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from:19/03/06 to:22/03/06	<b>Date of report:</b> 31/08/06
<b>Shifts: 9</b>	<b>Local contact(s):</b> A. Rossberg	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>C. Le Naour*, D. Trubert*, M.V. Di Giandomenico*, Institut de Physique Nucléaire Orsay</b> <b>C. Hennig*, ESRF-ROBL, FZR</b> <b>C. Den Auwer*, C. Fillaux*, A. Jeanson*, P. Moisy, CEA Valrhô</b>		

## Report:

XAS measurements on Pa samples were carried out on the Rossendorf Beam Line (BM20) at ESRF under dedicated ring conditions (6.0GeV at 200mA). Data were collected in the fluorescence mode with a Si (111) water cooled monochromator used in channel-cut mode. For all Pa samples, data were acquired at the Pa L<sub>III</sub> edge (16733 eV).

Unlike the other actinides U, Np, Pu that exhibit a linear trans dioxo bond in their higher oxidation states, Pa (V) species in aqueous solution, has been proved to possess one single oxo bond (in concentrated H<sub>2</sub>SO<sub>4</sub>) or no oxo bond in HF 0,5 M (User Report 32757). This experiment was performed with the aim of getting further information about the structure and the coordination of protactinium (V).

Samples prepared in phosphoric and perchloric acids could not be measured because of Pa precipitation. Polymerization of Pa(V) is known to occur with erratic induction time, especially in perchloric media. However the characterization of an aquo species of Pa(V) would assist in future analysis of protactinium complexes with various ligands. Despite these experimental difficulties, we would like to perform new XAS measurements with “fresh” samples by minimizing time between preparation and experiment on ROBL. This time can be reduced to about 10 hours (instead of more than 10 days) by informing in advance the local contact, the EHO and the Radiation Protection Group of ESRF and IPN Orsay.

In dilute HF media (<10<sup>-3</sup>M), mono-oxo-fluorocomplexe(s) is (are) described in the literature, unfortunately at tracer scale (C<sub>Pa</sub> < 10<sup>-10</sup>M). Only one oxo bond is therefore expected. The XANES spectrum registered during this experiment on the sample of following composition: 10<sup>-2</sup>M HF and 6.8 10<sup>-3</sup> Pa(V), does not exhibit the feature of a linear trans-dioxo bond. However, from our previous results (Pa-O @ 1.72 Å in

H<sub>2</sub>SO<sub>4</sub> and Pa-F @ 2.16 Å in HF 0.5 M), the difference between Pa-oxo and Pa-F distances is expected to be small, leading to an ambiguity with regards to the presence or not of a single oxo bond in these species.

Figure below presents the experimental and fitted Pa L<sub>III</sub> edge EXAFS spectra of samples in HF 10<sup>-2</sup> (red) and 0.5 M (blue). In HF 0.5 M, best fit parameters have been obtained with 7 fluoride ligands at 2.16(2) Å; this pure fluoride ligation agrees with quantum chemistry calculations, leading to PaF<sub>7</sub><sup>2-</sup> at 2.18 Å. On the other hand, in dilute HF medium, results of the fit tend to indicate the presence of one oxo bond at 1.71 Å and 7 F(or O) atoms at 2.13(2) Å. However, these results remain ambiguous, due to the too small difference between both distances. New measurements on Pa samples in diluted fluoride media at higher k values than recorded in this experiment could remove this ambiguity.

