



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.

	Experiment title: Spectroscopic approach of aqueous chemistry of Protactinium(V)	Experiment number: 20-01-645
Beamline: BM 20	Date of experiment: from: 8/06/2005 to: 12/06/2005	Date of report:
Shifts:9	Local contact(s): Ch Hennig	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Claire Le Naour*, Didier Trubert*, Maria Vita Di Giandomenico* CNRS/IN2P3/UPS Institut de Physique Nucléaire 91406 Orsay Cedex, France Clara Fillaux*, Christophe Den Auwer*, Philippe Moisy CEA/Valrhô, DEN/DRCP/SCPS, 30207 Bagnols sur Ceze Cedex, France Christoph Hennig* ESRF, ROBL - Forschungszentrum Rossendorf 38000 Grenoble, France		

Report:

Protactinium measurements were carried out on the ROBL beam line at ESRF (6.0 GeV at 200 mA) in fluorescence mode, at room temperature with a (111) water cooled monochromator in a channel cut mode and all data were acquired at the Pa L_{III} edge (16733 eV).

XAS measurements were performed on samples **I** and **II** in specific 600 µL cells for radioactive samples : Sample **I** 10 mM Pa(V) in H₂SO₄ 13M and sample **II** 10 mM Pa(V) in HF 0.5 M.

Data fitting was carried out in R space without any prior data filtering with Artemis code. Phases and amplitudes were calculated by Feff8.2 code from crystallographic structures of Na₁₀[(UO₂)(SO₄)₄](SO₄)₂·3H₂O (with Z=92 replaced by Z=91 in the Feff input file).

Figure 1 presents the EXAFS L_{III} edge of samples **I** and **II** (both raw EXAFS spectra and corresponding Fourier transform, FT). FT of sample **I** exhibits a single peak, H, suggesting that only one scatter contributes to the signal. According to the literature^{1,2}, seven fluoride ligands have been assumed to be in the first coordination sphere. Best fit parameters give the fluoride ligands at 2.16 Å ($\sigma^2 = 0.0050 \text{ Å}^2$) with R factor = 2.6%. The distances obtained by EXAFS agree well with the Pa-F distances in solid state Na₃PaF₈ (2.22 Å)³ and RbPaF₆ (2.18 Å)⁴. In the FT spectrum of sample **II**, peak D is clearly attributed to a short Pa-ligand bond. Combining this result with the XANES data and simulation of Figure 1 shows unambiguously that sample **II** exhibits a single short P-O bond in a monooxo form. Peak E contains second sphere O ligands and peak F originates from third sphere S ligands. Adjustment of the raw EXAFS spectrum was carried out according to the general formula $\text{PaO}(\text{SO}_4)^{\text{bid}}_n(\text{SO}_4)^{\text{mon}}_p$ from $n = 0$ to 3, $p = 0$ to 7. Because the coordination number in the equatorial plane of actinyls falls between 4 and 6, the coordination number of Pa-O is estimated between 6 and 7 ($2n+p = 6, 7$). Fits with only bidentate sulfates or only monodentate sulfates did not reproduce the experimental spectrum. Fits with $n = 1, p = 4$ or $n = 3, p = 1$ lead to a bad agreement and the optimum number for n was found to be 2. Within the uncertainty associated to amplitude estimation in EXAFS (and in the absence of experimental model compounds) the fit is more sensitive to number n than to number p because n contributes for 2 oxygen atoms and one sulfur atom. The value of p has then been fixed to 3 but the uncertainty is about ± 1 . Best fit structural parameters were obtained with one Pa-O bond at 1.72 Å ($\sigma^2 = 0.0033 \text{ Å}^2$), two bidentate sulfate ligands at 2.41 Å ($\sigma^2 = 0.0038 \text{ Å}^2$) and corresponding S atoms at

3.09 Å ($\sigma^2 = 0.0012 \text{ Å}^2$) and 3 monodentate sulfate ligands at 2.33 Å ($\sigma^2 = 0.0098 \text{ Å}^2$) and corresponding S atoms at 3.73 Å ($\sigma^2 = 0.0050 \text{ Å}^2$). The R factor is equal to 9.0%. Note that peak F is poorly reproduced in the fit (Figure 2b). This is attributed to an amplitude discrepancy between the fit and the experiment since the imaginary parts of the FT are in better agreement. In this scheme, peak G corresponds to multiple scattering contributions from the monodentate sulfate ligands.

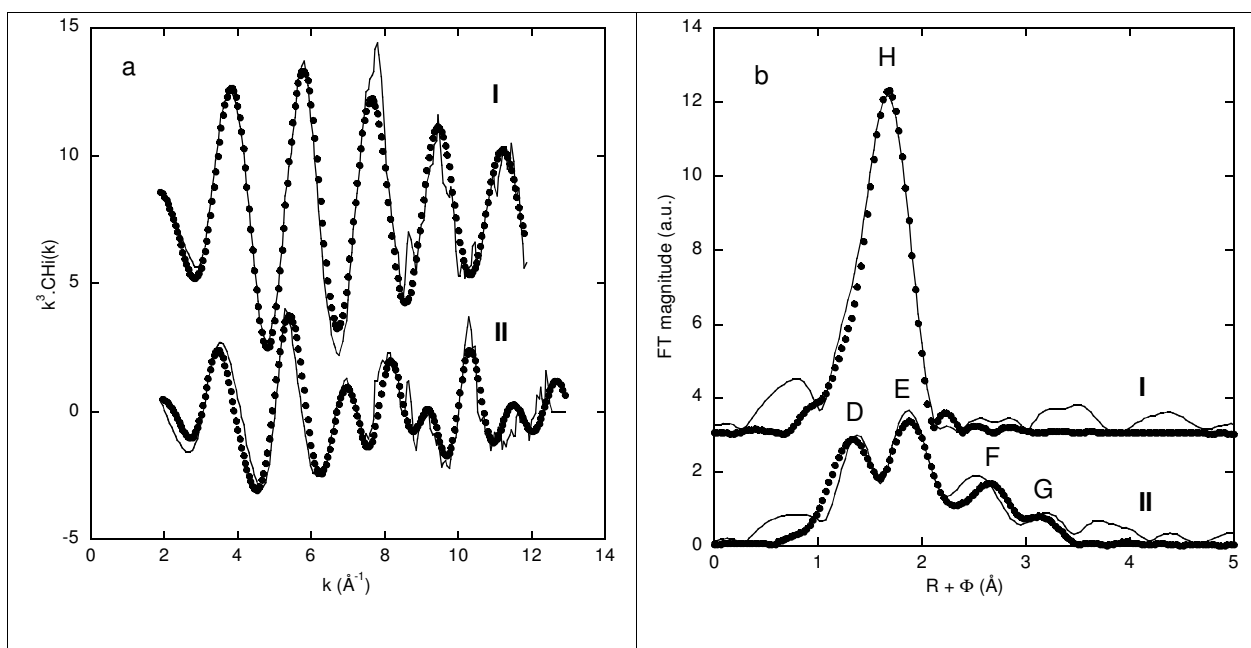


Fig 1 : L_{III} edge EXAFS spectra of samples I (hydrofluoric solution) and II (sulfuric solution). a) raw EXAFS spectra — and fitted curve •••••••• ; b) corresponding Fourier transform (not phase-shift corrected) and fitted curve ••••••••.

These results indicate unambiguously the presence of an oxo bound in H_2SO_4 13 M medium, as postulated for more dilute media where the species PaOSO_4^+ and $\text{PaO}(\text{SO}_4)_2^{2-}$ have been proposed.² Furthermore, the number of mono- and bi-dentate sulfate ligands deduced from EXAFS agrees with one of the formulations of the oxo-trisulfato-protactinate (V) proposed by Bagnall *et al.*⁵ These results report the first structural characterization in aqueous solution of a Pa-O oxo bond in a Pa(V) sulphato adduct. In contrast, no oxo bond has been found in the Pa(V) fluoro adduct.

Results were submitted and accepted for publication in Inorg. Chem.

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- 1) R. Guillaumont, G. Bouissières, and R. Muxart, *Actinides Rev.*, 1968, **1**, 135
- 2) R. Muxart, and R. Guillaumont, *Compléments au Nouveau Traité de Chimie Minérale-2-Protactinium*, Masson ed, Paris, 1974
- 3) Brown, D. ; Easey, J.; Rickard, C. E. *J. Chem. Soc. A* **1969**, 1161-1164.
- 4) Burns, J. H. ; Levy, H. A. ; Keller, O. L. *Acta Cryst.* **1968**, B24, 1675-1680.
- 5) Bagnall, K. W.; Brown, D.; Jones, P. J. *J. Chem. Soc.* **1965**, 27, 176-181.