

## Experiment Report Form

**The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL).** This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the FZD. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

### Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.


### Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

### 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 / experiment 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.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as "Times" or "Arial" , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

 ROBL-CRG	<b>Experiment title:</b>  <b>Investigation of the molecular structure of actinide solvent extraction compounds</b>	<b>Experiment number:</b>  CH-2969
<b>Beamline:</b>  BM 20	<b>Date of experiment:</b> from: 4/12/2009 to: 8/12/2009	<b>Date of report:</b>  1/07/2010
<b>Shifts:</b>	<b>Local contact(s):</b>  C. Hennig	<i>Received at ROBL:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  Clara Fillaux*, Christophe Den Auwer*, Gaëlle Dupouy*, Thomas Dumas*, Samir Dahou*, Xavier Crozes* CEA Marcoule, DEN/DRCP/SCPS, 30207 Bagnols-sur-Cèze, France		

## Report:

XAS measurements have been carried out on U(VI), Pu(IV), Np(IV) and Th(IV), in presence of nitric acid and tributylphosphate (TBP) solution. The data were acquired at the An L<sub>3</sub> edges, for each complex (17166 eV for U, 16300 eV for Th, 17610 eV for Np, 18057 eV for Pu).

Data fitting were carried out in R space, phases and amplitudes were calculated by Feff8 code on the basis of structures obtained from quantum chemical calculations on UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub>, Th(NO<sub>3</sub>)<sub>4</sub>(TBP)<sub>2</sub>, Np(NO<sub>3</sub>)<sub>4</sub>(TBP)<sub>2</sub> and Pu(NO<sub>3</sub>)<sub>4</sub>(TBP)<sub>2</sub> systems.

Three calculations were performed for the U(VI) complex: i) with two nitrates in bidentate coordination, ii) with one nitrate in bidentate coordination and one nitrate in monodentate coordination, iii) with two nitrates in monodentate coordination. Three calculations were also performed for the Pu(IV) complex: i) with four nitrates in bidentate coordination, ii) with three nitrates in bidentate coordination and one nitrate in monodentate coordination, iii) with two nitrates in bidentate coordination and two nitrates in monodentate coordination.

Figure 1 presents the Fourier transform of the EXAFS L<sub>3</sub> edge of U(VI) and Pu(IV) complexes. Fits performed with one or two monodentate nitrates did not reproduce the experimental spectra, for both U(VI) and Pu(IV) complexes.

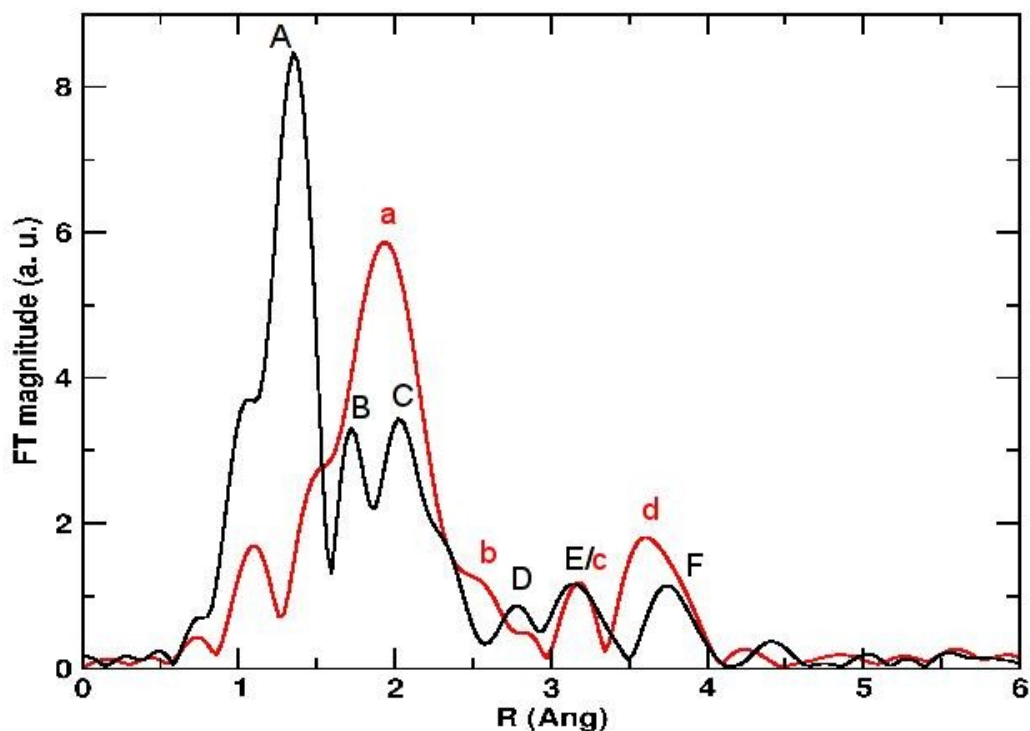


Figure 1: Fourier transform (not phase-shift corrected) of the  $L_3$  edge EXAFS spectra of U(VI) complex (black curve) and Pu(IV) complex (red curve).

For  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  the best fit is obtained with two nitrates in bidentate coordination. It gives two oxygen atoms at 1.76 Å ( $\sigma^2 = 0.0022$ ), two oxygen atoms of the phosphate group at 2.41 Å ( $\sigma^2 = 0.0050$ ), four oxygen atoms of the two bidentate nitrate ligands at 2.54 Å ( $\sigma^2 = 0.0048$ ), two corresponding nitrogen atoms at 2.99 Å ( $\sigma^2 = 0.0056$ ) and two phosphorus atoms at 3.62 Å ( $\sigma^2 = 0.0095$ ). In the FT spectrum, peak A is attributed to single scattering of oxygen atoms of the uranyl group, peak B is assigned to single scattering involving the oxygen atoms of the uranyl group and the oxygen atoms of the TBP group, peak C mainly contained single scattering signal due to the oxygen atoms of the nitrate group, peak D is assigned to single scattering of the nitrogen atoms and multiple scattering of the oxygen atoms of the uranyl group, peak E corresponds to single and multiple scattering of the phosphorus atom and peak F is assigned to single and multiple scattering signal due to the further oxygen atoms of the nitrate groups.

As for  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  the best fit for  $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$  is obtained with all nitrates in bidentate coordination. The EXAFS fit leads to a first shell with two oxygen atoms of the phosphate group at 2.33 Å ( $\sigma^2 = 0.0032$ ), eight oxygen atoms corresponding to the four bidentate nitrate ligands at 2.46 Å ( $\sigma^2 = 0.0065$ ), four nitrogen atoms at 2.91 Å ( $\sigma^2 = 0.0055$ ) and two phosphorus atoms at 3.73 Å ( $\sigma^2 = 0.0038$ ). In figure 1, peak a is assigned to single scattering of both oxygen atoms of the TBP group and oxygen atoms of the nitrate group. Peak b is assigned to single scattering of nitrogen atoms and peaks c and d are attributed to single and multiple scattering signals of phosphorus atoms and further oxygen atoms of the nitrate ligands, respectively.

Structural parameters given by the fitting procedure are consistent with distances obtained by DFT calculations. Data analysis for Th(IV) and Np(IV) complexes are currently under progress in order to compare the coordination sphere of U(VI), Th(IV), Np(IV) and Pu(IV) in presence of nitric acid and TBP solution.