

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: Molecular structure of actinide hexcyanometalates	Experiment number: 20-01-690
Beamline: BM29	Date of experiment: from: 10/03/2010 to: 12/03/2010	Date of report: 10/03/2011
Shifts: 9	Local contact(s): C. Hennig	<i>Received at ESRF:</i>

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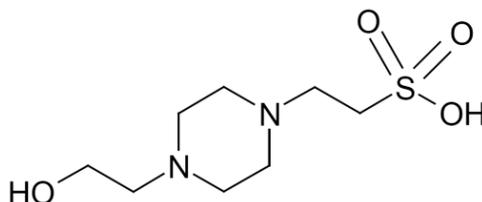
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Report:

In aqueous solution, synthesis with actinide elements at oxidation state +IV is always hampered by competition with hydrolysis. Clearly, the hydrolytic form of actinides and in particular actinide(IV) in medium acidic media is a key question in order to assess the reaction, incorporation or transportation mechanisms from the aqueous medium to the system of interest. A tremendous amount of data has been produced about the hydrolytic forms of actinides from strong acidic to natural water pH. It is far beyond the scope of this project to address all these forms. However we would like to report in this experiment on the behavior of neptunium(IV) in buffered HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) solutions. The scheme below shows the formula of HEPES. From literature data, it is believed that in water, the acidic proton is positioned either on the sulfonate group or on the amine function.



In this experiment, we have combined pHmetric measurements with *in situ* spectrophotometry and *post mortem* EXAFS studies to better understand the behavior of the neptunium(IV) aqueous ion in HEPES buffered acidic solution. The solution of Np(IV) in HCl has been obtained by reduction of Np(V) with NH₃OHCl. EXAFS measurements have been carried out *post mortem*. An aliquot of the above solution has been diluted in HEPES solution (14 μl of [Np] = 0.216 M in HCl at about 1M in 286 μl of HEPES solution at 0.25 M) and adjusted at designated pH with ammonia (called **Np-HEPES** in the text). The final Np concentration was 0.010 M. A spectrophotometric control of the solution has been carried out before and after sample measurement at the synchrotron, ensuring that no change of neptunium oxidation state has occurred during this time. EXAFS measurements were performed 4 hours after sample preparation. This short delay between sample preparation and measurement could only be achieved by a very good coordination between the RCTs of CEA Marcoule and ESRF. Note that we have observed a slow oxidation of Np(IV) into Np(V) with time higher than 10 hours (and strongly depending on the pH of the solution).

Figure 1 shows the UV-PIR spectrophotometric spectra of the **Np-HEPES** solution at various pH. Two sets of absorption bands are characteristic of Np(IV) in HCl (bottom curve) : one intense band at 960 nm, another intense band

at 723 nm with three shoulders at 695, 713 and 740 nm. The spectrum at pH = 1 is very similar to that of the aqueous form. From pH 2.5 and above, there is a Red shift of all the bands and a dramatic decrease of intensity. For instance, the band at 960 nm is shifted to 980 nm with significant broadening. However no precipitate of suspension is visible in the solution. At pH = 4.5, a very similar spectrum is observed with no significant change.

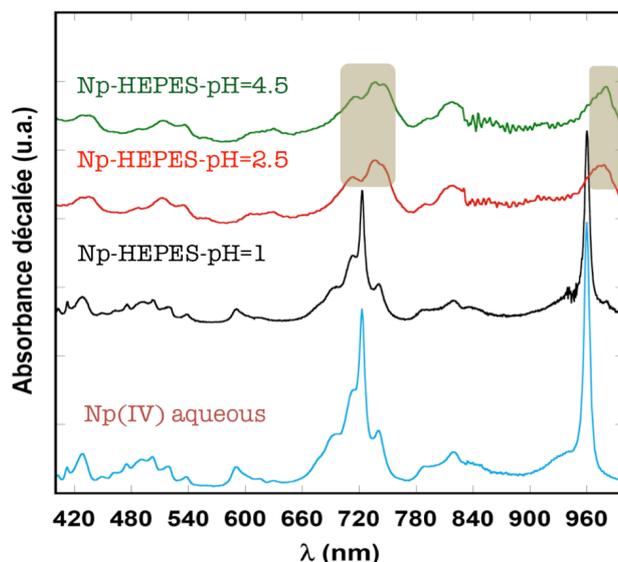


Figure 1 : Spectrophotometric measurements of **Np-HEPES** solutions at pH = 1.0, 2.5 and 4.5.

EXAFS measurements of two **Np-HEPES** solutions at pH = 2.5 and 4.5 show significant changes with respect to aqueous Np(IV) and the appearance of a long range contribution that may be attributed to Np-Np interactions. Figure 2 shows the Fourier transform of the EXAFS spectra together with best fit metrical parameters.

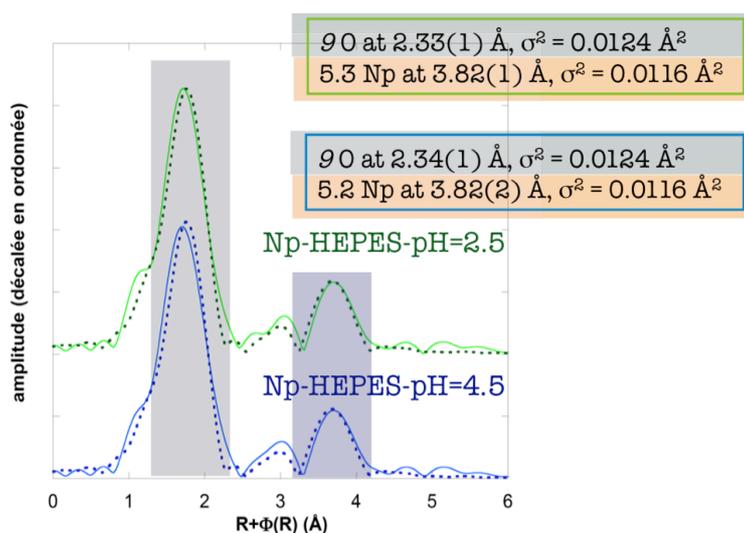


Fig. 2 : FT of the EXAFS spectra of **Np-HEPES** solutions at pH = 2.5 and 4.5.

As suggested by the spectrophotometric measurements, no difference occurs between the two pH values. Comparison of the fitted metrical parameters with the crystal structure of $[\text{Np}_2(\text{OH})_{10}\text{NH}_4]_n$ finds some similarities (on the average 9 O at 2.33 Å and 3 Np at 3.87 Å around each Np [1]). The exact mechanisms of formation and stabilization of the **Np-HEPES** clusters in solution is still not known as well as the molecular weight of the edifice.

In addition, slow oxidation of Np(IV) into Np(V) has been observed but not quantified. This oxidation occurs typically over few hours and increases with pH. A XANES and EXAFS measurement of the post mortem solution of **Np-HEPES** at pH = 4 and after 30 days clearly shows the presence of $\{\text{NpO}_2^+\}$ in the aqueous form (2 Oyle at 1.82(1) Å, $\sigma^2 = 0.0005 \text{ \AA}^2$ and 5 Oeq at 2.50(1) Å, $\sigma^2 = 0.0069 \text{ \AA}^2$). This result suggests the reversible state of these clusters in solution. In the future we shall perform complementary pH metric data with *in situ* spectrophotometric measurements in order to rationalize the speciation (and stoichiometry) of these species.