

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: Study of Thorium and Uranium complexation with alpha-hydroxy carboxylate ligands	Experiment number: CH-3082
Beamline: BM20	Date of experiment: from: 13/July/2010 to: 17/July/2010	Date of report: January 2011
Shifts: 10	Local contact(s): Andreas Scheinost	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Mireia Grivé (Amphos21) , *Elisenda Colàs (Amphos21), Lara Duro (Amphos21), *Isabel Rojo (Centre Tecnològic de Manresa).		

Report:

Introduction

Complexation of actinides by α -hydroxy carboxylate ligands (such as gluconate, $C_6H_{11}O_7^-$ and isosaccharinate, $C_6H_{11}O_6^-$) is of main interest on the context of radioactive waste disposal (Hummel et al., 2005). Nevertheless, there is a lack of information on the coordination number of these ligands with radionuclides, especially at high pH values. The general objective of this work is the spectroscopic study of Th(IV) complexes with gluconate and isosaccharinate ligands formed under alkaline environments.

The specific objectives of the work are:

- to gain information on the Th coordination chemistry with organic ligands, in terms of bond lengths and coordination numbers.
- to identify differences (if existing) among the coordination of thorium to gluconate and isosaccharinate.
- to investigate the possible change of coordination modes between Th and gluconate with pH.
- to study the role of calcium in the formation of mixed calcium-thorium-gluconate complexes.

Experimental

Several samples were prepared for their analysis:

- 1) Solid thorium oxohydroxide, aqueous thorium carbonate and aqueous thorium citrate samples, for comparison purposes.

- 2) Aqueous thorium gluconate samples at pH 12.0 and 7.6.
- 3) Aqueous thorium isosaccharinate samples at pH=12.0.
- 4) Aqueous thorium gluconate samples at pH=12.0 in the presence of calcium.

Aqueous samples were prepared from the oversaturation direction, mixing the appropriate amounts of ligand and thorium at 25°C in NaClO₄ (I=0.5M) solutions. The final pH was adjusted with NaOH. Samples were prepared under nitrogen atmosphere to avoid carbonate contamination.

Before the analysis, the samples were filtered with ≈20 nm or ≈1.2 nm filters to avoid the presence of solid thorium particles or colloids. Final thorium concentrations in the aqueous samples were ≈ 1·10⁻³ mol/dm³; ligand aqueous concentrations in solution varied between 0.01 and 0.5 mol/dm³.

The EXAFS spectra were collected in the fluorescence mode (except the solid thorium oxohydroxide, which was collected in the transmission mode) at room temperature.

Results

Preliminary data analysis was performed using the WinXAS (Ressler, 1998) software. Theoretical scattering amplitudes for each absorber and backscattered pair were calculated with the FEFF 8.20 code (Rehr and Albers, 2000). A single value of the shift in threshold energy, ΔE_0 , was allowed to vary for all coordination shells of a given sample. Principal component (PC) analysis was done with the PC application in Sixpack (Webb, 2005).

The analysis of solid thorium oxohydroxide indicates the coordination of ~8 oxygens at 2.43 Å, which is in agreement with the theoretical structure of thorianite (Whitfield et al., 1966). Th-Th interactions are not observed in the spectra due to the amorphous nature of the sample.

Aqueous thorium carbonate spectra was fitted (Figure 1.A) using thorium pentacarbonato aqueous complex (Th(CO₃)₅⁶⁻) as a model (Altmair et al., 2006). According to the results, ~9 oxygens appear to be coordinated to Thorium at 2.47 Å. The fit also suggests the presence of ~4.5 carbon atoms at 2.47 Å and ~4.5 oxygen atoms (O_{dist}) at 4.52 Å.

In the case of thorium gluconate and thorium isosaccharinate samples, the EXAFS spectra were fitted using the reference crystal structures of Mn(III) citrate (Matzapetakis et al., 2000) and Na(I) isosaccharinate (Bontchev and Moore, 2004).

In the aqueous thorium gluconate sample at pH=12 (Figure 1.B), aside from the Th-O shell at 2.42 Å (with a coordination number around 10), the next most intense feature corresponds to a Th-C interaction at 4.27 Å. For the aqueous thorium isosaccharinate sample at the same pH (Figure 1.C), the Th-C contribution appears at 4.19 Å. No Th-Th interactions are observed in thorium-gluconate or thorium-isosaccharinate samples.

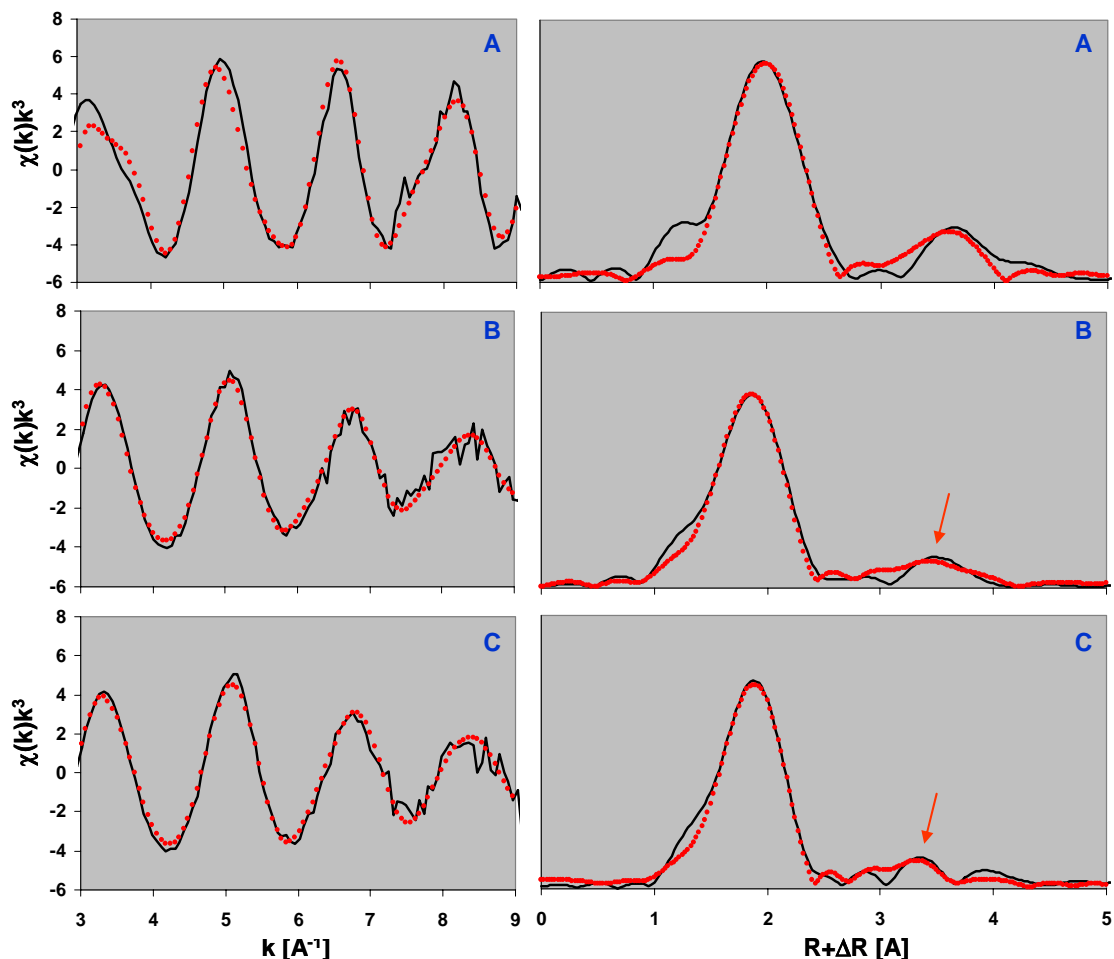


Figure 1: Thorium LIII edge k^3 -weighted EXAFS spectra (left) and their corresponding Fourier Transforms (right) for a) Thorium carbonate aqueous sample at pH=9.4; b) Thorium gluconate aqueous sample at pH=12; c) Thorium isosaccharinate aqueous sample at pH=12. Solid black line represents experimental data; red dots are the preliminary fit results. Red arrow indicates Th-C contribution for the organic ligands (see text).

Principal component analysis indicates that no important differences are observed between the Th-gluconate spectra at pH=7.6 or pH=12, and that similar aqueous complexes are being formed at both pH values. Likewise, no significant differences are observed in the spectra for thorium gluconate samples in the absence and presence of calcium. This may either indicate that the concentration of calcium in the samples is not high enough to allow the formation of a mixed calcium-thorium-gluconate complexes, or that Th-Ca path length is $R > 4 \text{ \AA}$. At such distances the large signal-to-noise ratio of the experimental data prevents a detailed analysis of the spectra.

Further work is still on going in order to both improve the fitting results and compare them with the data gathered from independent solubility experiments.

References

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