ROBL-CRG	**Experiment title:** **Thorium L_{III}-edge EXAFS measurements of solutions containing polyhydroxy ligands**	**Experiment number**: 20_01_007
Beamline: BM 20	**Date of experiment**: from: 4.2.1999 to: 11.2.1999 from: 3.6.1999 to: 8.6.1999	**Date of report**: 29.7.1999
Shifts: 12	**Local contact(s)**: T.Reich	*Received at ROBL:* 3.8.99

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Report:

Aims of the experiment and scientific background

Organic ligands are inherent components of low- and intermediate level waste. They originate from decontaminating processes in nuclear power stations (e.g. citric acid, oxalic acids, EDTA), from organic compounds added to cement to change its properties (e.g. gluconic acid (Gluc)) and from the degradation of polymeric materials present in the waste (ion exchange resins, cellulose, bitumen). The degradation of cellulosic materials under alkaline conditions results in the formation of polyhydroxy type ligands (PHL) such as α-isosaccharinic acid (ISA) [1]. Due to their strong complexing properties, PHL may reduce the sorption of radionuclides on the repository matrix by several orders of magnitude or enhance the solubility of the radionuclides (hydr)oxides precipitations. This might result in an enhanced release of radionuclides from the waste repository into the biosphere.

In a first step the EXAFS studies at ROBL included two goals: To investigate the complex-ation of Th(IV) with ISA and Gluc under highly alkaline condition and to gain experience with how active samples can be transported to ROBL (transport and import permission).

Experiments + Results

Th samples were prepared in a glove box by reacting Th with ISA and gluconic acid at pH 13.3 in 0.3 M NaOH The Th concentrations for the solutions were 0.1 -6.6 mM for ISA and1-10 mM for Gluc. The sampls were then packed into 4 ml PE cuvettes and tightly sealed. The EXAFS measurements were conducted in fluorescence mode (dilute samples) and transmittance mode (references).

Figure 1 shows the radial distribution functions of Th-ISA and Th-gluconic acid in comparison with a Th nitrate reference solution. The figure reveals that although structurally related, the spectra of Th/ISA and Th/gluconic acid are distinctly different beyond the first coodination shell. Data analysis suggests that the first coordination shell consists of 10 O atoms at distance of ~2.4 Å. The second shell of Th/ISA and Th/gluconic acid consists of C neighbouring atoms at ~3.1 Å and ~3.3 Å. Based on energy minimisation calculations, these distances are consistent with the polydendate binding of ISA and gluconic acid to the Th central atom. The structural origin of further Th shells is currently analysed using theoretical approaches.

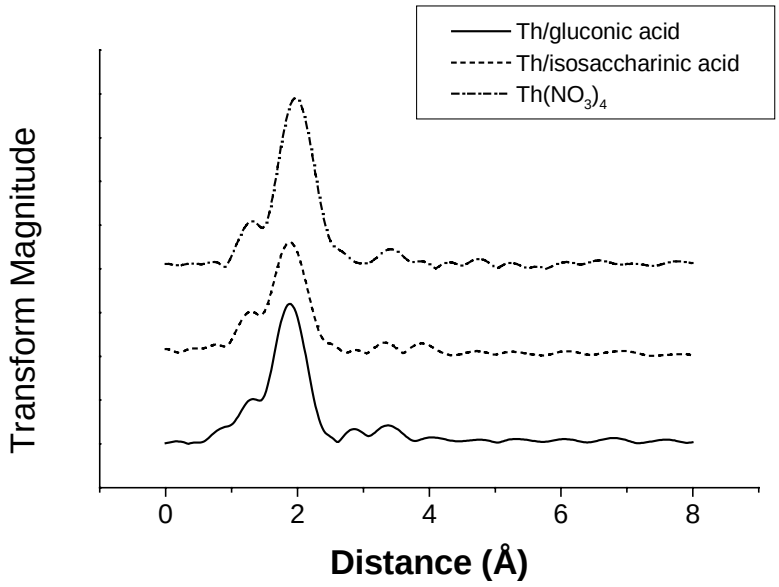

Fig. 1: Radial structure functions of Th-ISA, Th-gluconic acid and a Th nitrate solution

References

[1] Van Loon L.R. and Glaus M.A. *PSI-Bericht* **98-07** Paul Scherrer Institut Switzerland 1998. Also published as *Nagra Technical Report* NTB **97-04**, Wettingen, Switzerland 1998.