

ROBL-CRG

	Experiment title: Th(IV) Complexation by Humic Acids Studied by EXAFS	Experiment number: 20_01_022
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Report:

Structural parameters of a Th(IV) complex with natural humic acid (HA) from Aldrich were determined by EXAFS. The results were compared to those obtained for Th(IV) sorbed onto Bio-Rex70, a cation exchange resin having only carboxyl groups as proton exchanging sites. In addition, we compared our results with EXAFS data for the HA and Bio-Rex70 interaction with Th(IV) /1/ and Np(IV) /2/, respectively, as well as with data of Th(IV) hydrate /3/ and carboxylates /4/.

Experimental: Aldrich HA (AHA) and pre-equilibrated Bio-Rex70 from Bio-Rad were suspended in 0.1 M HClO₄. After addition of a 0.052 M Th(IV) stock solution the pH was adjusted to pH 1 and the suspensions were stirred for 48 h. The separated Th(IV) sorbates were studied in form of wet pastes. The resulting loadings were 41 mg Th/g AHA and 2 mg Th/g Bio-Rex70. Th L_{III}-edge EXAFS spectra were recorded at room temperature in fluorescence mode at ROBL.

Results and discussion: Fig. 1 shows the Th L_{III}-edge k³-weighted EXAFS oscillations and their corresponding Fourier transforms (FT). The EXAFS oscillations and FT are comparable for both samples. The FT are dominated by a peak which represents oxygen atoms coordinated to Th(IV). The EXAFS oscillations were fitted to the EXAFS equation involving one coordination shell of Th with oxygen as backscatterer. The obtained structural data are summarized in Tab. 1. Th(IV)-AHA and Th(IV)-Bio-Rex70 show comparable coordination numbers (N) and Th-O bond lengths (R). In both samples Th(IV) is surrounded by 11 oxygen atoms at a distance of 2.44 Å. Since Bio-Rex70 solely shows carboxyl groups as

proton exchanging sites we conclude that under the applied experimental conditions the interaction between AHA and Th(IV) is dominated by humic acid carboxyl groups, as expected for pH 1. However, the higher EXAFS-Debye-Waller factor, σ^2 , for the oxygen coordination shell of Th(IV)-AHA compared to Th(IV)-Bio-Rex70 and Th⁴⁺ (aq) indicates a greater bond lengths distribution in Th(IV)-AHA.

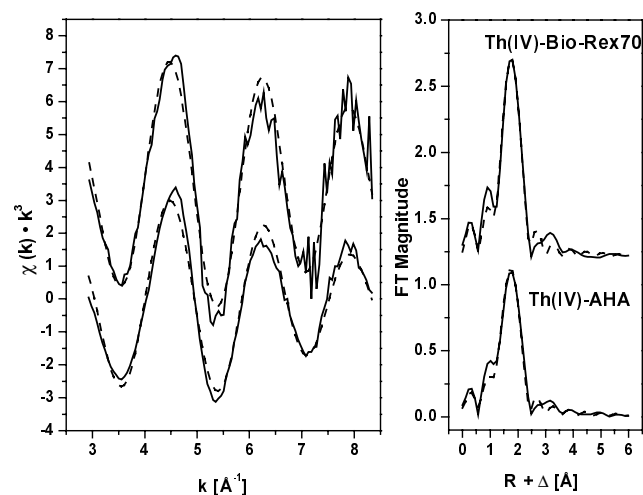


Fig. 1: Th L_{III}-edge k³-weighted EXAFS spectra and their corresponding FT. Solid lines: experiment, dashed lines: fit.

Tab. 1: EXAFS structural parameters in comparison to literature data. (95 % confidence limits for N an R).

Sample	Th-O			ΔE_0	Ref.
	N	R (Å)	σ^2		
Th(IV)-AHA	10.6 ± 1.5	2.44 ± 0.01	0.013	-17.3	
Th(IV)-BioRex70	11.0 ± 2.1	2.45 ± 0.02	0.009	-17.3	
Th(IV)-AHA	10.1	2.43	0.013	1.0	/1/
Th(IV)-BioRex70	9.4	2.44	0.012	1.0	/1/
Th ⁴⁺ (aq)	10.8 ± 0.5	2.45 ± 0.01	0.007	4.0	/3/

Within the experimental error, the obtained results agree with those determined by Denecke et al. /1/. Coordination number and bond length of Th(IV)-AHA are comparable with those reported for Th⁴⁺ (aq) /3/. That means that the interaction of Th(IV) with humic acid carboxyl groups induces no shortening of the Th-O bond lengths. Thus, a differentiation between coordinated water molecules and carboxylate groups of the HA is not possible. To identify the predominant binding mode of carboxylate groups onto Th(IV), the Th-O bond length is compared to those of Th(IV) model compounds. Monodentate coordinated carboxylate groups in different Th(IV) malonates /4/ show Th-O bond distances between 2.337 Å and 2.469 Å. The obtained bond length of 2.44 Å for Th(IV)-AHA lies in this range, indicating a predominantly monodentate coordination of humic acid carboxylate groups. The comparison of the Th(IV) data with those for the interaction of Np(IV) with AHA and Bio-Rex70 /2/ shows, that both tetravalent actinides are coordinated by about 11 oxygen. However, the Np-O bond distance is shorter (R=2.36±0.01 Å) than the Th-O bond length. The bond length difference (0.08 Å) is close to the difference of the effective ionic radii of Th⁴⁺ and Np⁴⁺ in aqueous solution (0.06±0.02 Å) /5/.

Acknowledgment: This work was supported by BMWi (no. 02E9299). *References:* /1/ Denecke, M.A. et al., J. Synchr. Rad. **6**, 394 (1999). /2/ Schmeide, K. et al., this report. /3/ Moll, H. et al., Inorgan. Chem. **38**, 1795 (1999). /4/ Zhang, Y.-J. et al., Polyhedron **19**, 1757 (2000). /5/ Neck, V. et al., Radiochim. Acta **89**, 1 (2001).