



ROBL-CRG

	Experiment title: EXAFS Study of the Np(V) Complexation by Humic Acids in Neutral Solution	Experiment number: 20_01_022
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Report:

Structural parameters for Np(V) humic acid (HA) complexes were determined by EXAFS. For the first time, the influence of phenolic OH groups on the Np(V) complexation by HA was studied with a chemically modified HA and Bio-Rex70, a cation exchange resin having only carboxyl groups as proton exchanging sites.

Experimental: Np(V) complexes were prepared from natural HA Aldrich (AHA), modified Aldrich HA with blocked phenolic OH groups (AHA-PB) /1/, synthetic HA type M42, and Bio-Rex70 from Bio-Rad. The phenolic OH group content of AHA and AHA-PB amounts to 3.1 and 1.1 meq/g. Np(V) humate solutions were prepared under N₂ at pH 7 with Np and HA concentrations of 0.88-0.90 mmol/L and of 8.1-10.8 g/L, respectively (0.1 M NaClO₄). The formation of Np(V) humate complexes was verified by NIR absorption spectroscopy. In addition, Np(V) was sorbed onto Bio-Rex70 at pH 7 (0.1 M NaClO₄). The sorbate had a loading of 121.3 mg Np/g Bio-Rex70. The Np(V) humates were studied in form of solutions, the Bio-Rex70 sorbate in form of a wet paste. Np L_{III}-edge EXAFS spectra were recorded at ROBL at room temperature in fluorescence mode (Np(V) humates) and in transmission mode (Np(V)-Bio-Rex70).

Results and discussion: The Np L_{III}-edge k³-weighted EXAFS oscillations and their Fourier transforms (FT) are shown in Fig. 1. The EXAFS oscillations were fitted to the EXAFS equation using a model with two Np coordination shells containing oxygen as backscatterer and including multiple scattering along the NpO₂⁺ unit. The axial coordination number was held constant at 2 during the fit. The data are shown in Tab. 1.

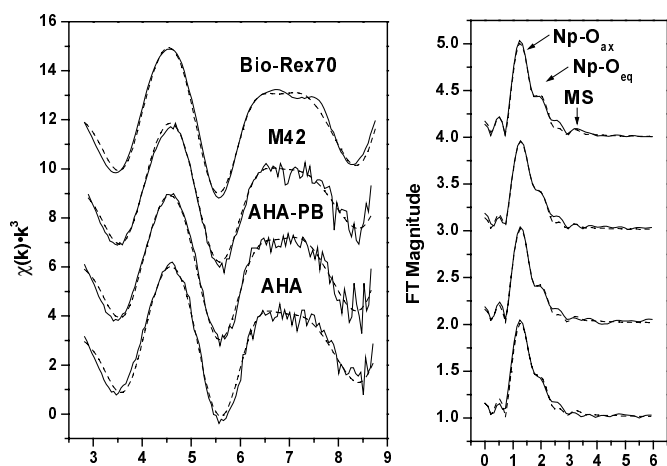


Fig. 1: Np L_{III}-edge k^3 -weighted EXAFS spectra and corresponding FT of Np(V) samples. Solid lines: experiment, dashed lines: fit, MS: multiple scattering along the NpO_2^+ unit.

Tab. 1: EXAFS structural parameters of Np(V) samples. (95 % confidence limits are given for N and R).

Sample	Np-O _{ax}			Np-O _{eq}			ΔE_0 (eV)
	N	R(Å)	σ^2	N	R(Å)	σ^2	
Np(V)-AHA	2	1.84 ± 0.01	0.0035	2.9 ± 0.7	2.48 ± 0.01	0.0047	-7.8
Np(V)-AHA-PB	2	1.85 ± 0.01	0.0034	2.8 ± 0.8	2.49 ± 0.01	0.0054	-8.0
Np(V)-M42	2	1.84 ± 0.01	0.0048	3.3 ± 0.9	2.48 ± 0.01	0.0078	-8.8
Np(V)-Bio-Rex70	2	1.85 ± 0.01	0.0034	2.9 ± 0.5	2.50 ± 0.01	0.0046	-8.2
$\text{NpO}_2(\text{H}_2\text{O})_x^+ / 2/$	1.9 ± 0.2	1.822 ± 0.003	0.0023	3.6 ± 0.6	2.488 ± 0.009	0.006	

Independent of the HA origin and their functionality, the axial (ax) and equatorial (eq) coordination numbers (N) and Np-O bond lengths (R) for all Np(V) humates are comparable with each other as well as with the data of Np(V)-Bio-Rex70. Due to the fact that the Np(V) humates of AHA-PB and AHA show comparable structural parameters it can be concluded that the blocking of humic acid phenolic OH groups has no influence on the local structure around Np in the Np(V) humates. Since Bio-Rex70 solely has carboxyl groups as proton exchanging sites, similar coordination numbers and bond lengths of Np(V) humates and Np(V)-Bio-Rex70 indicate that carboxylate groups dominate the interaction between Np(V) and HA at pH 7. However, a contribution of phenolic OH groups to the interaction between HA and Np(V) cannot completely be excluded, because the EXAFS results are average values over all interactions between HA and Np(V). There is the possibility that phenolic OH groups interacting with Np(V) show equatorial bond lengths similar to those of carboxylate groups. The equatorial Np-O bond lengths ($R_{\text{Np-Oeq}}$) of the humates are comparable with $R_{\text{Np-Oeq}}$ of monodentate coordinated carboxylate groups in a Np(V) malonate complex /3/. Due to the fact that $R_{\text{Np-Oeq}}$ of the humates are also comparable with $R_{\text{Np-Oeq}}$ of $\text{NpO}_2(\text{H}_2\text{O})_x^+$ (Tab. 1) /2/, a differentiation between monodentate coordinated carboxylate groups and water molecules is not possible. A predominant bidentate coordination of humic acid carboxylate groups to Np(V) can be excluded. $R_{\text{Np-Oeq}}$ of 2.60 ± 0.04 Å was found for bidentate coordinated carboxylate groups in a Np(V) formate complex /4/.

Acknowledgment: This work was supported by BMWi under contract no. 02E9299. *References:* /1/ Pompe, S. et al., Radiochim. Acta **88**, 553 (2000). /2/ Reich, T. et al., Radiochim. Acta **88**, 633 (2000). /3/ Grigoriev, M.S. et al., Radiokhim. **4**, 24 (1993). /4/ Grigoriev, M.S. et al., J. Neorgan. Chim. **39**, 1328 (1994).