

ROBL-CRG

	Experiment title: Neptunium(IV) Humate Complexation Studied by XAFS Spectroscopy	Experiment number: 20_01_022
Beamline: BM 20	Date of experiment: on: 30/09/00	Date of report: 16.03.2001
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Report:

For the first time, structural parameters of the near-neighbor surrounding of Np(IV) sorbed onto natural and synthetic humic and fulvic acids (HA, FA) were determined at pH 1 by XAFS spectroscopy. Bio-Rex70 was used as reference substance for humic substances.

Experimental: The Np loading of the wet pastes prepared at pH 1 from Aldrich HA (AHA), Kranichsee FA (KFA), synthetic HA type M42, and Bio-Rex70 (from Bio-Rad) was between 4 and 41 mg Np per g sorbent /l/. The samples were measured in transmission mode at the Rossendorf Beamline at the ESRF in Grenoble.

Results: The tetravalent oxidation state of Np and its stability in the humate and Bio-Rex70 complexes within the time of our experiment is verified by XANES spectroscopy. In Fig. 1, the XANES spectrum of Np(IV)-AHA is shown in comparison to that of the corresponding Np(V) sample. The spectrum of Np(IV) humate shows the characteristic near-edge features of Np(IV) compounds: A more intense 'white line' peak, but no additional shoulder on the high energy side of the peak as generally observed for Np(V) samples.

The Np L_{III}-edge k³-weighted EXAFS spectra of the Np(IV) samples and the corresponding Fourier transforms (FTs) are shown in Fig. 2 (solid lines: experiment, dashed lines: fit). Both the EXAFS oscillations and the FTs of all Np(IV) complexes are similar. The structural parameters are given in Tab. 1.

In the Np(IV) humate complexes, the Np ion is surrounded by about 11 oxygen atoms at a distance of 2.36 Å. Similar parameters are determined for the Np(IV) complex with Bio-Rex70, which has solely carboxylic groups as metal binding functional groups. This verifies that in the humate complexes predominantly the carboxylic groups are responsible for binding Np ions at pH 1. This was expected.

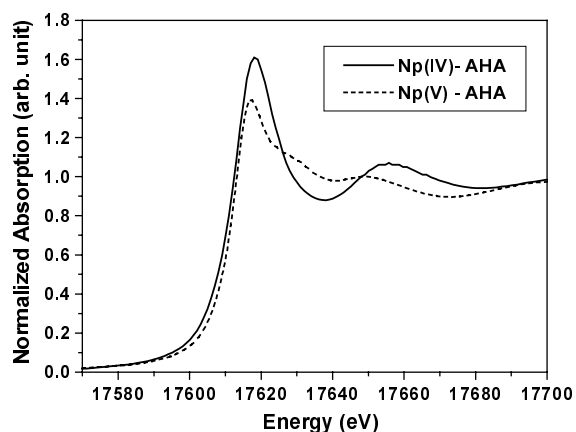


Fig. 1: Normalized Np L_{III}-edge XANES spectra.

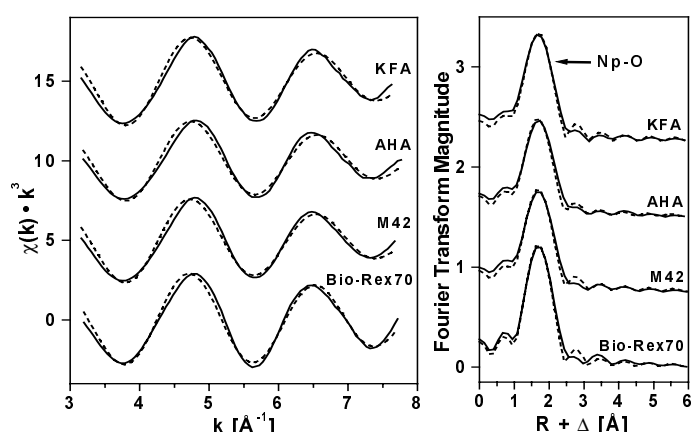


Fig. 2: Raw Np L_{III}-edge k^3 -weighted EXAFS spectra and corresponding FTs of Np(IV) samples.

Tab. 1: Structural parameters of Np(IV) samples

Sample	Shell	N	R [Å]	σ^2 [Å ²]
Np(IV)-KFA	Np-O	11.3±1.7	2.36	0.0162
Np(IV)-AHA	Np-O	10.1±1.7	2.36	0.0159
Np(IV)-M42	Np-O	11.0±1.7	2.36	0.0166
Np(IV)-Bio-Rex70	Np-O	10.2±1.3	2.37	0.0127
Np(IV) in 1 M HCl /2/	Np-O	11.2±1.1	2.40	0.0075
Np(IV) in 2 M H ₂ SO ₄ /3/	Np-O	11±1	2.39	0.0118
	Np-S	2.2±0.9	3.07	0.0070

$\Delta E_0 = -11.1$ eV; $R \pm 0.01$ Å; The 95 % confidence limits are given for N and R as estimated by EXAFSPAK.

Compared to the hydrated Np(IV) ion in hydrochloric or sulfuric medium /2,3/, the coordination number of the humates is similar, only the Np-O bond length is shortened by about 0.04 Å due to humate complexation. Since no carbon atoms of the binding humic acid carboxylate groups could be detected, it is not possible to determine separate coordination numbers for carboxylate groups and water molecules coordinated to Np by EXAFS analysis.

To identify the binding mode of the carboxylate groups, the bond distances of the Np(IV) humates are compared to those of Np(IV) model compounds which contain carboxylic groups. The results show that the bond distance of the Np(IV) humates is smaller than found for bridging and chelate forming carboxylate groups in Np(IV) oxalate ($R=2.39$ Å, 2.51 Å) /4/ or for bidentate binding carboxylate groups in Np(IV) formate ($R=2.50$ Å) /5/. We conclude that humic acid carboxylate groups are predominantly monodentately bound to Np(IV) ions. This has to be verified by future studies with further Np(IV) model compounds.

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References: /1/ Schmeide, K., et al., Proceedings of Internat. Conf. Actinide-XAS-2000, Grenoble, France, in press; /2/ Allen, P.G., et al., Inorg. Chem. 36, 476 (1997); /3/ Reich, T., et al., Radiochim. Acta 88, 633 (2000); /4/ Grigor'ev, M.S., et al., Radiokhim. 39, 419 (1997); /5/ Hauck, J., Inorg. Nucl. Chem. Lett. 12, 617 (1976).