

ROBL-CRG

Experiment title:**The Influence of Phenolic Hydroxyl Groups on the Complexation Behavior of Humic Substances with Uranyl(VI) Ions: EXAFS Investigations of solid UO_2^{2+} Complexes with Modified and Unmodified Humic Acids****Experiment****number:**

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Report:

To study the influence of phenolic OH groups on the short-range order surrounding of uranium(VI) in uranyl humate complexes we investigated solid uranyl humates of the modified synthetic humic acid (HA) type M1PB and of the modified natural HA Aldrich (A2/97PB) and Kranichsee (KHAPB) with blocked phenolic OH groups /1/. These samples were compared to uranyl humates of the original HA type M1, A2/97 and KHA.

Experimental: The preparation of the solid uranyl humates as well as their uranyl loadings are described in /2/. The samples dispersed in Teflon were pressed as 1.3 cm diameter pellets. U L_{III} -edge EXAFS transmission spectra were measured at room temperature at the Rossendorf Beamline at the ESRF. The monochromator, equipped with a Si(111) water cooled double-crystal system was used in the channel-cut mode.

Results: As examples, the k^3 -weighted U L_{III} -edge EXAFS and the corresponding Fourier transforms for the investigated uranyl humates of HA type M1 and M1PB as well as HA A2/97 and A2/97PB are depicted in Fig. 1 and Fig. 2. The EXAFS oscillations of all samples as well as the Fourier transforms are similar. The EXAFS oscillations were fitted to the EXAFS equation using a structural model with two coordination shells containing oxygen atoms as backscatterer and including multiple scattering effects along the uranyl unit (Tab. 1).

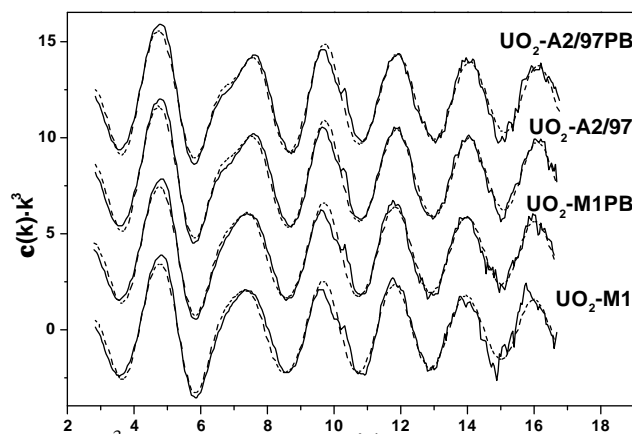


Fig. 1: k^3 -weighted U L_{III} -edge EXAFS spectra of solid uranyl humates of modified and unmodified HA. Solid lines: experimental data, dashed lines: fit results.

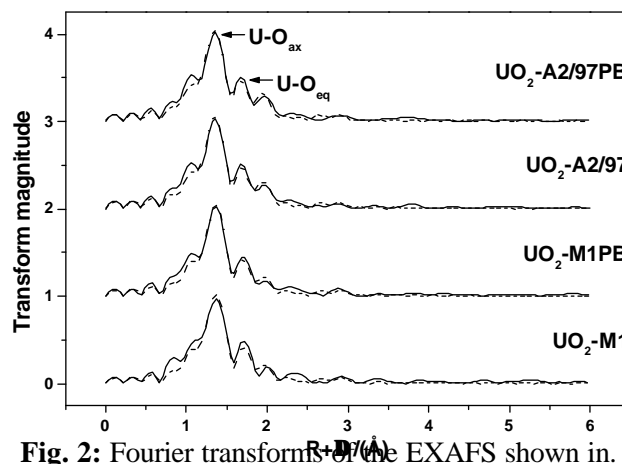


Fig. 2: Fourier transforms of the EXAFS shown in Fig. 1.

Tab. 1: EXAFS structural parameters. $\Delta E_0 = -13.6$ eV, $N_{ax} = 2$, errors in bond length (R) and coordination numbers (N) are ± 0.02 Å and $\sim 10\%$, respectively.

Sample	U-O _{ax}		U-O _{eq}		
	R (Å)	σ^2 (Å ²)	N	R (Å)	σ^2 (Å ²)
UO ₂ -M1	1.78	0.002	5.2	2.38	0.014
UO ₂ -M1PB	1.78	0.001	5.0	2.38	0.014
UO ₂ -A2/97	1.78	0.001	5.3	2.40	0.012
UO ₂ -A2/97PB	1.77	0.001	5.1	2.40	0.011
UO ₂ -KHA	1.78	0.001	5.2	2.39	0.012
UO ₂ -KHAPB	1.78	0.002	5.4	2.40	0.013

The modified HA show a smaller amount of phenolic OH groups than the unmodified HA /1/. Therefore, the spectra of the modified HA are more dominated by the interaction of UO_2^{2+} with carboxylic groups. The determined U-O_{eq} bond distances correspond to monodentate coordination of the carboxylic groups /3/. The structural parameters obtained for the solid uranyl humates of the unmodified HA do not differ from that of the modified HA. This indicates a comparable short-range order surrounding of the UO_2^{2+} ion. One can conclude that in the solid complexes the phenolic OH groups have only a small or no influence on the complexation of the UO_2^{2+} ions.

However, a contribution of phenolic OH groups to the complexation of UO_2^{2+} can not fully be excluded by the EXAFS results, because the obtained structural parameters represent an average over all interactions between HA and UO_2^{2+} . From EXAFS investigations concerning the complexation of pyrogallol with UO_2^{2+} at pH 4.8 /4/ it is known that phenolic OH groups can complex to the UO_2^{2+} ion with distances of 2.40 Å, which can not be distinguished from $R_{U-O_{eq}}$ of the humates.

References:

- /1/ Pompe, S., et al., Report FZR-272 (1999); /2/ Bubner, M., et al., Report FZR-272 (1999);
 /3/ Denecke, M., et al., Radiochim. Acta 79, 151, 1997; /4/ Roßberg, A., et al., Report FZR-247 (1999) p. 53

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