



ROBL-CRG

**Experiment title:****EXAFS Study of the Interaction of Uranium(VI) with Humic Substances****Experiment****number:**

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**Report:**

*Introduction:* The objective of this study was to obtain information about the binding of uranium(VI) onto functional groups of humic substances. Uranyl complexes of Kranichsee humic and fulvic acid (KHA and KFA: isolated from surface water of the mountain bog 'Kleiner Kranichsee' /1/), Aldrich humic acid (A2/97) as well as a synthetic HA type M42 /2/ were therefore investigated.

*Experimental:* The samples were prepared according to /3/. The uranyl loading was between 18 and 19 % of the carboxylic group capacity of the humic substances. Complex formation was confirmed by IR spectroscopy. The samples were dispersed in Teflon and pressed as 1.3 cm diameter pellets. The U content of the resulting pellets was 11 to 22 mg U. The EXAFS measurements were carried out at the Rossendorf Beamline at the European Synchrotron Radiation Facility in Grenoble. Uranium L<sub>III</sub>-edge X-ray absorption spectra were collected in transmission mode. The Si(111) double-crystal monochromator was used in the channel-cut mode.

*Results:* The k<sup>3</sup>-weighted EXAFS spectra and the corresponding Fourier transforms are shown in Figs. 1 and 2. In both figures the solid lines represent the experimental data and the dotted lines the theoretical fit of the data. A two-shell fit to the experimental EXAFS data was used with oxygen atoms as backscatterers. The multiple scattering along the uranyl unit at 3.6 Å was also included in the fit. The coordination number (N) for the axial oxygen atoms and ΔE<sub>0</sub> were kept constant at 2 and -13.6 eV.

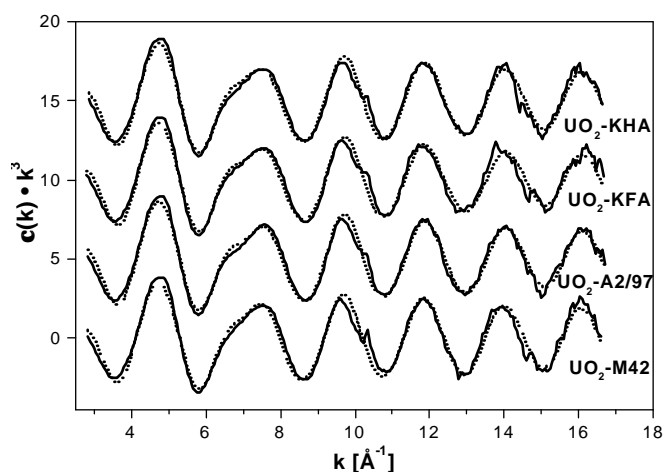


Fig. 1:  $k^3$ -weighted U  $L_{III}$ -edge EXAFS spectra of uranyl complexes with KHA, KFA, A2/97 and M42

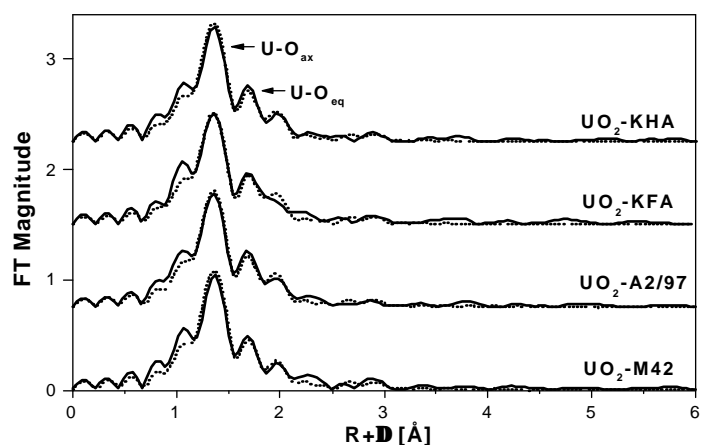


Fig. 2: Fourier transforms of the EXAFS spectra of uranyl complexes with KHA, KFA, A2/97 and M42

The EXAFS structural parameters of the uranyl humates are compiled in Tab. 1.

Tab. 1: Structural parameters of the uranyl humates

Sample	U - O <sub>ax</sub>		U - O <sub>eq</sub>		
	R [Å]	$\sigma^2$ [Å <sup>2</sup> ]	N	R [Å]	$\sigma^2$ [Å <sup>2</sup> ]
UO <sub>2</sub> -KHA	1.78	0.001	5.2	2.39	0.012
UO <sub>2</sub> -KFA	1.78	0.002	5.3	2.39	0.012
UO <sub>2</sub> -A2/97	1.78	0.001	5.3	2.40	0.012
UO <sub>2</sub> -M42	1.78	0.001	5.4	2.40	0.014

Error: N  $\pm$  10 %, R  $\pm$  0.02 Å

Axial U-O bond lengths (R) of 1.78 Å were determined for all uranyl humates. In the equatorial plane approximately five oxygen atoms were found at a mean distance of 2.40 Å. Since carboxylic groups are generally considered the main functional groups of the humic substances involved in the complexation of metal ions at pH  $\leq$  4, the results of this EXAFS study were compared with the mean values of the bond distances found for crystalline uranyl carboxylate complexes of known structures given in /4/. It turned out that the mean bond distance of 2.40 Å in the equatorial plane determined for the humates is the same as that found for the carboxylates where the uranyl ions are bound monodentately.

**Conclusion:** Both for natural humic substances (KHA, KFA, A2/97) and for the synthetic HA type M42 comparable structures of uranyl complexes were found with predominantly monodentate coordination of the humic acid carboxylic groups onto uranium(VI) ions.

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**References:** /1/ Schmeide, K., et al., Report FZKA 6124, Forschungszentrum Karlsruhe, 161 (1998); /2/ Pompe, S., et al., Radiochim. Acta **82**, 89 (1998); /3/ Bubner, M., et al., Report FZR-272, (1999); /4/ Denecke, M., et al., Radiochim. Acta **79**, 151 (1997).