ROBL-CRG	<b>Experiment title:</b> PRELIMINARY INVESTIGATION TO DETERMINE THE MAIN COMPLEX SPECIES IN THE AQUEOUS SYSTEM OF $UO_2^{2+}$ WITH PROTOCATECHUIC ACID BY EXAFS SPECTROSCOPY	Experiment number: 20_01_06
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Report:

## Experimental

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The speciation of the complexes on ionic strength of 0.1 M (NaClO<sub>4</sub>) and 25 C in the absence of CO<sub>2</sub> was calculated with the computer program RAMESES. The metal concentration was 1 mM  $UO_2(CIO_4)_2$  and the PCS concentration was 50 mM. Uranium(VI) hydrolysis was considered in the in the calculations.

The U L  $_{III}$ -edge spectra of the uranium(VI) complexes were measured at the Rossendorf Beamline using a Si(111) double-crystal monochromator in channel-cut mode. The fluorescence signal was measured with a 4-pixel germanium detector. The ionization potential of the U L  $_{III}$  edge was defined as 17,185 eV. The weights of the four detector channels were calculated according to their statistical signal-to-noise ratios. The dead-time corrected EXAFS spectra were analysed by the standard procedure, using the EXAFSPAK suite of programs and the theoretical scattering phases and amplitudes calculated with the scattering code FEFF6 /1/.

## **Results and Discussion**

The raw  $k^3$ -weighted U L<sub>III</sub>-edge EXAFS of the complex systems and their corresponding Fourier transforms (FT) are shown in Fig. 1 and the fit results in Tab. 1. During the fitting procedure the coordination number (N) of the axial oxygen of the uranyl unit was kept constant at N = 2. The average of the radial U-O<sub>ax</sub> distance between uranium and axial oxygen is 1.79 ± 0.02 Å. The average Debye-Waller factor is 0.002 Å<sup>2</sup>. The features in the k range from 6 Å<sup>-1</sup> to 8 Å<sup>-1</sup> and the radial distance of the equatorial oxygen change with the pH values (Fig. 1). The great distance of the equatorial oxygen of the 1:1 PCS complex at pH 4.3 indicates that the carboxylic group coordinates with the uranyl cation in a bidentate fashion (Tab. 1). The coordination number of carbon in the PCS complex is 2.4 atoms at pH 4.3. It is possible that at pH 4.3 two PCS ligands bind with the uranyl ion in a bidentate fashion. With increasing pH value, the bond distance of the equatorial oxygen decreases.

UO <sub>2</sub> <sup>2+</sup> :L, UO <sub>2</sub> <sup>2+</sup> :L		U-X equatorial			
PCS(L)	рН	Atom	R	$\sigma^{2*}10^{-3}$	N
1:1, 53%	4.30	0	2.45	8	5.7
		С	2.88	3	2.4
1:1, 46%	4.45	0	2.40	12	7.0
1:1, 23%	4.83	0	2.37	13	7.3
1:2, 30%					
1:1, 10%	5.04	0	2.38	10	6.0
1:2, 65%					
1:2, 100%	5.54	0	2.37	8	6.0
1:2, 100%	6.03	0	2.36	9	6.4
1:2, 90%	6.75	0	2.36	10	6.6

Tab. 1: Fit results for the second coordination shell (N - coordination number, R - radial distance in Å,  $\sigma^2$  - Debye-Waller factor in Å<sup>2</sup>).

At higher pH values, the PCS ligands coordinate with the uranyl cation in an o-diphenolic bonding fashion and the carboxylic group is not involved in the complexation. The calculated speciation of the PCS system shows at pH 4.8 the change from the carboxylic to the o-diphenolic coordination. The Debye-Waller factor for the equatorial oxygen has a maximum at this pH (Tab. 1). The similarity of the EXAFS spectra and coordination parameters of the uranium(VI) PCS and the BCT complexes increases with the pH /2/. The possible main complex species of PCA with the uranyl cation should be confirmed by principal component analysis of the EXAFS measurements. This can be used to validate the complexation constants for calculation of the speciation /3/.



Fig. 1: Left: Raw k<sup>3</sup>-weighted EXAFS spectra of PCS complexes sorted by pH values. Right: Corresponding Fourier- transforms without phase corrections.

## References

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- /2/ Rossberg A., et al., Annual Report FZR-247 (January 1999), p. 53
- /3/ Baraniak L., et al., Annual Report FZR-247 (January 1999), p. 31