



ROBL-CRG

**Experiment title: The application of iterative transformation factor analysis for the decomposition of multicomponent EXAFS spectra of uranium(VI) complexes with acetic acid**

**Experiment number:**  
20\_01\_018

<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 26/03/00 to: 27/03/00	<b>Date of report:</b> 27/03/01
<b>Shifts:</b> 6	<b>Local contact(s):</b> C. Hennig, T. Reich, A. Rossberg	<i>Received at ROBL:</i> 05/04/2001
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### Report:

Experimental

Eight solutions were prepared with 0.05 mol/l U(VI) and 1.0 mol/l acetic acid under norm conditions. The pH was varied in the interval from pH 0.10 to pH 4.48. The ionic strength was 1.2 mol/l. Figure 1 shows the pH-speciation of the complexes according to stability constants from the literature /1/. The U L<sub>III</sub>-edge EXAFS spectra were measured in transmission mode at ROBL.

### Results and Discussion

The Eigenanalysis of the EXAFS spectra yields that only two pure spectroscopic components (factors) are necessary to describe the variance in the spectra. By employing the iterative transformation factor analysis (ITT), the relative concentrations (matrix **C**) and the EXAFS spectra (matrix **R**) of the two factors result. The measured spectra (matrix **D**) can reproduced with two factors (Fig. 2, left). Therefore all complex species must consist of the fractions of the two isolated factors. Factor 1 consists of five equatorial oxygen atoms (O<sub>eq,1</sub>) at a short distance (2.41 Å). Factor 2 consists of six equatorial oxygen atoms (O<sub>eq,2</sub>) at a longer distance (2.46 Å) to the uranyl unit. The structural parameters from factor 1 are in agreement with those of the uranyl hydrate. For factor 2 the structural parameters indicate that the carboxylic groups of three acetate ligands are bidentate coordinated to the uranyl unit. The EXAFS spectra of the 1:1 and 1:2 uranyl acetates cannot be isolated since these complexes coordinate water and acetate simultaneously.

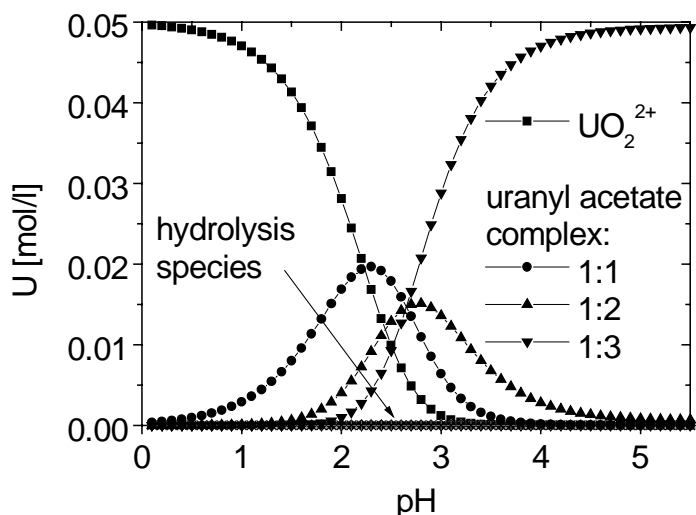


Fig. 1: Calculated pH-speciation (conditions: see experimental).

By multiplying the relative concentration of factors 1 and 2 by 5 and 6, respectively, one can plot the coordination numbers for  $O_{eq,1}$  and  $O_{eq,2}$  as a function of pH (Fig. 2, right). If one assume that 4 and 2 water molecules are coordinated in the 1:1 and 1:2 uranyl complexes then, the average  $O_{eq,1}$  and  $O_{eq,2}$  coordination numbers can be calculated from the speciation diagram (Fig. 1) for all pH values. The calculated values are in agreement with the experimental results (Fig. 2, right).

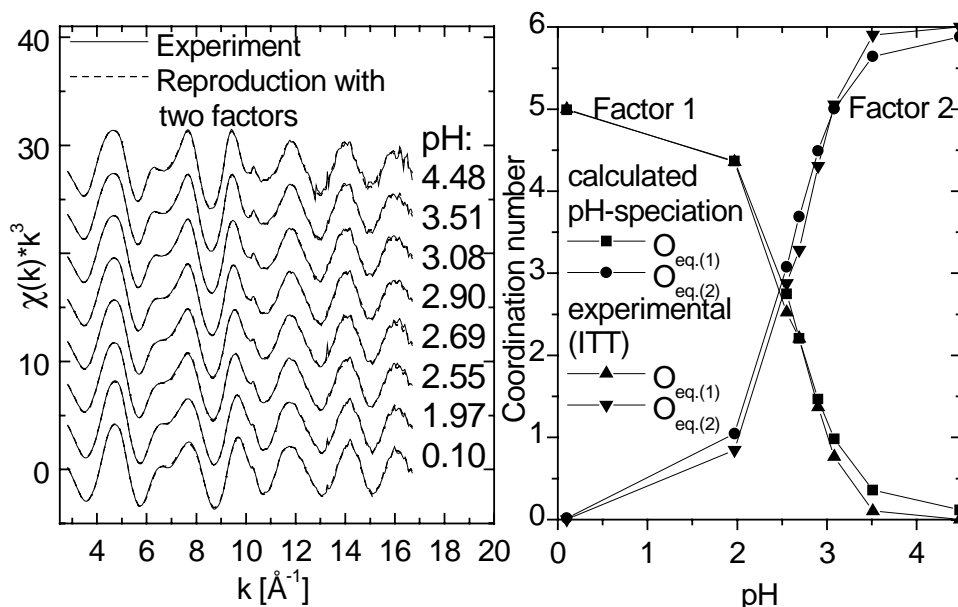


Fig. 2: The raw  $k^3$ -weighted U  $L_{III}$ -edge EXAFS spectra and their reproductions with  $\mathbf{D} = \mathbf{RC}$  (left). The result of the ITT and the calculated pH-speciation (right).

## References

/1/ Ahrland, S., Acta Chemica Scandinavica **5**, 199 (1951)