

Quantitative uranium speciation with U M_{4,5}-edge HERFD absorption spectra

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This report gives a brief description of the quantitative uranium speciation performed by iterative transformation factor analysis (ITFA) of High Energy Resolution X-ray Fluorescence Detection (HERFD) data collected at the M_{4,5} edge.

The HERFD method allows recording X-ray absorption spectra with substantially better energy resolution and permits the identification of the oxidation states and number of the 5*f* electrons of actinide systems. Moreover, the advances in factor analysis has made it possible to estimate the exact contribution of the different chemical states in the actinide system by ITFA program, where the exact composition can be found without the input of the solely separated compounds.^[1, 2]

We show here an example of the speciation studies of the magnetite nanoparticles co-precipitated with U(VI) solution.^[3] We used ITFA in order to decompose the spectral mixtures into the spectra and the fractions of the components (Fig. 1). It is clearly indicated in Fig. 1B that only the first three eigenvectors show a signal, while the following (4–6) consist of counting noise (ordinate) and noise in the monochromaticity; hence, only three components are necessary to describe the variation in the spectral mixtures. In the beginning, it was considered that the UO₂ sample contains 100 % of the U(IV) state, and UO₃ contains 100 % of the U(VI) state. The initial analysis showed that the Umh sample contains 100 % of the U(VI) and we used the spectrum of the Umh sample as input of the 100 % of the U(VI) fraction. The iterative target test (ITT) procedure was used to extract the spectrum of the third component and to determine the relative concentrations of all three components.^[4]

Figure 1C shows the spectra of the separated compounds corresponding to the U(IV), U(V) and U(VI) oxidation states. The analysis shows that all the samples Um1, Um3, Um6 and Um10 contain various fractions of the U(IV), U(V) and U(VI) valence states, being present simultaneously in the same sample. The results are summarized in Tab. 1. Such a quantitative empirical analysis can be applied to any spectrum measured at the actinide M_{4,5} edges.

Tab. 1: Fractions of U(IV), U(V) and U(VI) valence states in the Um1, Um3, Um6 and Um10 samples (values are given in %).

Sample	U(IV)	U(V)	U(VI)
Um1	20	80	0
Um3	0	80	20
Um6	0	72	28
Um10	1	62	37

[1] Rossberg, A. *et al.* (2003) *Anal. Bioanal. Chem.* **376**, 631–638.

[2] Rossberg, A. *et al.* (2009) *Environ. Sci. Technol.* **43**, 1400–1406.

[3] Pidchenko, I. *et al.* (2017) *Environ. Sci. Technol.*, accepted.

[4] Bryden, T. H. *et al.* (1988) *Anal. Chem.* **60**, 1154–1158.

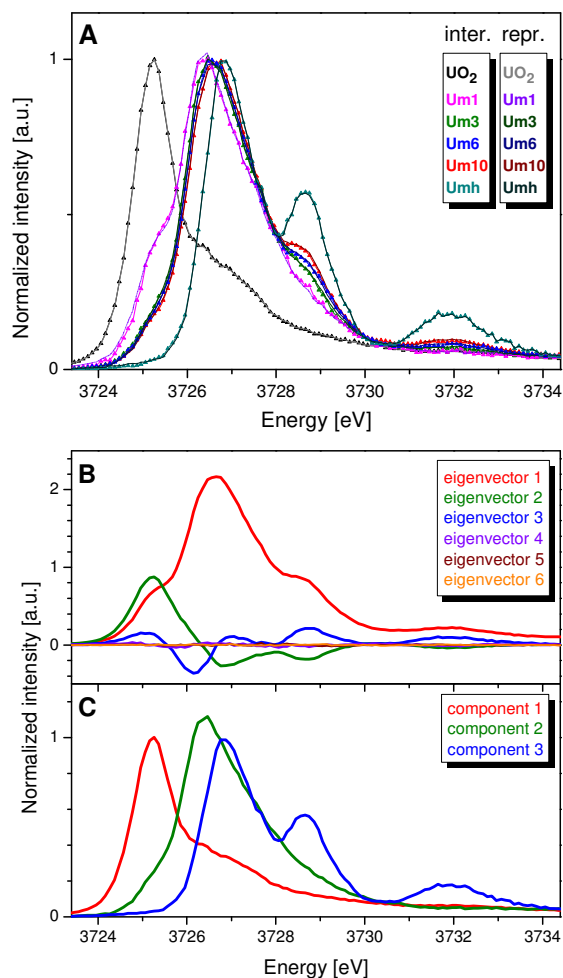


Fig. 1: Interpolated experimental (triangles) and reproduced (solid lines) U M₄ HERFD spectra of the samples containing 1,000 ppm U (Um1), 3,000 ppm U (Um3), 6,000 ppm U (Um6) and 10,000 ppm U (Um10) formed by co-precipitation of the U with magnetite (Fe₃O₄) nanoparticles and compared to the UO₂ and 3,000 ppm U(VI) adsorbed onto γ -Fe₂O₃ (Umh) serving as reference compounds (A). ITFA-extracted eigenvectors (B); isolated single component spectra belong to the U(IV), U(V) and U(VI) contributions (C).