

X-ray Photoelectron Spectroscopy Investigation of the Interaction of U(VI) and Fe(III) with Natural Humic Acid in Aqueous Solutions

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Abstract. Complexes of U(VI) and Fe(III) with natural humic acid (NHA) were studied by X-ray photoelectron spectroscopy (XPS). It follows from the analysis of the uranium and iron concentrations at the surface and in the bulk of the humates that the reaction in solution is heterogeneous. The NHA reacts as a particle. In solutions containing either U(VI) or Fe(III), NHA reacts similar with Fe(III) and U(VI). How-

ever, in a mixed solution of Fe(III) and U(VI), NHA reacts predominantly with iron. In comparison to Fe(III) complexes, the complexes with U(VI) are formed mostly in the inner of the NHA particle. Therefore, the concentration ratio U/Fe as measured by XPS increases by powdering of the particles. Salts of Fe(III) can be used to inhibit the uranium migration in form of its soluble humates.

The determination of radionuclide speciation and factors influencing radionuclide migration in the environment is an important task in current radioecological research. Humic substances are present throughout the environment and are the main organic component in natural waters. Uranium can form strong complexes with humic substances in natural waters leading to increased solubility of uranium and an enhancement of its mobility. As a result of forty years of uranium mining in the Ore Mountains (Erzgebirge) in Germany and Czech Republic, the danger occurred that uranium present in flooded mine shafts, rock piles, seepage and tailing waters can reach the drinking water reservoirs of the population in this region. This problem is also important for several regions in Russia. To improve the predictive capabilities of transport models used for risk assessment of abandoned uranium mines and evaluation of remediation strategies for contaminated sites, it is important to obtain a better understanding of the interaction of uranium with humic substances.

X-ray photoelectron spectroscopy (XPS) is a well-suited method for determining radionuclide speciation in environmentally relevant samples [1]. XPS allows to determine the relative radionuclide concentration, its oxidation state, the relative ionic composition, and the structure of the near-neighbour environment of the ac-

tinide ion in the compound. Previously, we used XPS to determine the chemical state of uranium in samples containing reactor fuel from "lava" and compounds growing in it as a result of the accident at the fourth block of the Chernobyl nuclear power plant [2]. XPS was also used to study the interaction of the uranyl group with calcite and diabase [3], and humic acids [4] in aqueous solutions. In the present work we investigated the interaction of the uranyl group, UO_2^{2+} , and Fe^{3+} ions with natural humic acid using XPS. The aim was to clarify the possibility of the formation of uranyl compounds and iron complexes at the surface of humic-acids particles and the relative complex stability.

Experimental

In the study of the interaction of UO_2^{2+} and Fe^{3+} ions with humic acid in aqueous solutions, we used the commercial natural humic acid (NHA) A2 (Aldrich). The elemental analysis gave the following composition: C 58.05; H 4.6; N 0.7; S 3.8; Fe 0.6; O 32.22% [5]. The NHA A2 contains a total of 7.4 meq/g acidic groups including 4.8 meq/g carboxylic groups.

Five different types of reaction solutions were prepared by dissolving uranyl acetate ($\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$; Merck), uranyl perchlorate ($\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$; synthesized from

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Merck), or iron(III) perchlorate ($\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$; Fluka) in purified water. Reaction solution 1 contained 0.09 mol l^{-1} uranyl acetate at pH 4.1. Solution 2 was 0.08 mol l^{-1} uranyl perchlorate at pH 3.6. Solution 3 had identical composition as solution 1 except that it was prepared from ^{14}C -labeled uranyl acetate. Solution 4 was 0.10 mol l^{-1} iron perchlorate at pH 2.0. Solution 5 were 1:1, 1:3, and 3:1 mixtures of uranyl and iron perchlorates with pH values ranging from 1.9 to 2.3.

Solid uranyl and iron humates were prepared by stirring deaerated NHA A2 (Aldrich) in an aqueous suspension with solutions 1–5 for three days under nitrogen atmosphere. Table 1 gives the approximate ratios expressed in meq (mmol · ionic charge) of metal ion and humic acid carboxylic groups, which were chosen for the sample preparation.

The solid reaction product was separated from the suspension by centrifugation and washed twice with purified water. The pH values given in Table 1 were measured after separating the solid in the aqueous supernatant. The reaction product was freeze-dried until the vapour pressure was below 10^{-2} mm Hg. The amount of uranium and iron in the humates given in Table 1 was determined by ICP-MS after oxidation of the organic material with HNO_3 in a microwave oven. The carbon content of the solid humate was determined by elemental analysis. From the carbon content of the humic acid and of the humate, a "theoretical" amount of humate resulting from 1 g of NHA was calculated. The calculation of the metal loading of the humic acid (meq/g NHA) was based on the metal content and on this "theoretical amount of humate".

The XPS spectra of the samples were measured at room temperature using a MK II VG Scientific spectrometer with Al K_{α} anode ($h\nu = 1486$ eV). The vacuum in the spectrometer was 10^{-7} Pa. The spectrometer resolution measured as the full-width at half-maximum of the $\text{Au}4f_{7/2}$ line was 1.2 eV. The energy scale of the spectra was calibrated relative to the C1s binding energy ($E_b=285.0$ eV) of the hydrocarbon layer at the sample surface. The uncertainties of the binding energy and the relative line intensity are 0.2 eV and 10%, respectively.

The samples were measured in two ways: (i) without any additional treatment the sample was introduced into the spectrometer; (ii) prior to measurement the sample was powdered in a mortar. In what follows, samples are referred to as non-powdered and powdered according to their treatments (i) and (ii), respectively. The concentration ratios measured for non-powdered samples correspond to the surface composition of the sample. Since new surfaces are created by powdering, the corresponding concentration ratios represent the values in the bulk of the sample.

Results and Discussion

Table 1 contains the results of the chemical analysis of the reaction products of NHA with UO_2^{2+} and Fe^{3+} ions, which were determined by ICP-MS. From analysis of these results one can conclude the following:

1. When comparing the reaction of NHA in aqueous solutions containing only UO_2^{2+} or only Fe^{3+} ions, similar amounts of meq U(VI) and Fe(III) are found per gram NHA. The reaction is pH controlled. The degree of reaction of UO_2^{2+} with NHA is independent of the type of starting uranyl compound, *i.e.*, $(\text{UO}_2(\text{CH}_3\text{COO})_2$ or $\text{UO}_2(\text{ClO}_4)_2$).
2. If UO_2^{2+} and Fe^{3+} ions can react simultaneously with NHA, even a 3:1 excess of UO_2^{2+} ions in relation to Fe^{3+} ions does not influence the capacity of iron to form complexes with NHA. However, even small amounts of Fe^{3+} ions present in the solution lead to an approximately tenfold decrease of the UO_2^{2+} ion's ability to form complexes with NHA. This is also reflected by comparing the ratios meq Fe(III)/meq U(VI) in the reaction mixtures with those of the reaction products. For samples B38 – B40 with 1.0, 3.0, and 0.3 meq Fe(III)/meq U(VI) in the mixtures, the corresponding ratios in the solid humate were 6.0, 16.4, and 4.0 meq/meq, respectively (see Tab. 1). Therefore, Fe(III) salts can be used to hinder the formation of uranyl humates and thereby hinder the migration of uranium ions in form of soluble NHA complexes.

Table 1 Conditions of sample preparation and analytical results for reaction of natural humic acid A2 (Aldrich) with U(VI) and Fe(III) solutions. The amount of uranium and iron in the humates was determined by ICP-MS.

Sample No.	Reaction mixture				Solid humate		Fe %	meq/g NHA
	No.	$\text{UO}_2^{2+}/\text{COOH}$ meq/meq	$\text{Fe}^{3+}/\text{COOH}$ meq/meq	final pH	U %	meq/g NHA		
B25	1	0.1	–	1.6	4.13	0.4	–	–
B26	1	0.5	–	2.3	19.4	2.2	–	–
B27	1	1.4	–	3.4	31.2	4.4	–	–
B28	1	3	–	3.7	36.3	5.7	–	–
B29	2	0.1	–	1.4	5.0	0.4	–	–
B30	2	0.4	–	1.7	12.6	1.3	–	–
B31	2	0.8	–	2.1	19.1	2.4	–	–
B32	2	2.4	–	3.3	34.7	5.2	–	–
B33	3	3.0	–	3.8	36.1	5.9	–	–
B34	4	–	0.1	1.3	–	–	1.2	0.7
B35	4	–	0.6	1.1	–	–	3.4	2.0
B36	4	–	1.2	1.1	–	–	4.6	2.7
B37	4	–	3.6	1.4	–	–	6.4	3.9
B38	5	0.9	0.9	1.2	4.8	0.40	4.4	2.4
B39	5	0.9	2.7	1.2	2.9	0.25	7.7	4.1
B40	5	2.6	0.9	1.5	7.8	0.7	4.6	2.8

According to the XPS spectrum, the valence band of the NHA A2 (Aldrich) ranges from 0 to 40 eV binding energy. This is due to the outer valence molecular orbitals (OVMOs) and inner valence molecular orbitals (IVMOs) in such acids from interacting C2s,p, and O2s,p shells of neighbouring atoms. The structure of the low-energy electrons at the top of the valence band are to a large degree due to C2p and O2p shells. But the IVMO electrons at the bottom of the valence band are mostly due to the C2s and O2s shells of neighbouring carbon and oxygen atoms.

In this energy range the structure of the XPS spectrum changes significantly when the NHA reacts with uranium(VI) solutions. Additional structures related to OVMOs and IVMOs of the uranyl humate appear in the valence band of NHA (Fig. 1). A significant increase in line intensity of OVMOs is observed at the top of the valence band. In addition, in the binding energy range from 15 to 20 eV, two maxima are clearly observed. They relate to electrons of IVMOs and can be assigned as $2a_{2u}$ and $2e_{1u}$ for a $[\text{UO}_2^{2+}\text{O}_6]^{10-}$ cluster with D_{6h} symmetry. Taking into account the relation between $\Delta E(2a_{2u} - 2e_{1u})$ and the U–O bond lengths r_1 and r_2 to the axial and equatorial oxygen atoms [6], respectively, the bond lengths for the powdered samples B32 (B33) are $r_1 = 1.74$ (1.73) Å and $r_2 = 2.39$ (2.40) Å. These values agree with those determined previously for other uranyl complexes with NHA [4].

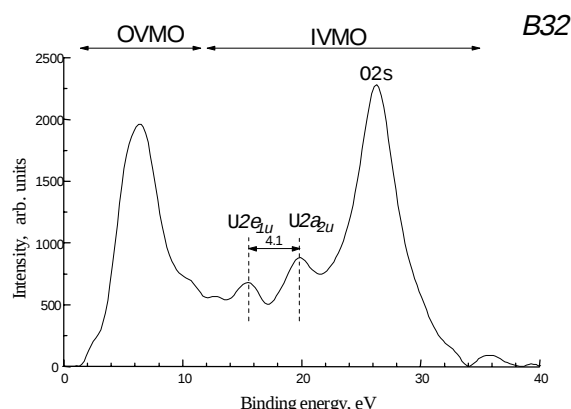


Fig. 1 XPS spectrum of outer and inner valence molecular orbitals (OVMO, IVMO) of uranyl humate sample B32 (powdered).

In the C1s spectrum of NHA one would expect a complicated structure since the carbon atoms are not chemically equivalent. The NHA A2 (Aldrich) has 4.8 meq/g carboxylic groups and 2.6 meq/g phenolic hydroxyl groups. Besides the main C1s line at 285.0 eV, which is due to the hydrocarbon layer at the sample surface, one would expect two additional maxima. The presence of $\equiv\text{C}-\text{OH}$ and $\equiv\text{COOH}$ groups would lead to maxima at 287 and 289.4 eV, respectively [7]. Indeed, at the high-energy side of the C1s line at $E_b = 285.0$ eV, an additional maximum occurs at $E_b = 289$ eV in the XPS of the reaction products. The peak intensity is proportional to the amount of $\equiv\text{COOH}$ groups. Due to the limited energy resolutions of these spectra, it is difficult to separate the C1s line related to carbon of the $\equiv\text{C}-\text{OH}$ group.

In the binding-energy region of the U4f electrons, the XPS spectrum of the uranyl humates consists of two main lines with a spin-orbit splitting Δ_{so} of 10.8 eV and two satellite lines. These monopole satellites with an intensity of 12% of the main line appear at 3.7 eV toward higher binding energy (Fig. 2). This satellite structure is characteristic for uranium in uranyl compounds containing U(VI) [2]. The U4f_{7/2} binding energy for the uranyl compounds at the surface of the humic acid equals 382.6 ± 0.1 eV. This is in good agreement with the corresponding value of $E_b = 382.7$ eV for $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and does not significantly differ from $E_b = 382.9$ eV for U4f_{7/2} in $\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ and $E_b = 382.9$ eV in $\text{UO}_2(\text{ClO}_4)_2(\text{DMSO})_5$.

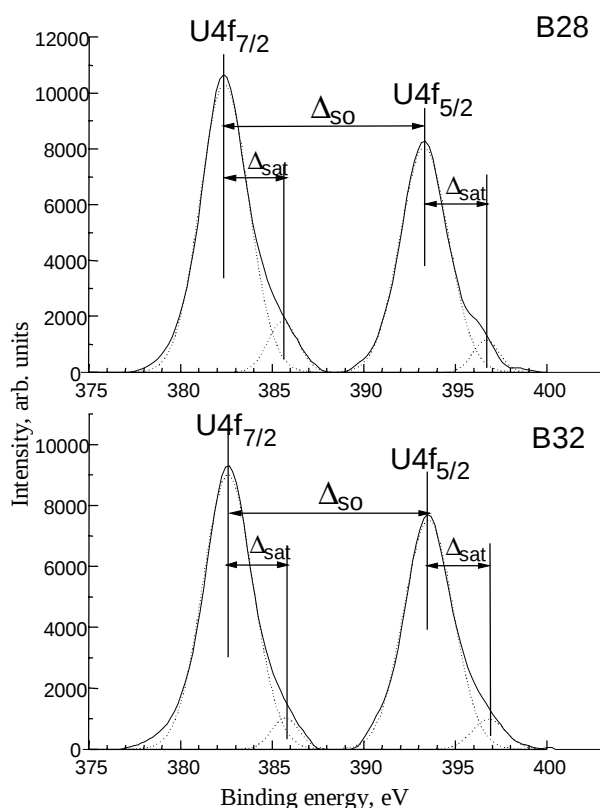


Fig. 2 U4f XPS spectra of uranyl humate samples B28 (top) and B32 (bottom). Both spectra were measured on non-powdered samples.

The Fe2p_{3/2} binding energy of the samples equals 712.1 ± 0.2 eV, which indicates the presence of Fe(III). The absence of a Cl2p line at 208 eV binding energy in the XPS spectra indicates that the ClO_4^- group is not part of the complex. As in our previous study of humic acids, we observed a weak N1s line with a binding energy of $\sim 400.5 - 401.0$ eV indicating the presence of HNR_2^+ groups [4].

The comparison of XPS line intensities of powdered and non-powdered samples allows to conclude on differences in the concentration of Fe(III) and U(VI) in the bulk and at the surface of the NHA particles. Some indirect and also some direct data indicate that the complex formation with uranyl proceeds to a larger degree in the bulk of the particle and not

at the surface. And *vice versa*, the Fe^{3+} ions are accumulated to a much larger extent at the surface of the particles than in their bulk. The dependency of the relative $\text{U4f}_{7/2}/\text{C1s}$ and $\text{Fe2p}_{3/2}/\text{C1s}$ line intensities of the powdered and non-powdered samples on the amount of meq U(VI) or Fe(III) per 1 g NHA is an indirect evidence (Figs. 3, 4). For the UO_2^{2+} ion the corresponding relative intensities are higher for the powdered samples (bulk) (Fig. 3). In case of Fe^{3+} , the $\text{Fe2p}_{3/2}/\text{C1s}$ ratio is larger for the non-powdered samples (surface) than for powdered ones (Fig. 4). These data are indirect evidence since the C1s electron line is not well suited as a standard due to the presence of hydrocarbon contamination at the surface. Also, a small change in the relative concentration of carbon atoms at the surface of the particle compared to the

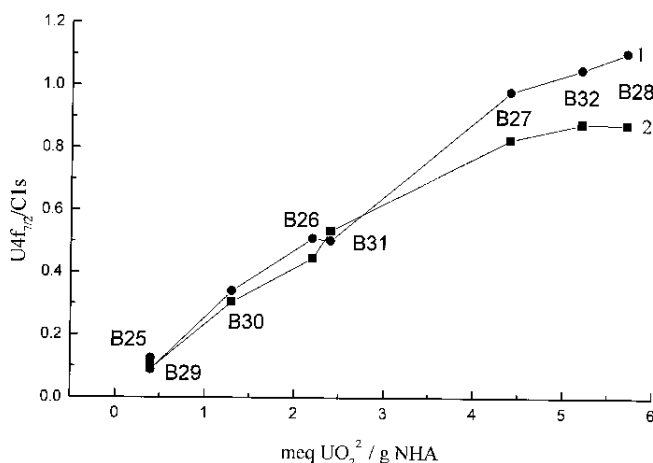


Fig. 3 Dependency of the relative $\text{U4f}_{7/2}/\text{C1s}$ line intensity on the relative concentration meq UO_2^{2+} /g NHA of the complexes. Curve 1 (circles) – powdered samples (bulk); curve 2 (squares) – non-powdered samples (surface).

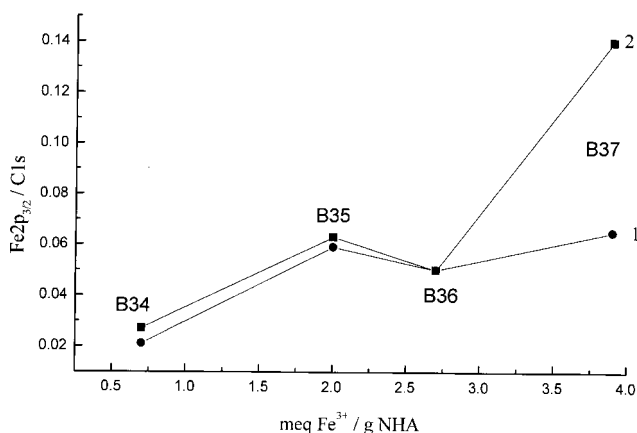


Fig. 4 Dependency of the relative $\text{Fe2p}_{3/2}/\text{C1s}$ line intensity on the relative concentration meq Fe^{3+} /g NHA of the complexes. Curve 1 (circles) – powdered samples (bulk); curve 2 (squares) – non-powdered samples (surface).

bulk is possible. The dependency of the relative line intensity $\text{U4f}_{7/2}/\text{Fe2p}_{3/2}$ on the relative concentration of UO_2^{2+} and Fe^{3+} ions (Fig. 5) belongs to the direct evidence. The relative in-

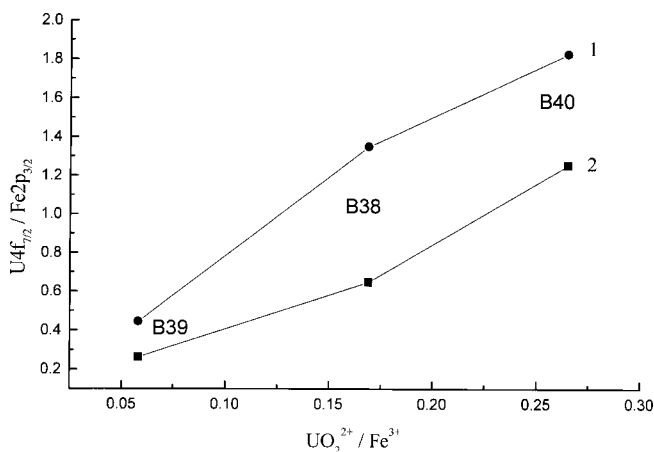


Fig. 5 Dependency of the relative $\text{U4f}_{7/2}/\text{Fe2p}_{3/2}$ line intensity on the relative concentration meq UO_2^{2+} /meq Fe^{3+} in the humates. Curve 1 (circles) – powdered samples (bulk); curve 2 (squares) – non-powdered samples (surface).

tensity is much higher for powdered than for non-powdered samples.

The difference in the distribution of components in the bulk and at the surface of the NHA particles is also supported by the S2p spectra. Both at the surface (non-powdered samples) and in the bulk (powdered samples), the S2p line of sulfate with a binding energy of approximately 168.2 eV and the S2p line of organic sulfide with an energy of 164.4 ± 0.2 eV are observed [7]. The ratio of sulfur atoms of the sulfate to sulfur atoms of the sulfide equals 0.5 ± 0.1 at the surface. For the majority of samples, this ratio is approximately two times smaller in the bulk.

In summary, we conclude the following: In the absence of iron ions, the uranyl ions and iron ions react similar with NHA. However, if UO_2^{2+} and Fe^{3+} ions react simultaneously with NHA, Fe(III) complexes are formed predominantly.

The reaction of NHA with solutions containing UO_2^{2+} and Fe^{3+} ions is heterogeneous. At the surface of the particle, the concentration ratios of the complexes are different from those in the bulk of the particle. The UO_2^{2+} ions prefers to participate in the complex formation in the bulk of the particle; but the Fe^{3+} ion at its surface. The sulfur atoms in the NHA A2 was found in two nonequivalent chemical states corresponding to SO_4^{2-} and SR_2 or HSR.

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