### AN X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF URANYL – CHITOSAN INTERACTION

by

# Alexander N. VELESHKO<sup>1</sup>, Irina E. VELESHKO<sup>1</sup>, Anton YU. TETERIN<sup>2</sup>, Konstantin I. MASLAKOV<sup>1</sup>, Labud VUKČEVIĆ<sup>3</sup>, Yury A. TETERIN<sup>1</sup>, and Kirill E. IVANOV<sup>1</sup>

Received on June 24, 2008; accepted on October 2, 2008

An X-ray photoelectron spectroscopy study of uranium sorption by spherically-granulated chitosan in sulphate solutions, as well as the study of the nature of the U(VI) – chitosan interaction was carried out in this work. The X-ray photoelectron spectroscopy analysis showed that the uranyl – chitosan interaction results in the formation of complexes with aminogroup nitrogen, and possibly chitin ring oxygens and free hydroxyl groups in the equatorial plane. Under the UHV in the spectrometer chamber, the uranyl–amin and uranyl–hyroxide bonds were shown to break and tetravalent uranium compounds were shown to form on the sample surface. Hydroxyl groups were shown to evaporate. The calculated  $\Delta G^0 = -1.3$  kJ/mol can be an evidence of several concurrent processes, some of which require energy, as well as of the formation of a surface chemical compound.

Key words: chitosan, uranyl, X-ray photoelectron spectroscopy, sorption

#### INTRODUCTION

Modern uranium hydrometallurgy sets a great number of tasks to be solved. The processing of low-concentration solutions and prevention of environment contamination being the most important ones. Sorption methods employing inorganic sorbents on the basis of titanium salts and organic ionites have been the most developed ones for the extraction of uranium from natural and mine waters [1, 2].

Since recently, complex-forming fibrous sorbents were proposed to be used for the extraction of

Nuclear Technology & Radiation Protection Scientific paper

UDC: 661.879.1:543.428.4

BIBLID: 1451-3994, 23 (2008), 2, pp. 43-50

DOI: 10.2298/NTRP0802043V

Authors' addresses:

<sup>1</sup> Russian Research Centre "Kurchatov Institute"

1, Kurchatov square

Moscow 123182, Russia

<sup>2</sup> N. S. Kurnakov Institute of Inorganic Chemistry,

1, Kurchatov square

Moscow 123182, Russia

<sup>3</sup> Faculty of Natural Sciences and Mathematics

University of Montenegro

P. O. Box 211, Podgorica, Montenegro

E-mail address of corresponding author: teterin@ignp.kiae.ru (Yu. A. Teterin)

trace-amounts of uranium from natural and waste waters [3]. These sorbents are compositions of thin porous acrylic fiber with finely dispersed polymeric complex-forming sorbents strongly fixed inside them. They can be used both as filters and in columns. The uranium sorption rate in the dynamic mode was 90%.

The development of technological methods for the minimization of industrial wastes is the issue of the day now. With this in mind, a sorbent on the basis of a natural biopolymer, chitosan, is especially promising. Chitosan's unique properties worth mentioning are: the presense of several functional groups in its structure, including aminogroups, high sorptive ability to heavy metals, low ash content, bio-compatibility and bio-destructivity to the level safe for humans and the natural environment [4]. Raw material sources for this bio-polymer are available and wide-spread. Therefore, chitosan production tends to grow and prices to fall.

Industrial chitosan is produced in the form of 10 mm scales or powders. Obviously, the factor defining the sorptive ability to metal ions is their diffusion in the surface layer. It is known that amorphous chitosan has a higher sorption efficiency. One way to make chitosan amorphous is the reprecipitation from solutions. This also enables us to produce spherically granulated sorbents [5, 6]. Lacing also leads to crystal structure regularity breakdown and

to an increase in durability [7]. These sorbents were used for the extraction of  $Cu^{2+}$  ions from sulphate solutions. The total static exchange capacity (TSEC) was 5.6 mmol/g for dry sorbents [8].

References [4, 9, 10] give the data on sorption properties of chitosan to uranium. However, some of the problems have not been fully researched yet. For example, it's not clear how to reach the highest capacity. According to calculations taking into account the content of amides and the equimolar structure of the formed complex, it is around 6 mmol/g. Besides, there is still no consensus on the nature of U(VI) – chitosan interaction. The authors of [10] have suggested the following composition of the complex:  $UO_2^2$  is surrounded by two hydroxyl groups and a single amide group, as well as a water molecule or the hydroxyl group's third carbon atom of the glucosamine ring.

It's known that acid leaching provides the most complete uranium extraction from ores. This method uses sulphuric acid formed from sulphur oxidation in the air, under pressure or by bacteria [1]. Therefore, U(VI) sorption was conducted from aqueous solutions of UO<sub>2</sub>SO<sub>4</sub>.

The present work is dedicated to the study of the laws of uranium sorption by spherically-granulated chitosan in sulphate solutions and the determination of the nature of U(VI) – chitosan interaction. X-ray photoelectron spectroscopy (XPS) was employed for this purpose.

#### **EXPERIMENTAL**

XPS spectra of the studied samples were measured with an electrostatic spectrometer MK II VG Scientific using non-monochromatized AlK<sub> $\alpha$ 1,2</sub> (hv == 1486.6 eV) radiation at room temperature. The resolution of the device was 1.2 eV, measured as full width on the half-maximum (FWHM) of the Au4f<sub>7/2</sub> line on the standard rectangular golden plate. The binding energies (BE)  $E_b(eV)$  were measured relatively to the BE of C1s electrons from hydrocarbons absorbed on the surface of the sample, accepted to be equal to 285.0 eV. For the gold standard, calibration binding energies  $E_b(C1s) = 284.7 \text{ eV}$  and  $E_b(Au4f_{7/2})$ = 83.8 eV were used. The FWHM were measured relatively to the width of the C1s line of hydrocarbons, accepted to be equal to 1.3 eV. The error in the determination of electron BE and line widths did not exceed 0.1 eV and that of the relative line intensities was less than 10%.

The studied samples were prepared as thin films or finely dispersed powders on a double-sided conductive adhesive tape. For all the samples, the following spectra were measured: valence band 0-50 eV BE, the U4f, the N1s, the O1s, and the C1s. U4f spectra enable us to determine uranium valency. Calibration by the C1s peak was done for each measurement, since the

strongly charged samples (up to 5 eV BE) and their charging times were unstable. In other words, the C1s peak was measured before and after each spectrum. It lowered the BE error down to 0.1 eV. After the initial study, samples 1, 2, and 3 were left in the spectrometer chamber for a day. After that, they were studied again in order to understand the influence of UHV on their stability. Thereafter, terms 1a, 2a, and 3a (samples studied on the first day) and 1b, 2b, and 3b (samples studied on the second day) were introduced (tab. 1).

For all the samples, quantitative elemental and ionic analysis was done. It was based on the fact that spectral intensity is proportional to the number of certain atoms in the studied sample. The following ratio was used:  $n_i/n_j = (S_i/S_j)(k_j/k_i)$ , where  $n_i/n_j$  is the relative concentration of studied atoms,  $S_i/S_j$  – the relative core-shell spectral intensity, and  $k_j/k_i$  – the relative experimental sensitivity coefficient. The following coefficients relative to C1s were used: 1.00 (C1s), 2.64 (O1s), 1.68 (N1s), 36.0 (U4f<sub>7/2</sub>), 2.16 (S2p) [11].

The new formed chitosan granules (NFCG) with a diameter of 3 mm produced according to [6] were used as sorbents. Studies of the sorption properties of the granulated chitosan and its modifications were conducted in static conditions of the  $\rm UO_2SO_4$  solution of a 0.75-1400 mg/l concentration. As a tag, the  $\rm ^{233}U$  radionuclide was used. The specific activity of the solutions amounted to  $\rm 10^5\text{-}10^6$  Bg/l.

The sorption experiments were done in the following way: the  $UO_2SO_4$  aqueous solution of a given concentration containing <sup>233</sup>U was mixed with granulated chitosan of the quantity providing the constant ratio V/m = 125.

Previous experiments on U(VI) sorption by spherically granulated chitosan showed that the most effective sorption takes place when pH = 5. Therefore, the pH of the experimental solution was corrected and controlled with the pH-meter "HANNA 8314". The content of uranium hydrolysis products was determined by the activity of the solution. The sorbent in the solution was mixed over a necessary period of time, at a constant pH. At the end of the process, solid and liquid phases were separated by filtering on the plastic net with a diameter of 0.25 mm. The granules were then washed in water acidified with HNO<sub>3</sub> to pH = 5, so as to remove the residual products of the hydrolysis. After that, the granules were placed in a 10 ml glass and solved in 1% acetic acid. The products of uranium hydrolysis were separated by centrifugation and solved in 1 mol of HNO<sub>3</sub>. Uranium content was measured with the spectrometer-radiometer "Quantulus 1220" in standard potassiumless dishes in a liquid scintillator "HiSafe".

The samples for the XPS studies were prepared in the following way:

Sample 1 (film) was obtained as a result of  $^{238}$ U sorption on NFCG from a  $UO_2SO_4$  solution (molecular mass 170 kDa; 1 Da = 1.6605  $10^{-27}$  kg) over an hour.

Sample	U <sup>4+</sup> 4f <sub>7/2</sub>	U <sup>6+</sup> 4f <sub>7/2</sub>	N1s	S2p	O1s	C1s
1a.1st day film +U	380.3 (1.5)	382.3 (1.5)	399.4 (1.5) 401.6		532.7 (2.4)	285.0 (1.3) 286.7 288.4
1b. 2 <sup>nd</sup> day film +U	380.7 (1.5)	382.5 (1.5)	399.9 (1.7) 401.6		532.4 (2.4)	285.0 (1.3) 286.7 288.3
2a. 1st day granules +U	380.7 (1.5)	382.4 (1.5)	400.1 (1.5) 401.5		531.3 (1.5) 533.1	285.0 (1.3) 286.5 288.2
2b. 2 <sup>nd</sup> day granules +U	380.8 (1.5)	382.5 (1.5)	399.7 (1.5) 401.9		531.4 (1.5) 533.1	285.0 (1.3) 286.6 288.2
3a. 1st day chitosan powder			399.6 (1.3)		533.2 (1.5)	285.0 (1.3) 286.5 288.2
3b. 2 <sup>nd</sup> day chitosan powder			399.7 (1.2)		533.2 (1.3)	285.0 (1.3) 286.5 288.2
4. Powder +U	380.7 (1.4)	382.3 (1.4)	399.7 (1.2) 401.9	160.5 (1.3) 165.8	531.3 (1.4) 533.0	285.0 (1.3) 286.6 288.4
5. Powder of UO <sub>2</sub> SO <sub>4</sub> nH <sub>2</sub> O		383.1 (1.8) 385.9 sat		169.6 (1.9)	532.4 (1.5)	285.0 (1.3)
Chitosan [18]			399.9			
Chitin [18]			401.6			
Cellulose [15]					532.5	
UO <sub>2</sub> [14]		380.9			530.5	285.0
γ-UO <sub>3</sub> [14]		382.4			531.4	285.0

Table 1. Electron binding energies  $E_{\rm b}({\rm eV})$  of compounds and complexes. Biding energy distances to the shake-up satellites are given in parentheses

After the sorption, the granules were separated, washed in a HNO $_3$  lean solution ( $\sim$ 0.001 M) and dried in the air. The water content of the air-dried granules was 6-8%. To prepare the film, the granules were solved in acetic acid ( $\sim$ 200  $\mu$ l of CH $_3$ COOH). The solution was put on an aluminum substrate and dried in the air. As a result, a  $\sim$ 5  $\mu$ m thick film was obtained. The  $^{238}$ U content in the film was  $\sim$ 5-8 mg. The chemical reaction of this process is shown at (a).

Sample 2 (powder). The  $^{238}$ U sorption on NFCG from a UO<sub>2</sub>SO<sub>4</sub> solution (molecular mass 170 kDa) lasted an hour. After that, the granules were separated, washed in HNO<sub>3</sub> ( $^{\sim}0.001$  M) and dried in the air. The water content in the air-dried granules varied from 6-8%. To prepare the powder, the granules were milled in a ball mill ( $d_{\text{particle}} \sim 20 \, \mu \text{m}$ ). The uranium content in the film was  $\sim 170 \, \text{mg/g}$ . The chemical reaction of this process is shown at (b).

Sample 3 (powder). Chitosan powder after the milling of the air-dried granules in a ball mill ( $d_{\text{particle}} \sim 20 \text{ um}$ ).

Sample 4 (powder) – powderized complex chitosan – U(VI).  $^{238}$ U sorption on chitosan powder from the UO<sub>2</sub>SO<sub>4</sub> solution (molecular mass 170 Da) was done over an hour. To prepare the powder, the granules were milled in a ball mill ( $d_{particle}$  ~20  $\mu$ m). After the sorption, chitosan powder was separated from the solution by centrifugation, washed in HNO<sub>3</sub> (~0.001 M) and air-dried.

Sample 5 (powder). 0.5 g of powderized  $UO_2SO_4 \times nH_2O$  obtained by reprecipitation of  $UO_2SO_4 \times 3H_2O$  with  $NH_4OH$  and dilution of  $UO_2(OH)_2$  in a 1-3 M solution of  $H_2O_4$ . The solution was steamed to humid salts and air-dried at t=30 °C. The dry salt was washed thrice in ethanol and air-dried. The salt  $UO_2SO_4 \times nH_2O$  was ground in a porcelain mortar.

#### RESULTS AND DISCUSSION

To evaluate the sorbate—sorbent interaction energy, a sorption isotherm was drawn and the TSEC for U(VI) on NFCG was calculated (fig. 1). The calculations were done using the linear Freundlich equation [12]:

$$\ln A \quad \ln K \quad \frac{1}{n} \ln C \tag{1}$$

where C is the sorbate equilibrium concentration in solution [mg/ml], K – the sorption equilibrium constant, and A – the equilibrium sorption at a given temperature [mg/g].

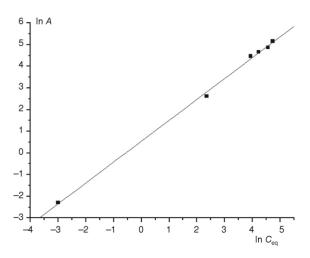


Figure 1. Sorption isotherm for U(VI) on NFCG from UO<sub>2</sub>SO solution; pH = 5, T = 298 K, V/m = 125

The calculation of the coefficient K in the linear Freundlich equation was done using the least squares method. The calculated mean-square error R = 0.998

indicated the adequacy of the chosen mathematic model for the studied sorption process. The coefficient K was 1.71. The TSEC for U(VI) on NFCG was experimentally established to be 0.7 mmol of U(VI)/g of dry sorbent.

The chemical potential was calculated using the Van't Hoff isotherm equation:

$$\Delta G^0 = RT \ln K$$
 (2)

where  $\Delta G^0$  is the Gibbs function [J/mol], R – the universal gas constant [J/mol], T – the temperature [K], and K – the reaction equilibrium constant.

As a result,  $\Delta G^0$  was 1,3 kJ/mol. Such a low  $\Delta G^0$  can be an evidence of several concurrent processes, some of which require energy, or, of the formation of a surface chemical compound [12].

The valence electronic configuration and ground state of the uranium atom is:  $^{92}\text{U6s}^26\text{p}^65\text{f}^36d7\text{s}^2$   $^{5}\text{L}_{6}^{0}$ . This proves that an uranium ion can have several oxidation states.  $\text{UO}_2$  and  $\text{UO}_3$  are known to be the most stable uranium oxides. Electron BE for various uranium electronic shells in oxides and metal are known. Thus, the U4f XPS exhibits a spin-orbit split doublet ( $\Delta E_{\text{sl}} = 10.8 \, \text{eV}$ ) [13]. Satellites at  $\Delta E_{\text{s}}$  to the right side of the basic peaks, are observed in U4f XPS of uranium oxides. The peak positions and satellite separations are different for uranium ions of different oxidation states. Thus, the U4f<sub>7/2</sub> BE ( $E_{\text{b}}$ ) are: metallic U– $E_{\text{b}} = 377.4 \, \text{eV}$ ,  $\Delta E_{\text{sl}} = 10.8 \, \text{eV}$  [13];  $\text{UO}_2 - E_{\text{b}} = 380.9 \, \text{eV}$ ,  $\Delta E_{\text{s}} = 6.9 \, \text{eV}$ ;  $\gamma$ -UO<sub>3</sub> –  $E_{\text{b}} = 382.4 \, \text{eV}$ ,  $\Delta E_{\text{s}} = 3.7 \, \text{eV}$  [14]. Uranium BE for other shells and compounds are also known [14].

The XPS from the studied chitosan and its complexes with uranium in the BE range of 0-1200 eV exhibits peaks attributed to elements included in the studied compounds, as well as Auger- (CKVV and OKVV) lines (fig. 2). This BE range can be conditionally subdivided into three parts [14]. The first one, 0-15 eV, shows the structure attributed to electrons from the outer valence molecular orbitals (OVMO), built mostly from the incompletely filled outer U5f,6d,7s, C2p, O2p, and N2p atomic orbitals AOs (fig. 2b). This spectral range exhibits a sharp peak attributed to U5f electrons not participating in the formation of the chemical bond. The U5f intensity at  $E_{\rm h}$  = = 1.9 eV can serve as a quantitative parameter of uranium ionic composition in a compound [14]. The second one, 15-40 eV, shows the structure due to inner valence molecular orbitals (IVMO) built mostly from the completely filled inner valence U6p, C2s, O2s, and N2s AOs. The IVMO structure features correlate with uranium close environment parameters in compounds [14]. The third range above 50 eV exhibits the core electron shells related structure. The core shells do not participate in the formation of molecular orbitals. However, this spectral range can exhibit a structure attributed to the spin-orbit interaction with the splitting  $\Delta E_{\rm sl}({\rm eV})$ , multiplet splitting  $\Delta E_{\rm ms}({\rm eV})$ , many-body

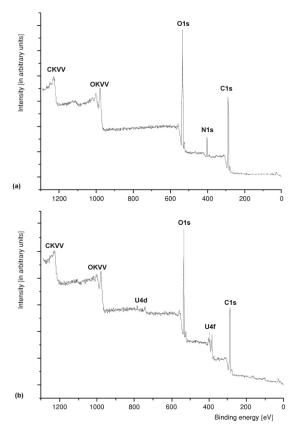


Figure 2. Survey XPS from (a) – sample 3a, and (b) – sample 4

perturbation, dynamic effect, etc. [14]. Since these structure parameters correlate with various properties of the studied compounds, they are used along with traditional XPS parameters, such as electron BE, peak intensities, chemical shifts, and energy differences between the XPS peaks. To simplify the discussion, both molecular and atomic terms will be used below.

Low binding energy XPS (0-50 eV). The low BE XPS from the studied complexes exhibit U5f peaks and OVMO bands formed from the outer valence U5f,6d,7s, C2p, O2p, and N2p shells, as well as an IVMO structure due to the U6p, C2s, O2s, and N2s shells. In the O2s BE range, a wide structured line is observed. For chitosan (sample 3), the FWHM of this line is ~4 eV, while the O1s peak is much narrower  $(\Gamma \sim 1.5 \text{ eV})$ . The structure in the O2s BE range is attributed to IVMO formation. The U5f and U6p peak are observed to be of low intensity which complicates a correct elemental and structural analysis. However, the low BE XPS yields some qualitative conclusions. Indeed, after chitosan (sample 3) stayed for 24 hours in the spectrometer chamber under the UHV, the low BE XPS did not sustain any significant changes. However, in the same XPS from the complexes (samples 1, 2) the intensity of the U5f peak rose significantly. It indicates the decrease of U<sup>6+</sup> and an increase of U<sup>4+</sup> on the sample surface. In this spectrum, a U5f peak is also observed in sample 4. This analysis is

possible because in the low BE XPS from studied materials (insulators) at 1.9 eV BE only the U5f peak occurs.

Core electron shells XPS (above 50 eV binding energy). The quantitative elemental and ionic XPS analysis usually employs the most intense peaks from the included elements [15]. In our case, they were the C1s, O1s, N1s, S2p, and U4f ones (tab. 1). The S2p and U4f spectra are observed as spin-orbit split doublets with  $\Delta E_{\rm sl}$  =1.1 eV and 10.8 eV [13], respectively. Although the C1s, O1s, and N1s peaks are single, these spectra are observed structured due to the presense of carbon, oxygen, and nitrogen ions of different oxidation states (figs. 3-5). The C1s spectrum consists of several peaks attributed to carbon ions of different oxidation states (fig. 3a). This spectrum allows only a qualitative attribution of spectral lines to polimer carbon ions. Thus, the peak at 285.0 eV is attributed to the saturated hydrocarbons (for example,  $-CH_3$ ), the one at 286.7 eV – to carbon ions bound with one oxygen, and the one at 288.4 – to carbon ions bound with two oxygen ions. Also, the C1s spectrum from chitosan contains three peaks, where the middle one is more than twice more intense than the side ones. It has to be noted that the C1s spectra did not change during the time the samples stayed in the spectrometer chamber.

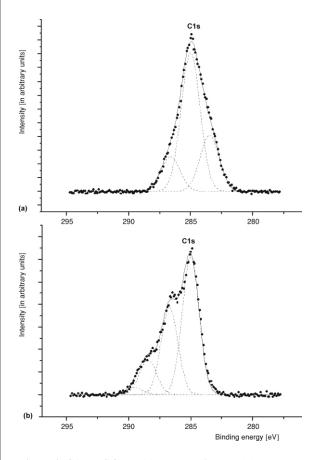


Figure 3. C1s XPS from (a) – sample 3a, and (b) – sample 1a

The O1s XPS from chitosan (sample 3a) shows up as a relatively symmetric sharp ( $\Gamma$  = 1.5 eV) peak with a small shoulder on the lower BE side. This shoulder can be attributed to the –OH-group. The fact that, in the XPS from the complex (sample 4), the low BE shoulder rises can be explained by the presense of extra hydroxyl groups. Similar considerations can be applied to the XPS from samples 1 and 2.

The O1s XPS from the complex (sample 2) consists of the two peaks (tab. 1, fig. 4) at 531.3 and 533.1 eV. Using the following equations [16]:

$$E_{\rm b}({\rm eV}) = \frac{2.27}{R_{\rm M-O}({\rm nm})} = 519.4$$
 (3)

from where

$$R_{\text{M-O}}(\text{nm}) = \frac{2.27}{E_b = 519.4}$$
 (4)

on the basis of O1s BE, one can evaluate interatomic distances  $R_{\text{A-O}}$  (nm) to oxygen in the studied samples, which are 0.191 and 0.166 nm.

The N1s XPS from chitosan (sample 3) exhibits one sharp ( $\Gamma$  = 1.3 eV) peak at  $E_{\rm b}$  = 399.7 eV (tab. 1). After the formation of chitin-uranium complexes (samples 1, 2, and 4), an extra peak on the higher binding energy side at  $E_{\rm b}{\sim}401.6$  eV shows up in the N1s spectrum. The intensity of this peak decreases in time, which may be an indication of the disintegration of the uranium-nitrogen bond in studied materials.

The XPS from chitosan (sample 3) did not detect a S2p peak within the measurement error. However, the XPS from the complex (sample 4) exibited low intense S2p peaks at 160.5 and 165.8 eV (tab. 1). The higher binding energy peak can be attributed to the  $SO_3^2$  group, while the one at 160.5 eV must be related to the sulphur bound with other included ions [15].

The U4f XPS from  $\rm UO_2SO_4 \times nH_2O$  (Sample 5) consists of a doublet with a relatively sharp peak. On the higher BE sides, at a distance from these peaks and at 2.8 eV, 20% intensity shake up satellites are observed (tab. 1). This is a typical XPS for  $\rm U^{6+}$  [14]. The U4f XPS from the uranium-chitosan complex film (sample 1) exhibits the two chemically inequivalent uranium states,  $\rm U^{4+}$  and  $\rm U^{6+}$  (fig. 5). During the time spent in the spectrometer chamber, an increase in the  $\rm U^{4+}$ component was observed (fig. 5b). It can be explained by UHV influence and suggests that only  $\rm U^{6+}$  ions were initially present in the studied complex. A similar picture was observed for all the other studied complexes (samples 2 and 4).

Quantitative analysis results. The error in the XPS quantitative elemental and ionic analysis of the studied compounds and complexes can grow because of the extra spectral structure in the core level XPS range, due to the secondary electronic processes (many-body perturbation). Since the many-body perturbation results in the shake up satellites on the higher BE side of the basic peaks, their intensity can be par-

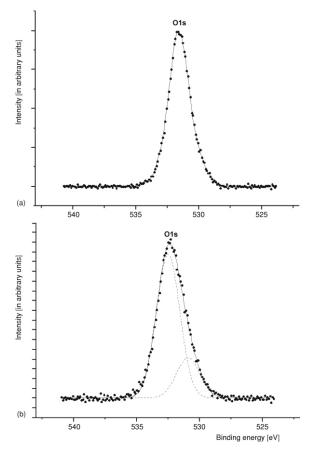


Figure 4. O1s XPS from (a) - sample 3a, and (b) - sample 4

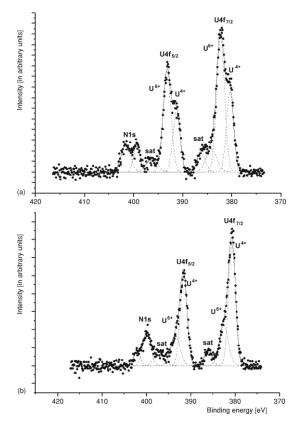


Figure 5. U4f and N1s XPS from (a) – sample 1a, and (b) – sample 1b

tially taken into account (fig. 4). All these fact can lead to an error of more than 10%. The XPS quantitative elemental and ionic analysis of the surfaces (~5 nm) of the studied samples relative to carbon was done with this in mind:

- $\begin{array}{lll} \text{1. Sample 1a} & & C_{1.00}O_{0.53}N_{0.06}(N_{0.037},\,N_{0.023}) \\ & & U_{0.011}\,\,(U_{0.004}^4,\,U_{0.007}^6) \\ \text{Sample 1b} & & C_{1.00}O_{0.50}N_{0.07}(N_{0.050},\,N_{0.020}) \\ & & U_{0.010}\,\,(U_{0.007}^4,\,U_{0.003}^6) \end{array}$
- 2. Sample 2a  $-C_{1.00}O_{0.60}N_{0.14}(N_{0.114}, N_{0.026})$  $U_{0.010} (U_{0.005}^4, U_{0.005}^6)$ 
  - $\begin{array}{cccc} \text{Sample 2b} & & C_{1.00}C_{0.005}, C_{0.005}, \\ & & C_{1.00}C_{0.50}N_{0.13}(N_{0.120}, N_{0.010}) \\ & & U_{0.009}(U_{0.007}^4, U_{0.002}^6) \end{array}$
- $\begin{array}{lll} \text{3. Sample 3a} & & C_{1.00}O_{0.54}N_{0.13} \\ \text{Sample 3b} & & C_{1.00}O_{0.54}N_{0.12} \end{array}$
- $\begin{array}{l} \ C_{1.00} O_{0.53} N_{0.07} (N_{0.063}, \, N_{0.007}) \\ U_{0.007} (U_{0.005}^4, \, U_{0.002}^6) \\ S_{0.013} \, (SO_3^2 \, ) \, S_{0.015} (S\!-\!A) \end{array}$ 4. Sample 4

The obtained data differ slightly from initial calculation results for the bulk of the samples. The difference can be explained by the fact that the XPS deals with a 5-10 nm thick surface.

Our XPS analysis shows that the uranyl chitosan interaction results in the formation of complexes with amide nitrogen, and possibly, chitin ring oxygens and free hydroxyl groups in the equatorial plane. Indeed, in the spectrometer chamber, under UHV influation, uranyl-amide and uranyl-hyroxide bonds broke and tetravalent uranium compounds were shown to form on the sample surface. The hydroxyl group evaporated (see quantitative analysis data for samples 1 and 2).

#### **CONCLUSIONS**

The XPS analysis shows that the uranyl – chitosan interaction results in the formation of complexes with amide nitrogen, possibly, with chitin ring oxygens and free hydroxyl groups in the equatorial plane. Under UHV in the spectrometer chamber, uranyl-amide and uranyl-hyroxide bonds were shown to break and tetravalent uranium compounds to form on the sample surface. Hydroxyl groups were hown to evaporate.

The calculated  $\Delta G^0 = -1.3$  kJ/mol can be an evidence of several concurrent processes, some of which require energy, as well as the formation of a surface chemical compound.

#### REFERENCES

Kats, J., Seaborg, G., Mors, L., Chemistry of Actinides (in Russian), Mir, Moscow, 1991

- [2] \*\*\*, Uranium Chemistry (in Russian) (Ed. B. N. Laskorina), Nauka, Moscow, 1981, pp. 58-67
- [3] Myasoedova, G. V., Zaharchenko, E. A., Molochnikova, N. P., Proceedings, Fifth Russian Conference on Radiochemistry, Dubna, Russia, October 23-27, 2006, p. 109
- Muzarelli, R. A., Natural Chelating Polymers: [4] Alginic Acid, Chitin and Chitosan, Oxford, Pergamon Press, 1973
- Mironov, A. V., Vedenina, O. L., Vihoreva, G. A., Kildeeva, N. R., Abulov, A. I., Production of Granulated Chitosan (in Russian), Him. Volokna (Chem. Fibers), 2005, 1, pp. 26-29
- Rumyantseva, E. V., Chernyshenko, A. O., [6] Neborako, A. A., Saraeva, E. Yu., Vihoreva, G. A., Kildeeva, N. R., Proceedings, Eighth Int. Conf., Modern Tendencies in the Studies of Chitin and Chitosan, Kazan, Russia, June 13-17, 2006, pp. 126-130
- Wan Ngah, W. S., Endud, C. S., Mayanar, R., Removal of Copper (II) Ions from Aqueous Solution onto Chitosan and Cross-Linked Chitosan Beads, React. and Funct. Polym., 50 (2002), 2, pp. 181-190
- Rumyantseva, E. V., Vihoreva, G. A., Kildeeva, N. R., [8] Neborako, A. A., Saraeva, E. Yu., Galbraih, L., Sorption of Copper Ions by Granulated Chitosan (in Russian), Him. Volokna (Chem. Fibers), 2006, 2, pp. 6-10
- Piron, E., Domard, A., Interaction between Chitosan and Uranyl Ions - Part 1. Role of Physicochemical Parameters, International Journal of Biological Macromolecules, 21 (1997), pp. 327-335
- Piron, E., Domard, A., Interaction between Chitosan and Uranyl Ions - Part 2. International Journal of Biological Macromolecules, 22 (1998), pp. 33-40
- \*\*\*, Auger and X-Ray Photoelectron Spectroscopy Surface Analisys (in Russian) (Eds. D. Briggs, M. P. Sich), Mir, Moscow, 1987
- Frolov, Yu. G., The Course of Colloid. Surface Phenomena and Disperse Systems (in Russian), 2<sup>nd</sup> ed., Himiya, Moscow, 1989, pp. 129-153
- Fuggle, J. C., Martensson, N., Core-Level Binding Energies in Metals, Journal of Electron Spectroscopy and Related Phenomena, 21 (1980), 3, pp. 275-281
- Teterin, Yu. A., Teterin, A. Yu., Structure of X-Ray Photoelectron Spectra of Light Actinide Compounds, Russian Chemical Reviews, 73 (2004), 6, pp. 541-580
- Nefedov, V. I., X-Ray Photoelectron Spectroscopy of Chemical Compounds (in Russian), Khimiya, Moscow,
- Sosulnikov, M. I., Teterin, Yu. A., X-Ray Photoelectron Spectroscopy Study of Calcium, Strontium, Barium and Their Oxides (in Russian), DAN SSSR, 317 (1991), 2, pp.
- [17] Wells, A., Structural Inorganic Chemistry (Ed. M. A. Poray-Koshts), (in Russian), Mir, Moscow, 1987, Vol. 2
- Teterin, Yu. A., Biotechnology for Waste Management and Site Restoration (Eds. C. Ronneau, O. Bitchaeva), NATO ASI-Series, Kluwer Academic Publichers, Series 2 Environment, 1997, Vol. 34, pp. 135-139

## Александар Н. ВЕЛЕШКО, Ирина Е. ВЕЛЕШКО, Антон J. ТЕТЕРИН, Константин И. МАСЛАКОВ, Лабуд ВУКЧЕВИЋ, Јуриј А. ТЕТЕРИН, Кирил Е. ИВАНОВ

### ИСТРАЖИВАЊЕ УРАНИЛ – ХИТОСАН ИНТЕРАКЦИЈЕ РЕНДГЕН-ИНДУКОВАНОМ ФОТОЕЛЕКТРОНСКОМ СПЕКТРОСКОПИЈОМ

У овом раду приказано је проучавање сорпције уранијума сферно гранулираним хитосаном у сулфатном раствору и природе U(VI) — хитосан интеракције посредством рендген-индуковане фотоелектронске спектроскопије. Фотоелектронском спектроскопском анализом потврђено је да интеракција уранил — хитосан добија облик комплекса са азотном аминогрупом, са могућим кисеоницима хитинског ринга и слободним хидроксилним групама у екваторијалној равни. У спектрометарској комори у ултрависоком вакууму, показало се да се везе уранил-амина и уранил-хидроксида кидају, а да се легура тетравалентног уранијума образује на површини узорка док хидроксилне групе испаравају. Израчунати  $\Delta G^0 = -1,3$  kJ/mol може се сматрати показатељем више конкурентних процеса од којих неки захтевају енергију, као и назнаком формирања површинских легура.

Кључне речи: хишосан, уранил, ренд ген-индукована фошоелек шронска сцек шроской ија, сор ција