

THE LEVEL OF THE URANIUM, RADIUM, AND OTHERS RADIONUCLIDES CONCENTRATION IN OBJECTS OF ENVIRONMENT AND BIOOBJECTS IN POWERFUL INDUSTRIAL CENTER

*N.P. Dikiy, E.P. Bereznyak, Yu.V. Lyashko, E.P. Medvedeva, D.V. Medvedev
National Scientific Centre Kharkov Institute of Physics and Technology*

INTRODUCTION

The problems of actinides migration and distribution in different medium are very importance and actual. Actinides geochemical mobility is higher in contaminated ecosystem.

A substantial public discussion was devoted to influencing of sulfate, phosphate, and carbonate complexation on uranium distribution in the ecosystem and on the health effects. Depleted uranium is less radioactive than natural uranium. The risks from the chemical toxicity of uranium and its different effects on human health and disease considered [1].

Natural uranium found in water, soil, and rocks with an average concentration in the earth's crust of 2.7 mg/kg, or 0.0004%. It occurs as a mixture of three radioactive isotopes ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.0055%) [2]. Radioactivity of natural uranium 25.280 Bq/g depends on the percentage and on specific activity of the three isotopes ^{238}U (12.455 Bq/g), ^{235}U (80.011 Bq/g) and ^{234}U ($2.31 \cdot 10^{-6}$ Bq/g). Uranium is present in oxidation states 0, +2, +3, +4, +5 and +6, being the prevalent forms the tetravalent U(IV), found in most minerals and U(VI), which represents the more suitable state [3]. Elemental uranium dissolve in the strong acids (H_2SO_4), while it is stable in a strong base solution. Divalent uranium compounds (+2), as UO exist only in the solid-state [4]. Trivalent compounds readily oxidized in water solution. Pentavalent uranium is compounds oxidized by oxygen in presence of air, and gives tetravalent and hexavalent by disproportionation in absence of air. The tetravalent uranium compounds, stable in the absence of air, comprise the oxide UO_2 , different salts and basic salt as $\text{UO}(\text{NO}_3)_2$ and UOCl_2 . The chemistry of uranyl (UO_2^{+2}) cation is the most dangerous for the environmental and biological behavior. Uranyl cation is a "yard" cation that strongly interacts with inorganic oxygen donor ligands and organic ligands like carboxylic and amino carboxylic acids, phenols and biological substances [5]. The complex formation, equilibrium involving uranyl complexes and coordination of number inorganic and organic ligands are very importance for examination of determinant for environmental fate of (UO_2^{+2}), and its absorption and bioavailability in humans.

The aim of the present study is to investigate the uranium mobility and concentration process in drinking water, soil, aquatic plant (hydrophyte) and patients' kidney stones in the region of Kharkov.

2. MATERIALS AND METHODS

There are the samples of drinking water, soils from neighborhood in Kharkov, river plant "*Pistia stratiotes*"

and kidney stones from 24 patients (the age group was 40-68) of Regional Clinical hospital N17.

The determination of uranium content in samples was performed by gamma spectrometer method on Ge(Li)-detector with the volume of 50 cm³ and resolution of 3.2 keV at 1332 keV line. To reduce the influence of background, the detector is equipped with a three-layer Pb-Cu-Al protection. The more significant error is for ^{238}U , the activity of which was calculated from activity of ^{235}U (line of 186 keV is equal sums of line from $^{226}\text{Ra} + ^{235}\text{U}$). The errors of measurements were from 7 to 25%.

Samples irradiated by bremsstrahlung from the linear accelerator electron NSC KIPT with energy 23 MeV and current 500 μA . Activation of samples carried out on air, the temperature of samples in the course of the activation did not exceed 40°C. The limit of detection elements for photo activation analysis was 10^{-4} – 10^{-7} % wt. Gamma-activation analyses are no destroying for native samples.

The IR-spectroscopy is suitable method, which give information about the composition of kidney stones and identify not only the molecular species present in stone but also the crystalline form.

The ^{235}U yield in the nuclear reaction calculated with the help of the program complex PENELOPE.

As experimental model, drinking water (5-10 l) was chosen with pH=6.8. The Fe_2O_3 nanoparticles used as sorbent for ^{235}U in drinking water relativity FeCl_3 .

Samples of soil (15x15 cm² and h=10 cm) from the neighborhood in Kharkiv on virgin soil or in the forest. Two samples were took on arable land. Soil samples dried at room temperature then sieved through a 1-mm mesh to remove the roots of plants and stones and homogenized prior to analysis.

Samples of "*Pistia stratiotes*" (dry roots and leaf) from the Seversky Donets were taken in October. Investigation of radionuclide activity in dry samples was in air.

The kidney stones from 24 patients of both sexes washed many times with distilled water, and then completely dried at room temperature. After drying kidney stones crushed in agate mortar. For IR-spectroscopy analysis, the samples were prepared in the form of transparently compressed tablets from a mixture of KBr, which served as the matrix and the test substance (in amount of 1%, 100 mg sample). The tablets had a rectangular shape and of sizes 25x5 mm. The pressure was 9200 kg/cm². To exclude the absorption bands of the matrix, a tablet of pure potassium bromide, pre dried at 180°C for 10 hours, placed in comparison channel of the device. The powders were ground and mixed in a special closed box; pressing performed immediately before

measuring spectra. The evaluation carried out on the spectrum of polystyrene with a known frequency of absorption maxima. Correction averaged $10 \dots 5 \text{ cm}^{-1}$. The IR spectrometer IRS-29 (LOMO) used to record absorption spectra in the infrared range. The spectra were recorded in the spectral range $1000 \dots 100 \text{ cm}^{-1}$ (middle infrared region) [6,7].

Crystal-optical investigations carried out on POLAM-L211, MIN-8 microscopes with the use of immersion liquids (IZH, OVIZ sets).

3. RESULTS AND DISCUSSION

The production of activity maximum of $^{235,238}\text{U}$ sorption was with use nanoparticles Fe_2O_3 (40 nm) pH=3.2. In the studied ecosystems, Fe-compounds are major sorbents of uranium during migration and concentration process [8].

The specific activity of $^{235,238}\text{U}$ were $1.2 \cdot 10^{-6}$ and $1.8 \cdot 10^{-6} \text{ Bk/dm}^3$. There were $^{90}\text{Sr} - 7.7 \cdot 10^{-4}$, $^{232}\text{Th} - 1.1 \cdot 10^{-7} \text{ Bk/dm}^3$ in drinking water. The low-level $^{235,238}\text{U}$ sorption was connected with there is uranium in drinking water as stable anion tri-carbonate complexes.

On fig. 1 shows the gamma spectrum of soil sample. In general, uranium is more closely associate with iron and manganese, due to its strong sorption by iron oxides. The ^{238}U content in different types soil has differences, for example: serozems – 31.5 Bq/kg, gray-brown – 27.8 Bq/kg, chestnut – 26.6 Bq/kg, chernozems – 21.6 Bq/kg, gray forest – 17.8 Bq/kg, sod-podzolic- 15.2 Bq/kg, podzolic – 8.9 Bq/kg, peaty – 6.3 Bq/kg.

Therefore, for the Kharkov region there are the series actinides migration $\text{Ra} > \text{U} > \text{Th}$.

On fig. 2 the gamma spectra of the irradiated sample of roots of “*Pistia stratiotes*” are given. There are radionuclides of these samples (^{40}K , ^{131}I , ^7Be , ^{226}Ra , ^{228}Ac , ^{214}Pb , ^{214}Bi , ^{208}Tl , ^{212}Pb , ^{137}Cs , ^{235}U). “*Pistia stratiotes*” content of elements in leaf and roots has the peculiarities. The content of elements in root there are Mn, Co, Ni, Mo, I, Pb, As and U. The leaf include element U too. The content U in root is $3.74 \cdot 10^{-6} \text{ g/g}$, in leaf – $5.27 \cdot 10^{-7} \text{ g/g}$.

According these results uranium impregnated not only water, soil and plants and it becomes hazardous to biological organisms in a large geographic area. High levels of urinary excretion of uranium are frequently associated with accumulation of uranium in the kidneys [9]. Renal storage occurs after uranium intakes ($10\text{--}50 \mu\text{g/kg}$ body weight) and may produce chemical changes in the proximal renal tubules and indicate damage in renal glomeruli [10]. The elevation concentration of uranium in drinking water provide some evidence of adverse renal effects as assessed by biomarkers of proximal tubule damage. The kidney and in particular epithelial cells of the proximal tubules may be the target, for example, of uranium and of others actinides. The precise mechanism nephrotoxicity by uranium has not recognized. However, the inflammatory process as usually is escorting the formation of reactive oxygen species, followed by lipid peroxidation and glutathione oxidation in the cell membrane [11]. It is possible that uranium – induced nephrotoxicity is link to impairment of electron transfer to free radical products (R, RO,

ROOH, H_2O_2) and to the oxidative cell stress. The oxidative dysfunction might play a fundamental role in renal toxicity to uranium and others actinides. Uranium-induced nephrotoxicity might be one of possibility in formation of kidney stones.

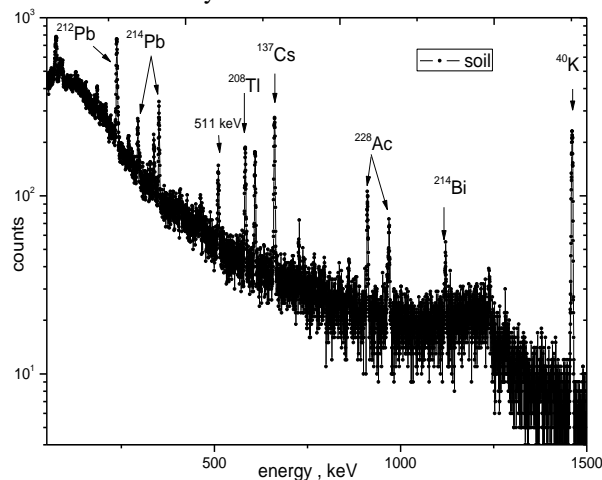


Fig. 1. The energy spectrum of soil sample

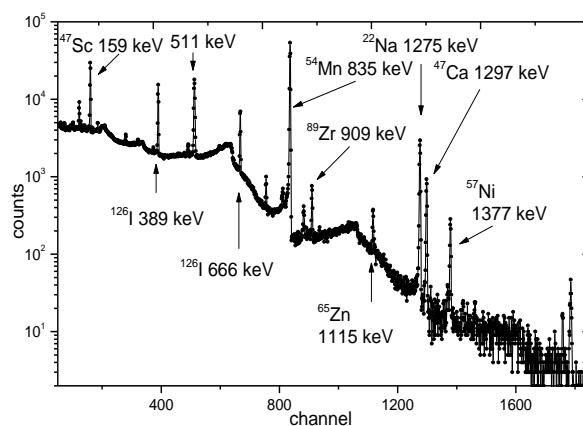


Fig. 2. The energy spectrum of root *Pistia stratiotes* after irradiation on electron accelerator

An important chemical property of uranium is its strong reducing ability. The aqueous solutions of UO_4 hydrolyzed. In bone and tooth's uranium is being deposited on the surface of smallest hydroxyapatite crystals by ion exchange of Ca^{+2} ions labile form per UO_2^{+2} . Each ion of UO_2^{+2} strongly binds with two phosphate groups on the surface of the crystals, releasing two Ca^{+2} ions [12]. The form of uranium ions in the body is UO_2^{+2} . Uranium and other actinides are alpha emitters and they long detained in the human body.

The average content of uranium in some types of kidney stones (calcium oxalates, calcium oxalate dehydrates, calcium phosphates, urate, magnesium ammonium phosphate, pure uric acid and others) was performed using Ge(Li)-detector relativity of standard-uranium and composed from 1 to 100 ppb.

The wide range of chemical compounds identified in the samples of different types of kidney stones. There are whevellite (calcium oxalate monohydrate – $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, whevellite - $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, hydroxyapatite - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, uric acid - $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$, aragonite – CaCO_3 and others mixed compounds.

Fig. 3 show IR spectra the sample of kidney stones N1 with bands corresponding to different types vibration of main structural fragments of organic and nonorganic compounds with sharp maximums (415, 440, 470, 515, 560, 600, 775, 955, 1030, 1100, 1310, 1400, 1600, 3100, 3300, 3420 cm^{-1}). There are wide maximums which are characteristic into whevellite ($\text{O}-\text{C}=\text{O}$) 415, 440, 470, 560, 600, 1030 cm^{-1} (70%), into phosphates (PO_4^{3-}), 515, 775, 955, 1310 cm^{-1} – into apatite (20%).

Fig. 4 show IR spectra the samples of kidney stones N2. The characteristic bands namely 420, 440, 470, 480, 515, 640, 660, 775, 870, 950, 1080, 1300, 1330, 1360, 1600, 3060, 3130, 3240, 3330, 3420 cm^{-1} are very similar with the sample N1.

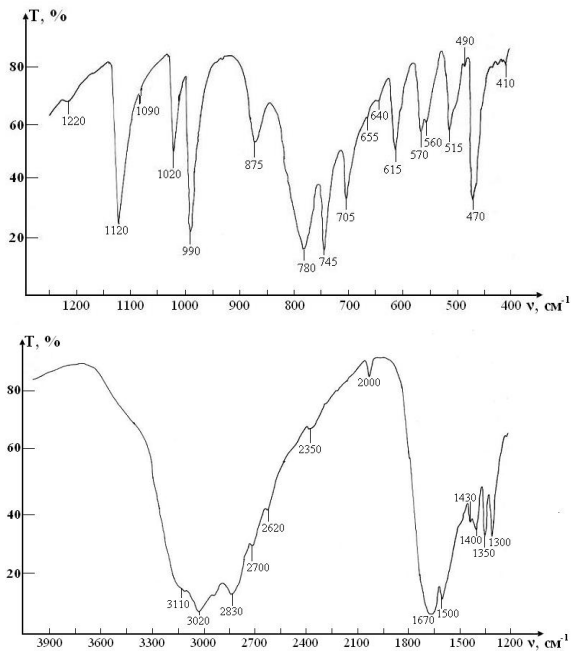


Fig. 3. IR-absorption spectra the sample kidney stones N1

Fig. 5 show the microphotograph of sample N2 in immersion liquid in transmitted light.

Fig. 6,7,8 show the microphotograph of sample N3 in immersion liquid in transmitted light.

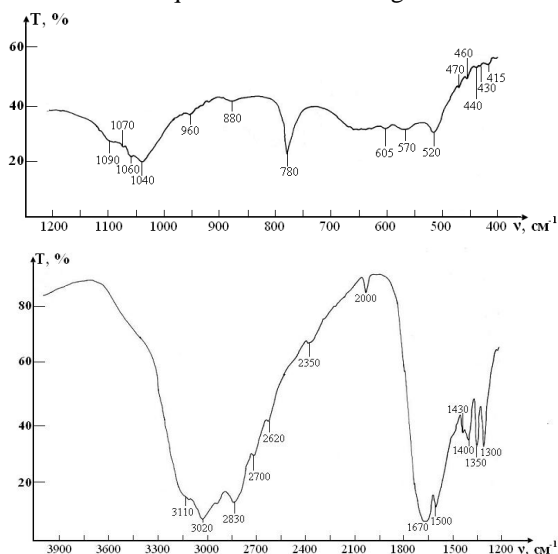


Fig. 4. IR-absorption spectra the sample kidney stones N2

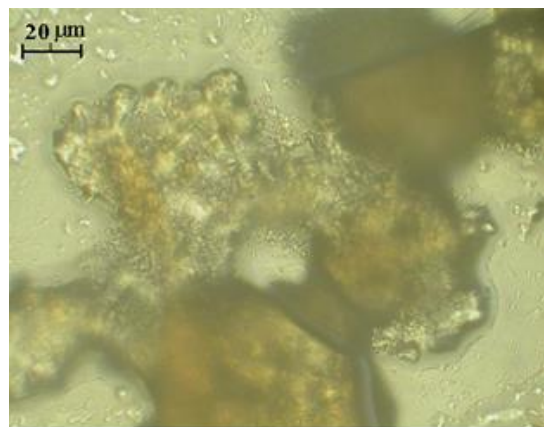


Fig. 5. The microphotograph of sample N2 in immersion liquid in transmitted light. The grain of whevellite with texture of strips. Without analyzer

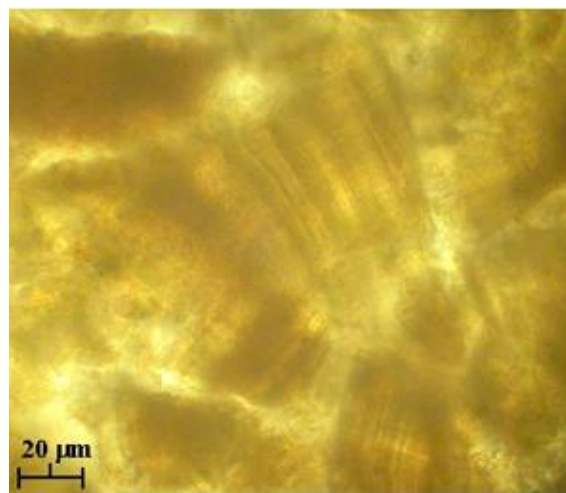


Fig. 6. Microphotograph of sample a kidney stone N3 in immersion liquid in transmitted light. Vevellite grains with a banded texture

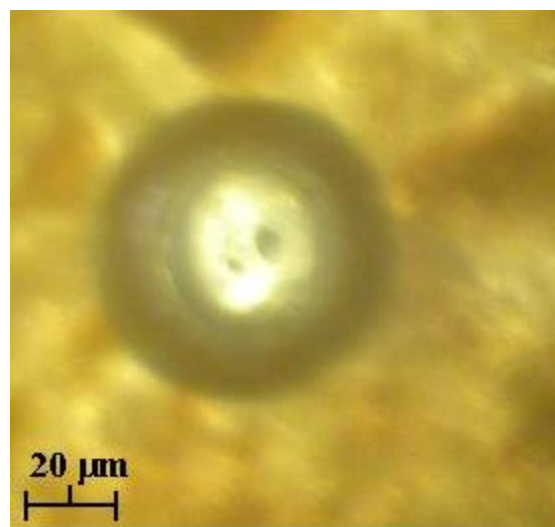


Fig. 7. Microphotograph of sample a kidney stone N3 in immersion liquid in transmitted light. Spherical inclusion

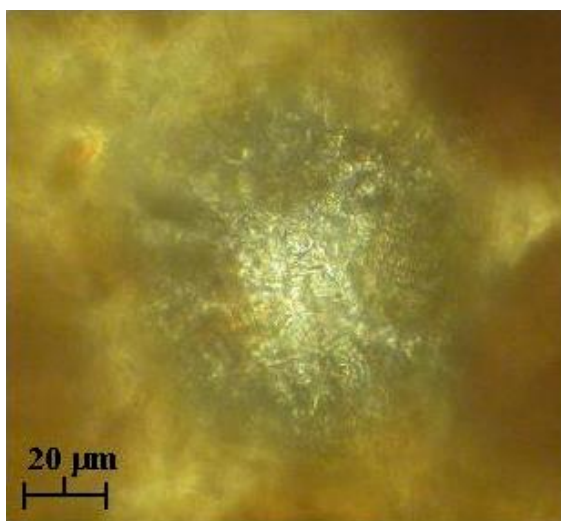


Fig. 8. Microphotograph of sample kidney stone N3 in immersion liquid in transmitted light. Spherical inclusion with a polycrystalline center

Fig. 6,7,8 show the sample N3, which consist of crystal phase with transparent and translucent grains ~15-30 μm and grain-yellow color. There are multitude of quantity impregnations.

3. CONCLUSIONS

The specific activity of ^{235}U and content of native U for the Kharkiv region in drinking water, soil, of roots and leaf of hydrophyte "*Pistia stratiotes*", and the samples of kidney stones of patients of Regional clinical hospital N17 carried out by using gamma activation analysis on linac accelerator of NSC KIPT.

The $^{235,238}\text{U}$ activity is one of dangerous actinide. It was registered in whole research samples the following level: for drinking water – from $1.2 \cdot 10^{-6}$ to $1.8 \cdot 10^{-6}$ Bq/dm, for soil – 26.6 - 8.9 Bq/kg, for native U in the root of "*Pistia stratiotes*" – $3.74 \cdot 10^{-6}$ g/g, in the leaf of "*Pistia stratiotes*" – $5.27 \cdot 10^{-7}$ g/g, the activity of ^{235}U in the root "*Pistia stratiotes*" – $2.6 \cdot 10^{-8}$ Bq/kg and at last, for the samples of kidney stones from 1 to 100 ppb.

The infrared spectral analysis the whole samples have the common feature for all types of kidney stones in patients of the Kharkiv region.

The level of the uranium in native U and ^{235}U not exceeds the background value for the Kharkiv region.

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