Preparation and property studies of new detectors of transuranium elements

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The possibility to use porous scintillators based on the organic molecular crystal of *p*-terphenyl for determination of α-nuclides in the environmental water has been shown. The technological methods of the porous scintillator preparation have been improved. As a selective sorbent for transuranium elements, the strong-basic anion-exchange resin VP-1Ap was used. The operation efficiency of the prepared material has been checked using model systems of ^{239}Pu reference solutions.

Показана возможность применения пористых сцинтилляторов на основе органического молекулярного кристала *п*-терфенила для определения α-нуклидов в водных объектах окружающей среды. Усовершенствованы технологические приемы изготовления пористых композитов. В качестве селективного к трансурановым элементам сорбента выбран сильноосновный анионит ВП-1Ап. Исследование работоспособности предлагаемого материала проводилось на модельных системах на основе образцовых радиоактивных растворов ^{239}Pu.

The problem of environmental protection has been steadily gaining worldwide importance. Technological activities of the humankind result in environmental pollution with artificial radionuclides, thus arousing a special interest in radiation monitoring and radiation safety. Improvement of the existing means of radiation monitoring and creation of new efficient instruments and methods is a challenging task for scientists from the major world countries. The largest fraction of radioactivity that entered the ecosystem after the Chernobyl catastrophe has been located in aqueous objects. Monitoring of the radionuclide levels in these objects is highly important because of their ability to migrate through alimentary channels. The choice of the most appropriate monitoring method depends upon what kind of ionizing radiation is to be recorded. For detection of β-nuclides, liquid scintillators and organic single crystals are commonly used, while for γ-nuclides the best performance is provided by solid inorganic materials such as NaI and CsI. Substantial problems exist in detection of α-nuclides, which are absorbed in the surface layer due to their short free path length. The monitoring of α-nuclides is further complicated by the value of their total maximum acceptable concentration in water (1 Bq/l).

The toxicology of transuranium elements is rather complicated due to double-sided nature of biological effects of uranium upon organism [1]. In many cases, low concentrations of the element to be detected on the background of high concentration of the matrix components is an obstacle to its direct determination. Consequently, the analysis must be preceded by various procedures of separation and concentration of the element in question. Numerous methods for separation of uranium from a mixture of cations have been described. As an example,

one could note joint extraction of U and Th by trioctylphosphine oxide, their quantitative extraction by caprylic acid and analysis of the re-extract by mass spectrometry with inductively bound plasma [2]. However, this procedure is time-consuming, it produces large amounts of organic wastes, and the separation efficiency of many matrix components (e.g., Fe) is clearly insufficient [3]. This makes the liquid extraction method unsuitable for routine analyses of large sample sets. Among methods used to concentrate uranium ion, the most common are those of extraction chromatography and ion exchange.

Extraction chromatography is relatively simple, but it does not provide long-term stability due to losses of the extractant in the eluent. Extraction by solvents and ion exchange are popular because of their ability to ensure simultaneous concentration and separation of ions [4, 5]. The ion exchange method is well suited for sorption of ions from water. The most commonly used in transuranium extraction is Chelex-100 resin. It has been shown [6] that, Chelex-100 should be used in the ammonium form to obtain the maximum extraction degree. Recently, the use of U/TEVA (EiChrom, Darien, IL) anion exchange resin for purification of U-containing solutions was reported [7–9], but the U/Th separation was not improved. Also known are ion exchange resins [10] which are used in combination with HCl as eluant to remove U(VI) from solutions. The experimentally obtained distribution coefficients show that U(VI) is absorbed in 9–12 M HCl, but is weakly retained with 0.1 M HCl [11]. A procedure for uranium sorption from mineral solutions using BioRad AG1-X8 anion exchange resin has been developed [12] with subsequent detection by a liquid scintillation counter. Cation exchange methods [13, 14] as well as the use of other eluants for uranium separation [15, 16] have also been reported. To determine uranium traces in water, an analytical procedure has been proposed basing on selective sorption of uranium by a chelating resin (SRAFION NMRR) and determination of the retained uranium by neutron activation analysis [17].

Recently, detection of radionuclides in water media using porous scintillators has been proposed [18, 19]. These porous scintillators are organic matrices with through pores containing a selective complexing substance fixed on their surface. The structure of the material allows the analyzed liquid to

pass through it. The element to be detected is accumulated in the scintillator volume, which provides both concentration of the radionuclides and 4π geometry of radiation detection. The objective of this work was to develop new composite materials for radiation monitoring and to apply those for detection of α-radiation in aqueous media of the environment, taking as an example selective determination of ^{239}Pu and ^{241}Am in environmental waters. Within the scope of the work, studies have been carried out in the following directions: selection of a selective sorbent for concentration of transuranic elements; studies of sorption properties of the sorbent using model solutions of uranyl nitrate; development of preparation technology of porous scintillators for detection of α-radiation; studies of scintillation properties of the prepared material (light yield, transparence); studies of sorption properties of the prepared material using reference model solutions of ^{239}Pu and ^{241}Am.

As sorbents for transuranic elements, anionites AM-2B, AMP, AM(p) and VP-1Ap were used. First, we have studied the sorption properties of the pure sorbents using model solutions of uranyl nitrate in the static sorption mode. To that end, sorbent granules were ground in an agate mortar into a powder with the grain size of 35 to 50 μm. The sorbent weights in 20 ml of the solution were placed into a Teflon vessel with a lid and kept for 72 hours to complete the sorption. In the first series of experiments, the solution contained 0.1, 1, 10 and 100 μg/ml of uranyl nitrate, the solution pH was varied within 3 to 12, and the sorbent weights, within 0.01 to 1.0 g. The residual uranium content in the solvents after sorption was monitored by a Trace Scan Advantage "Thermo Jarrell Ash Company" atomic emission spectrometer with induction-coupled plasma. The second set of experiments was carried out using VP-1Ap anionite. At the determined optimum pH and sorbent weight values (9 and 0.01 g, respectively), the uranium separation selectivity was studied. Accompanying ions K, Cs, Ba, Sr, Co, Y (10 μg/ml each) were introduced into the solution. Before introduction of the sorbent, the solution was passed through a paper filter to remove the residues of polyvalent metal hydroxides. After the static sorption process was finished, the concentrate was separated from the solution by filtering, washed with distilled water, dissolved in 1M HNO_3, and the content of

metal ions was determined by AAS-ETA method (using a "Saturn" spectrometer).

Next, the process of ^{239}Pu removal from the solution by porous scintillators was studied. The porous scintillators shaped as cylindrical pellets of 32 mm dia. and 1.5 mm height were made by uniaxial pressure compaction of an appropriately prepared uniform mixture of organic scintillation material granules, a sorbent and a pore-forming agent. The organic matrix for preparation of the porous scintillator was diphenylbutadiene activated *p*-terphenyl, while ammonium hydrocarbonate was used as the pore-forming agent. The mass ratio of the scintillator (PTP), sorbent (VP-1Ap), and pore-forming agent (NH_4HCO_3) was 4:1:1. The granules of the said substances had linear dimensions of 0.3, 0.035 and 0.05 mm, respectively. The compaction was carried out in a steel mould at 400 MPa for 15 min at room temperature. The compacted pellets were placed into a quartz ampoule and heated in a water bath at 80°C for 2 hours. Before preparation of porous scintillators, the pore-forming agent was dried in a desiccator over phosphorus oxide for 3 days, and the sorbent was treated with 0.01 % solution of surfactant sodium lauryl ethoxysulfate. The mixture of the sorbent, pore-forming agent and *p*-terphenyl was mixed in a Pulverisette-5 ball mill at 150–170 rps for 20 minutes.

Further, using the same optimum conditions (pH = 9, sorbent mass 0.01 g) we studied sorption of ^{239}Pu and ^{241}Am from model solutions with activities ^{239}Pu 50 Bq/ml and ^{241}Am 100 Bq/ml. To that end, we introduced 0.01 g of anionite into a Teflon conical cuvette, added 1 ml of the radionuclide solution and waited 5 hours for sorption to be completed. Then the sorbent was dried under a quartz lamp. ^{239}Pu and ^{241}Am solutions of specified activities were prepared proceeding from the reference radioactive solutions diluted with bidistilled water. Powder emitters were prepared in the following way: 0.1 g of polyvinyl pyrrolidone was solved in 1 ml of ethanol, the sorbent after sorption was added, and the mixture was applied in drops onto organic glass substrate of 4×4 cm^2 area and 2 mm thickness. To prepare the calibration samples, 1, 3, 5 ml ^{239}Pu solutions of 50 Bq/ml activity and ^{241}Am solution of 100 Bq/ml were applied in drops onto the organic glass substrate and kept under a quartz lamp until the solution was fully evaporated.
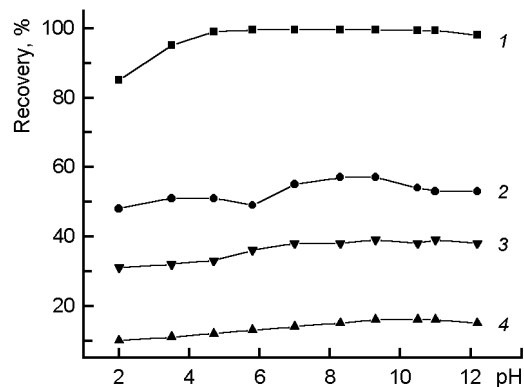

Fig. 1. Sorption degree of uranyl ion by different sorbents as function of the solution pH: VP-1Ap (*1*), AMP (*2*), AM(p) (*3*), AM-2B (*4*).

Concentrating of plutonium ions by the porous scintillator was carried out in static mode. For sorption, the pellet was kept for 72 hours in 20 ml of ^{239}Pu solution with 50 Bq/ml activity. The scintillation characteristics of porous scintillators after sorption were measured using a standard radiometric circuit comprising a BUS 2-94 preamplifier, a BUI-3K linear amplifier and an AMA 03-F multi-channel pulse amplitude analyzer. As photoreceiver, we used a R 1307 Hamamatsu photomultiplier with 3-inch photocathode diameter. The scintillations were excited by an "external" ^{238}Pu α-radiation source ($A = 10^4$ Bq). All pressure-compacted samples were put into optical contact with the PMT.

To choose the most suitable sorbent for transuranium elements, we studied properties of medium basicity anionite AM-2B and strongly basic anionites AMP, AM(p) and VP-1Ap [20, 21]. In Fig. 1, the sorption degree of uranyl ions by different sorbents is shown as a function of the solvent pH. The strongly basic anionite VP-1Ap appeared to be the most efficient, with sorption degree close to 100 % in a broad pH range. It can be seen from Fig. 1 that it is just the pH range from 6 to 10 that is the optimum sorption region. Further experiments were carried out at pH = 9.0, because at this pH value hydroxides of calcium, magnesium and some polyvalent metals precipitate readily from water. Using the dependence of uranium sorption degree upon the sorbent mass, volume capacity of the anionite with respect to UO_2^{2+} was calculated, yielding 3.9 mmol/g. It has been shown that not less than 0.01 g anionite is required for analysis of 100 ml water.

Table. Selectivity of uranium extraction by anionite VP-1Ap, solution volume 100 ml, sorbent mass 0.5 g

Element	Content in the sorbent prior to sorption, mg/g	Amount introduced into the testing solution, mg/l	Content in the sorbent after sorption, mg/g	Content in the testing solution, mg/l
Ba	<0.005	10.0	<0.005	9.95
Sr	0.10	10.0	3.06	6.94
Cs	<0.005	10.0	<0.005	10.1
K	1.65	10.0	1.82	10.1
Co	<0.005	10.0	<0.005	9.98
Y	<0.005	10.0	<0.005	10.0
U	<0.005	10.0	9.98	0.87

In Table, results are presented for sorption selectivity of uranyl ions by the anionites. The values given were obtained by measuring the content of the elements in the anionite after sorption and averaged over 7–10 experiments. The introduced concentrations of Ba, Sr, Cs, K, Co, Y are close to common concentrations of these elements in environmental waters. It can be seen that the accompanying ions are practically not sorbed by the anionite in the course of analysis. It is important to note that alkali and alkali earth metals having artificial and natural radioactive isotopes (that could affect substantially the analysis results) are practically absent in the sorbate. Thus, isotopes ^{40}K, ^{137}Cs, ^{139}Ba, etc. can increase the analytical signal, while stable isotopes of these elements can decrease the effective capacity of the sorbent. The behavior of barium is known to be a good model of its chemical analog radium. The absence of barium in the sorbate implies that ^{226}Ra, which can be present in natural waters, is unlikely to affect determination of transuranium elements.

The main condition for operability of porous scintillators is the presence of sufficient number of through pores. As gas-forming substance, we used ammonium hydrocarbonate, which has the decomposition temperature 36°C. As a result of thermal decomposition of ammonium hydrocarbonate, pellets were obtained with through pores of 25 to 70 μm in diameter (Fig. 2). The penetrability degree of the pellets, as estimated from water filtration rate in dynamic mode, was 10 ml·min^{-1}. It was found by hydrostatic weighing that the porosity of the pellets was close to 40 %. The exchange capacity of porous scintillators with respect to uranium was 75 % of the sorbent capacity, i.e., 2.9 mmol/g. To avoid the influence of such sorbent properties as hardness and hydrophobicity upon mechanical properties of pressure-compacted samples, the preparation technology of porous scintillators was improved as follows. The pore-forming agent was dried in a desiccator over phosphorus oxide, and the sorbent was treated with a surfactant solution. To ensure uniform distribution of the sorbent over the material volume, the component mixture was mixed in a ball mill. Fig. 3 shows the luminescence spectrum of porous scintillator composed of the organic matrix, sorbent and pore-forming agent. Such spectrum shape is typical for *p*-terphenyl activated with diphenylbutadiene. One can assume that neither anionite nor ammonium hydrocarbonate affect the spectrum shape, i.e., they do not act as luminescence quenchers or luminescent dopants.

In Fig. 4, the radioluminescence spectra of porous scintillators are presented. It can be seen that there is an α-peak in the spectrum of pressure-compacted samples with an "internal" source. Its value has been estimated to correspond to the presence of 30 Bq ^{239}Pu in the pressure-compacted sample. The difference between the introduced (50 Bq) and found (30 Bq) values is within the limit of measurement errors. It is known that α-particles, when passing through substance, are attenuated due to ionization and excitation of atoms and molecules, as well as due to dissociation of molecules. Therefore, realization of 4π-geometry for their detection is a complicated problem. To improve the detection accuracy at low activities of transuranium elements, we used ^{241}Am (α-particles with $E_\alpha = 5.4$ MeV, γ-radiation photons with $E_\gamma = 59.6$ keV). Calibration of the equipment was carried out using powder emitters of known activ-

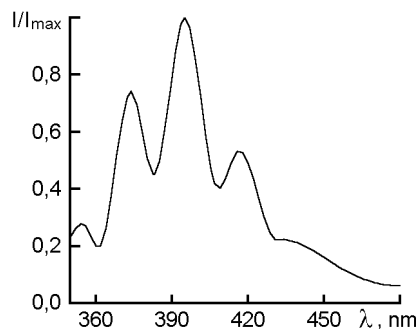Fig. 2. Image of the porous scintillator (optical microscope MBS-9, ×6).

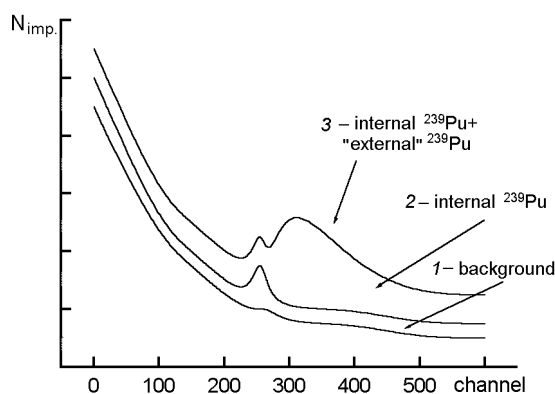Fig. 3. Luminescence spectrum of porous scintillator.

Fig. 4. Radioluminescence spectra of porous scintillators: background emission of pressure-compacted sample (*1*); emission of pressure-compacted sample with an "internal" source (*2*); emission of pressure-compacted sample with an "internal" source under irradiation by an "external" source (*3*).

ity. It has been shown that a clear correlation exists between the values of pulse counting rate.

In conclusion, basing on the results of our study, a new method has been proposed to determine α-emitters in potable and natural water. A selective sorbent has been chosen for concentration of transuranium elements, namely, a strongly basic anionite VP-1Ap, and its properties have been studied. It has been shown that the sorption degree of α-emitters by the anionite is close to 100 % in a broad pH range; an optimum pH range for sorption (6 to 10) has been determined. Technological procedures for preparation of porous scintillators have been improved. Mixing of the component mixture in a ball mill before pressure compaction has been proposed, as well as treatment of the sorbent by a surfactant solution. Using the prepared scintillators, activities were measured of model solutions containing ^{239}Pu. The results obtained showed the presence in the pressure-compacted sample of 30 Bq ^{239}Pu, which amounts 60 % of the introduced activity.

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Виготовлення та дослідження властивостей нових детекторів трансуранових елементів

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Показано принципову можливість використання пористих сцинтиляторів на основі органічного молекулярного кристала *n*-терфенілу для визначення α-нуклідів у водних об'єктах довкілля. Удосконалено технологічні прийоми виготовлення пористих компо-зитів. Як селективний до трансуранових елементів сорбент, використано сильнооснов-ний аніоніт ВП-1Ап. Дослідження працездатності запропонованого матеріалу проведено на модельних системах на основі зразкових радіоактивних розчинів ^{239}Pu.