

EXTRACTION OF RADIONUCLIDES ^{137}Cs , ^{90}Sr , ^{90}Y AND UO_2^{2+} FROM AQUEOUS SOLUTIONS USING SOLID-PHASE EXTRACTANTS IMPREGNATED WITH CALIX[4]ARENE PHOSPHINE OXIDES

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The extraction of radionuclides ^{137}Cs , ^{90}Sr , ^{90}Y , and UO_2^{2+} was studied using solid-phase extractants SPE-TBP, SPE-C45 and SPE-CIP67 depending on the acidity of the aqueous solution. SPE-C45 and SPE-CIP67 are porous styrene-divinylbenzene copolymer pellets impregnated with calix[4]arene tetraphosphine oxide C45 (5,11,17,23-tetrakis-diethylphosphinomethyl-25,26,27,28-tetrapropoxycalix[4]arene) and CIP67 (5,11,17,23-tetrakis-dipropylphosphinomethyl-25,26,27,28-tetrapropoxycalix[4]arene). Commercial solid-phase extractant SPE-TBP based on tributylphosphate was used for comparison. The influence of the radionuclides contact time with extractant on the establishment of extraction equilibrium was analyzed. It was shown that the equilibria in the systems using SPE are established in 3-4 hours.

A significant influence of the acidity of the aqueous solution on the extraction efficiency of the radionuclides was found: an increase in acidity leads to an increase in the distribution coefficients.

The influence of the nature of cations on the extraction efficiency is shown. The extraction of the radionuclides increases in the following series: $\text{UO}_2^{2+} > ^{90}\text{Y} > ^{90}\text{Sr} > ^{137}\text{Cs}$.

It was revealed that the extraction of the radionuclides depends on the length of the alkyl radical at the phosphorus atom of the macrocyclic skeleton of calix[4]arene phosphine oxide. Cations are extracted more efficiently with calix[4]arene of shorter alkyl radical length at phosphorus atom. The ability of SPE-calixarenes towards the studied radionuclides exceeds the extraction ability of SPE-TBP and varies in the following order: SPE-TBP < SPE-CIP67 < SPE-C45.

The conducted studies have shown the possibility of using the studied solid-phase-liquid extraction systems in the organization of radiation control of natural waters. In this case, the method of solid-phase extraction is convenient for radionuclide extraction, as it is simple and allows minimizing waste.

Keywords: radionuclides, solid-phase-liquid extraction, calixarene, phosphine oxide, radioactive waste.

Introduction

At this stage of development of civilization, there is a growing demand for energy. At the same time, the anthropogenic load (greenhouse gases and other harmful substances) increases. This leads to environmental pollution and negatively affects the integrity of ecosystems. Therefore, interest in nuclear energy has increased. Nuclear power plants are an environmentally friendly source of energy with a minimum amount of harmful substances entering the atmosphere. During the operation of a nuclear power plant, a large number of radioactive isotopes are formed in the reactor. In case of possible accidents at nuclear power plants and radioactive waste processing plants, radioactive isotopes may enter the environment. Particularly dangerous are the long-lived radionuclides uranium-235, plutonium-239 and their fission products strontium-90 and cesium-137. These radionuclides have long-term radiotoxicity, harming not only the health of the body, but also the environment as a whole. One of the

environmental problems is also its pollution by depleted uranium [1, 2], which is used for the production of warheads for armor-piercing projectiles. At the same time, depleted uranium is the most potentially dangerous to human health due to the formation of a large number of aerosols.

To assess the impact of radiation on the environment and, above all, on the human body, there is a need to create radiation monitoring [3]. When organizing radiation environmental monitoring, one of the methods for assessing the degree of technogenic load on the environment of cities and on the health of the population living in them is monitoring the pollution of atmospheric precipitation, surface water and soil [4, 5].

In this case, the main interest is those radionuclides that, accumulating in the external environment, pose a serious threat due to their biological activity and toxic properties [6]. An important component of radiation monitoring is the assessment of radionuclide content in surface and technogenic waters [7, 8].

Low contents of radionuclides and large amounts of other elements necessitate their preliminary concentration. One of the most appropriate ways to solve this problem is the use of liquid-liquid extraction [9, 10]. However, the organic solvents used are usually toxic, flammable and expensive. Therefore, the search for new extraction systems for the isolation and separation of radionuclides is one of the most important scientific and practical problems of radiochemistry.

New systems must be as efficient as traditional ones, but at the same time more environmentally friendly. They must not contain toxic extractants or solvents ("green extraction"), and waste solutions must be easily recycled or destroyed.

As an alternative to liquid-liquid extraction, there has recently been increased interest in the development and use of the solid-phase extraction method, which combines sorption and extraction methods. Solid-phase extractants (SPE) are porous materials impregnated with a complexing agent solution capable of forming complexes with metal ions and extracting them from aqueous solutions [11-13]. The advantage of SPE is their high capacity, characteristic of extractants, and the simplicity of the technological process for extracting metal salts, characteristic of sorbents.

Solid-phase extraction is characterized by wider possibilities for varying the nature and strength of interaction of the sample with the sorbent and eluent than liquid extraction. Through specific interactions, it is possible to selectively concentrate and extract each of the specific compounds or separate them from interfering components [14].

The use of solid extractants for decontamination of liquid radioactive waste allows to significantly reduce the volume of waste and facilitate its disposal. One of the common solid extractants produced commercially and used in extraction technologies is a porous copolymer of styrene and divinylbenzene impregnated with tributyl phosphate (SPE-TBP) [15]. At the same time, SPE-TBP has insufficient complexing ability and low selectivity towards actinides and lanthanides. The use of extraction methods for the extraction of radionuclides involves the introduction into the system of complexing ligands that have high selectivity [11].

For this purpose, multifunctional supramolecular receptors (synthetic cyclic and macrocyclic ligands, crown ethers and their derivatives, calixarenes, heterocyclic nitrogen- and sulfur-containing compounds, bifunctional neutral organophosphorus compounds [11, 12, 13, 16] are widely used.

In recent years, research in the development of selective extractants has been focused on calixarenes [11, 12, 17, 18].

Calix[4]arenes, due to their unique spatial structure, have great potential for modifying the macrocycle. This makes it possible to build specific receptors capable of recognizing with high selectivity various cations, anions or neutral molecules. The ability of calix[4]arenes to form stable supramolecular complexes determines the widespread use of calix[4]arenes and their derivatives in extraction technologies [11, 18].

A promising direction in the design of highly selective extractants is the functionalization of the macrocyclic ring of calix[4]arenes with phosphine oxide groups. The phosphine oxide groups are spatially oriented in such a way that their oxygen atoms form pseudocavities with the size and topology of complementary metal cations (Figure 1) [19].

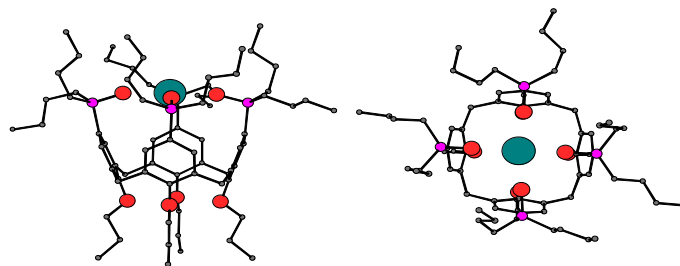


Fig. 1 The energetically minimized structure of calixarene phosphine oxide complex with metal cation: a) side view; b) projection from above [19].

By changing the conformation of the macrocyclic skeleton of calix[4]arene, it is possible to purposefully design molecules that are selective complexing agents with respect to radioactive elements and other metal cations.

Calixarene phosphine oxides have high complexing properties and can be used as extractants for the creation of new SPEs. Evaluation of the possibility of their use in the processing of liquid radioactive waste is an important task of applied radiochemistry.

In this work the extraction of ^{137}Cs , ^{90}Sr , ^{90}Y , and UO_2^{2+} from nitric acid solutions using SPEs based on phosphorus-containing calix[4]arenes C45 and CIP67 differing in the length of alkyl radicals at the phosphorus atom was investigated.

Method

Reagents. To study the extraction of radionuclides ^{137}Cs , ^{90}Sr , ^{90}Y , and UO_2^{2+} were used model solutions of ^{137}Cs with a specific activity of $8.6 \cdot 10^7 \text{ Bq/dm}^3$, ^{90}Sr with a specific activity of $1.8 \cdot 10^8 \text{ Bq/dm}^3$, ^{90}Y with a specific activity of $1.8 \cdot 10^8 \text{ Bq/dm}^3$ and uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ with a metal ion concentration of 1.52 mg/dm^3 . The required acidity of the solution was created with nitric acid.

Samples of SPE-C45 and SPE-CIP67 which are porous pellets of styrene-divinylbenzene copolymer (production of enterprise “Smoly”, Kamianske) impregnated with calix[4]arene tetraphosphine oxides C45 (5,11,17,23-tetrakis-diethylphosphinoylmethyl-25,26,27,28-tetrapropoxycalix[4]arene) and CIP67 (5,11,17,23-tetrakis-dipropylphosphinoylmethyl-25,26,27,28-tetrapropoxycalix[4]arene), which differ in the length of the alkyl radical at the phosphorus atom were used.

Calix[4]arenes C45 and CIP67, as well as SPEs based on them SPE-C45 and SPE-CIP67 were synthesized and characterized at the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine [19]. The solid extractant was obtained in the form of granules of size (63-100 μm). The mass fraction of calixarene in the sorbent is 40 wt. %. Commercial SPE-TBP based on tributyl phosphate was used for comparison [20, 21]. Figure 2 show the chemical structures of calixarenes C45 and CIP67 [19].

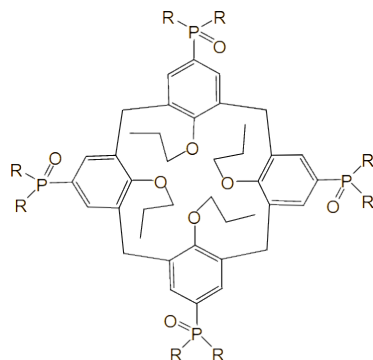


Fig. 2 Structures of calixarene phosphine oxide C45 ($\text{R} = \text{C}_2\text{H}_5$) and C67 ($\text{R} = \text{C}_3\text{H}_7$).

Study of extraction properties. The extraction properties of SPEs were determined with solutions of ^{137}Cs , ^{90}Sr , ^{90}Y , and UO_2^{2+} at a mass ratio of solid and liquid phases 1:100. SPEs suspension was mixed with the solution containing the investigated radionuclide with the given acidity of the solution (0; 0.1; 0.5 and 1 mol/dm^3) at 293 K. The experiment was carried out in static mode. The time of equilibrium establishment was determined experimentally. The equilibrium phases were separated by cen-

trifugation, after which a sample of the aqueous phase was taken for analysis. Sampling was carried out using micropipette dispensers Eppendorf Pipette 4700 (Germany).

Radiometric measurements of the dry residue of radionuclide samples were carried out using an α - β -automatic device NRR-610 "Tesla" (Czech Republic). The relative errors in radioactivity measurements did not exceed 2%.

The activities of ^{90}Sr , ^{90}Y and ^{137}Cs in the solid phase were calculated from the change in the activity of the radionuclide in the aqueous phase before and after contacting the aqueous solution with the solid extractant.

The UO_2^{2+} content in the solid phase was calculated from the change in uranium concentration in the aqueous phase before and after contacting the aqueous solution with the solid extractant. The initial and equilibrium concentrations of uranium were determined by the luminescent method using a Hitachi spectrofluorimeter (Japan).

The extraction capacity of the investigated SPEs for radionuclides ^{90}Sr , ^{90}Y , ^{137}Cs and UO_2^{2+} was characterized by extraction coefficients (R), which were calculated according to the formula

$$R = \frac{A_0 - A_i}{A_0} \cdot 100, \% \quad (1)$$

where A_0 and A_i are the initial and equilibrium activities of ^{90}Sr , ^{90}Y and ^{137}Cs in the aqueous phase, imp/sec (or UO_2^{2+} concentration, mol/dm³).

At intervals, aliquots of the solution over the sorbent were taken and the radioactivity of the dry residue was determined. The constant radioactivity value of two consecutive samples indicated that sorption equilibrium was reached. The time corresponding to the establishment of thermodynamic equilibrium in the system was determined graphically from the dependence of the extraction coefficients (R) on the contact time of the solution with SPE.

Results and discussions

Based on the data on the dependence of the extraction factors (R) on the time of contact with SPE for the radionuclides ^{90}Sr , ^{90}Y and ^{137}Cs , kinetic curves were constructed (Figures 3-5).

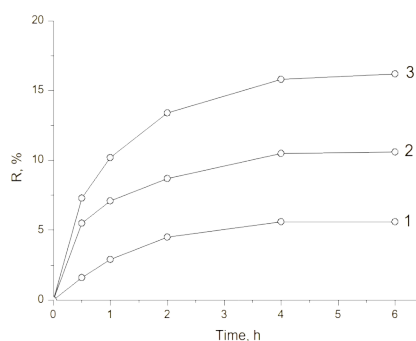


Fig. 3 Extraction kinetics ^{137}Cs : 1) SPE-TBP, 2) SPE-CIP67, 3) SPE-C45

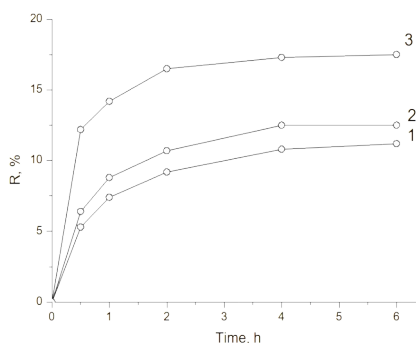


Fig. 4 Extraction kinetics ^{90}Sr : 1) SPE-TBP, 2) SPE-CIP67, 3) SPE-C45

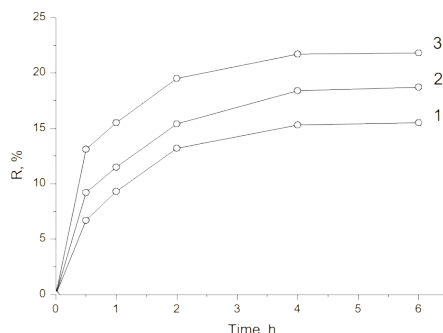


Fig. 5 Extraction kinetics ^{90}Y : 1) SPE-TBP, 2) SPE-CIP67, 3) SPE-C45

Analysis of kinetic curves showed that sorption equilibrium in the studied systems occurs after 3-4 hours. The process of radionuclide extraction occurs in 2 stages - fast and slow. The first stage is responsible for the process of saturation of the SPE surface with radionuclides, which occurs in a fairly short period of time. The second stage, corresponding to some "straightening" on the kinetic curve, indicates complete saturation of the sorbent surface with radionuclides and subsequent slow diffusion into the sorbent. This suggests that the rate of extraction by the solid extractant is controlled by a slower intradiffusion mechanism. For systems with uranium, the sorption kinetics at different pH values were investigated.

A significant contribution to the kinetics is made by the chemical interaction during the extraction process. The extraction kinetics for such systems is most accurately described by a pseudo-second-order model [22]. This indicates a significant influence of chemical interaction between extractants and radionuclides on the process rate.

Based on the data obtained, the empirical parameters of the pseudo-second-order kinetic model were calculated using equation:

$$R = \frac{k_2 R_e^2 t}{1 + k_2 R_e t} \quad (2)$$

where k_2 – rate constant, R_e – equilibrium extraction coefficient.

The initial extraction rate was calculated using the equation

$$h = k_2 R_e^2 \quad (3)$$

The results are shown in Tables 1 and 2.

Table 1. Parameters of equations 2 (k_2 , hours $^{-1}$) and 3 (h , hours $^{-1}$) dependence of extraction coefficients $R(\%)$ on time $t(\text{hours})$ for SPE systems with radionuclides.

| Radionuclides | SPE-TBP | | | SPE-C45 | | | SPE-CIP67 | | |
|-------------------|---------|------------------|------|---------|------------------|------|-----------|------------------|------|
| | R_e | $k_2 \cdot 10^2$ | h | R_e | $k_2 \cdot 10^2$ | h | R_e | $k_2 \cdot 10^2$ | h |
| ^{137}Cs | 7.7 | 4.8 | 2.9 | 18.1 | 6.9 | 22.6 | 11.2 | 14.1 | 17.6 |
| ^{90}Sr | 12.2 | 10.9 | 16.3 | 17.8 | 23.6 | 74.7 | 13.4 | 11.9 | 21.1 |
| ^{90}Y | 17.5 | 6.7 | 20.4 | 22.6 | 10.9 | 55.4 | 20.4 | 6.9 | 28.7 |

Table 2. Parameters of equations 2 (k_2 , hours $^{-1}$) and 3 (h , hours $^{-1}$) dependence of extraction coefficients $R(\%)$ on time $t(\text{hours})$ for SPE systems with UO_2^{2+} at different pH.

| pH | SPE-C45 | | | SPE-CIP67 | | |
|----|---------|------------------|------|-----------|------------------|------|
| | R_e | $k_2 \cdot 10^2$ | h | R_e | $k_2 \cdot 10^2$ | h |
| 2 | 82.5 | 1.2 | 79.6 | 75.1 | 1.1 | 59.4 |
| 4 | 79.0 | 1.4 | 87.1 | 74.6 | 0.9 | 48.8 |
| 6 | 71.7 | 1.7 | 89.2 | 67.6 | 1.1 | 50.7 |

In all studied systems extraction coefficients and initial extraction rate increase in the series SPE-TBP < SPE-CIP67 < SPE-C45. The extraction coefficient for systems with UO_2^{2+} decreases with increasing pH. At the same time, the initial extraction rate does not show such a trend.

The effect of addition of nitric acid on the equilibrium extraction coefficients is shown in Table 3. For all systems, an increase in extraction coefficients with increasing acid concentration is observed. Even small additions of acid significantly increase the extraction coefficient. Further increases in acid concentration have only a minor effect on the extraction.

Table 3. Effect of nitric acid concentration on extraction coefficients.

| Ion | SPE-TBP | | | | SPE-C45 | | | | SPE-CIP67 | | | |
|-------------------------------|---|------|------|------|---------|------|------|------|-----------|------|------|------|
| | c(HNO ₃), mol/dm ³ | | | | | | | | | | | |
| | 0 | 0.1 | 0.5 | 1.0 | 0 | 0.1 | 0.5 | 1.0 | 0 | 0.1 | 0.5 | 1.0 |
| ¹³⁷ Cs | 5.6 | 22.8 | 25.6 | 27.5 | 16.2 | 29.2 | 33.5 | 34.9 | 10.6 | 25.6 | 29.5 | 31.4 |
| ⁹⁰ Sr | 11.2 | 34.9 | 37.5 | 38.8 | 17.5 | 44.9 | 49.9 | 52.8 | 12.5 | 37.1 | 42.7 | 44.9 |
| ⁹⁰ Y | 15.5 | 38.2 | 43.7 | 48.2 | 21.8 | 48.5 | 57.7 | 62.9 | 18.7 | 43.4 | 48.9 | 53.4 |
| UO ₂ ²⁺ | 43 | 51 | 68 | 73 | 62 | 84 | 90 | 96 | 58 | 75 | 88 | 91 |

For the analyzed systems, depending on the nature of extracted particles, the extraction coefficients change in the following series $\text{UO}_2^{2+} > ^{90}\text{Y} > ^{90}\text{Sr} > ^{137}\text{Cs}$. This behavior of the systems is due to the specificity of complexation of the extracted particles with TBP and calixarenes.

Conclusions

Experimental studies of solid-phase extraction of radionuclides ^{137}Cs , ^{90}Sr , ^{90}Y , and UO_2^{2+} from aqueous solutions using SPEs were carried out. Calix[4]arene phosphine oxides C45 and CIP67, which differ in the length of the alkyl radical at the phosphorus atom, were used as complexing reagents of SPEs. A significant influence of the acidity of the aqueous solution on the efficiency of the radionuclide extraction has been shown. Analysis of the extraction coefficients of radionuclides in two-phase systems SPEs-water allowed us to construct the series: $\text{UO}_2^{2+} > ^{90}\text{Y} > ^{90}\text{Sr} > ^{137}\text{Cs}$. A comparative analysis of the radionuclides extraction coefficients shows that the extraction ability of solid extractant SPE-calixarenes significantly exceeds the extraction ability of SPE-TBP one and varies in the series: SPE-C45 > SPE-CIP67 > SPE-TBP. The reasons for the identified patterns are of interest for further research. The obtained results open the prospect of using of the calixarene based SPEs for the extraction of radionuclides from aqueous solutions.

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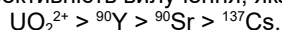
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Вилучення радіонуклідів ^{137}Cs , ^{90}Sr , ^{90}Y та UO_2^{2+} досліджували з використанням твердофазних екстрагентів SPE-ТБФ, SPE-C45 та SPE-CIP67 залежно від кислотності водного розчину. SPE-C45 та SPE-CIP67 є пористими гранулами стирол-дивінілбензолного сополімеру, імпрегнованими калікс[4]арентетрафосфіноксидами C45 (5,11,17, 23-тетракіс-діетилфосфіноілметил-25,26,27,28-тетрапропосикалікс[4]арен) і CIP67 (5,11,17,23-тетракіс-дипропілфосфіноілметил-25,26,27,28-тетрапропосикалікс[4]арен). Як сорбент для порівняння використовували комерційний твердофазний екстрагент SPE-ТБФ на основі трибутилфосфату. Проаналізовано вплив часу контакту радіонуклідів з екстрагентом на встановлення екстракційної рівноваги. Показано, що рівноваги в системах з використанням твердофазних екстрагентів встановлюються за 3-4 години.

Виявлено значний вплив кислотності водного розчину на ефективність вилучення радіонуклідів: збільшення кислотності призводить до зростання коефіцієнтів розподілу.

Показано вплив природи катіонів на ефективність вилучення, яка зростає в наступному ряду:



Виявлено, що вилучення радіонуклідів залежить від довжини алкільного радикала при атомі фосфору макроциклічного кістяка калікс[4]аренфосфіноксиду. Катіони ефективніше вилучаються калікс[4]ареном з меншою довжиною алкільного радикалу. Здатність твердофазних екстрагентів імпрегнованих каліксарен фосфіноксидами до вилучення досліджуваних радіонуклідів перевищує екстракційну здатність SPE-ТБФ і змінюється в наступному порядку: SPE-ТБФ < SPE-CIP67 < SPE-C45.

Проведені дослідження показали перспективність використання каліксареновмісних твердофазних екстрагентів в радіаційному контролі природних вод, оскільки вони є селективними, зручними у використанні і не потребують використання органічних розчинників.

Ключові слова: радіонукліди, твердофазна екстракція, каліксарени, фосфіноксиди, радіоактивні відходи.

Конфлікт інтересів: автори повідомляють про відсутність конфлікту інтересів.

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