Application of Phosphorus-Containing Ion Exchangers for the Recovery and Separation of Uranium and Transuranic Elements - 11490

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ABSTRACT

Selective recovery and separation of actinides from nitrate solutions generated in the spent nuclear fuel processing makes an important task of the applied radiochemistry. A number of new organic phosphorus-containing ion exchange resins developed in the last 10-15 years for water treatment, effluent decontamination, and hydrometallurgy seemed promising to address the problem.
The batch, kinetic, and flow sorption studies were conducted for NpO_2^+, Pu^{4+}, Th^{4+}, UO_2^{2+}, Am^{3+}, Eu^{3+}, Fe^{3+}, Al^{3+} ions in nitrate solutions. The S-957 cationite revealed the highest batch exchange capacity (BEC) by thorium. The determined BEC value by plutonium was 25-30 mg/cm^3; for practical purposes it remained constant within the 2 thru 7 $mole/dm^3$ range of HNO_3 concentration.
In further studies the S-957 cationite showed the highest selectivity towards Pu^{4+} species; maximum distribution coefficient (K_d) values for plutonium of $\sim 10^3$ cm^3/g have been observed.

The selectivity series for S-957 could be written as follows:
$Pu^{4+} > Th^{4+} > UO_2^{2+} >> NpO_2^+ >> Am^{+3} \approx Eu^{+3}$.

Results of the flow runs showed that the effective sorption of Pu occurs within the entire investigated range of plutonium and HNO_3 concentrations. The breakthrough sorption capacity value of S-957 by Pu reached 50-60 mg/cm^3. Stripping of Pu from the resin is conducted by a nitric acid solution in the presence of reducing agents.

The difference in the affinity of the sorbent towards 4+ and 3+ ions allows direct separating of Pu and Am pair provided the oxidation state of plutonium in the solution is maintained at 4+. Similarly, the separation of Np and Pu pair is possible if the oxidation state of Np in the solution is maintained at 5+, and that of Pu at 4+.

S-957 showed the superior qualities for the recovery of uranium from sulfate-containing solutions arisen in the uranium ore processing. Its flow capacity by uranium from sulfate-containing solutions is at least two times as much as the capacity of other investigated ion exchangers.

The results obtained allowed recommending the S-957 sorbent for the recovery of uranium and for different high level radioactive waste processing applications.

INTRODUCTION

Recovery of uranium from natural objects as well as the recovery and separation of transuranics from solutions of different composition make a challenging task of the applied radiochemistry. To date various extraction processes and sorption techniques based on vinylpyridine anionites [1] are widely used for the purpose.

Modern ion exchangers with phosphorus-containing functional groups look promising for the radiochemical technology. In [2, 3] a possibility for the recovery of uranium and thorium from nitrate solutions on different phosphorus-containing sorbents has been shown. The S-957 sorbent containing phosphonic and sulfonic functional groups has been found to be the most suitable for radiochemical processes. And in this work the attention was focused at the study of the possibility of separating transuranic elements in different oxidation states using S-957 sorbent. The results obtained are reported below.

EXPERIMENTAL

Before the experiments the sorbent was successively conditioned with 5% solution of sodium carbonate solution and 3 mole/dm³ HNO₃ solution. After this treatment the sorbent was thoroughly rinsed with distilled water and dried in the air to the constant weight.

Batch studies were performed by contacting an aliquot weight of the air-dry sorbent with an aliquot of the solution for the period of time required to attain the equilibrium. Then the sorbent was separated from the solution by filtering through a paper filter and the filtrate was analyzed to determine the concentration of the component under study. The analytical data obtained were used to calculate the mass distribution coefficient (K_d, cm³/g) values of the element and the batch exchange capacity (BEC, mg/g of the sorbent) according to the equations given below:

$$K_d = (C_o - C_{eq}) \cdot V / (C_{eq} \cdot m) \qquad\qquad (Eq.1)$$
$$BEC = (C_o - C_{eq}) \cdot V / \cdot m \qquad\qquad (Eq.2)$$

where C_o and C_{eq} (g/dm³) denote the adsorbed ion concentrations in the feed and in the equilibrium solution, respectively;

V (cm³) is the solution volume;

m (g) is the sorbent mass.

Flow runs were conducted in the column chromatographic mode by passing the feed solution at a constant flow rate through glass columns loaded with the S-957 bed. The emerging filtrate was analyzed to determine the adsorbed ions concentration which, in its turn, was used to calculate the sorbent breakthrough capacity (SBC).

The Pu^{+4}, UO_2^{+2}, NpO_2^{+}, Am^{+3}, and Eu^{+3} ion concentration was determined by radiometry using Pu-239, U-233, Np-237, Am-241, and Eu-152 tracers, respectively.

RESULTS AND DISCUSSION

In Fig.1 the effect of HNO₃ concentration within the range of 1.5-8 mole/dm³ on the mass distribution coefficients of individual U-233, Am-241, Eu-152, Np-237, and Pu-239 species in tracer amounts of ~1×10⁵ Bq/dm³ on S-957 sorbent is given. The experiments were conducted in batch mode at the volume/mass liquid/solid phase ratio of 100/1 and the contact time of 24 hours.
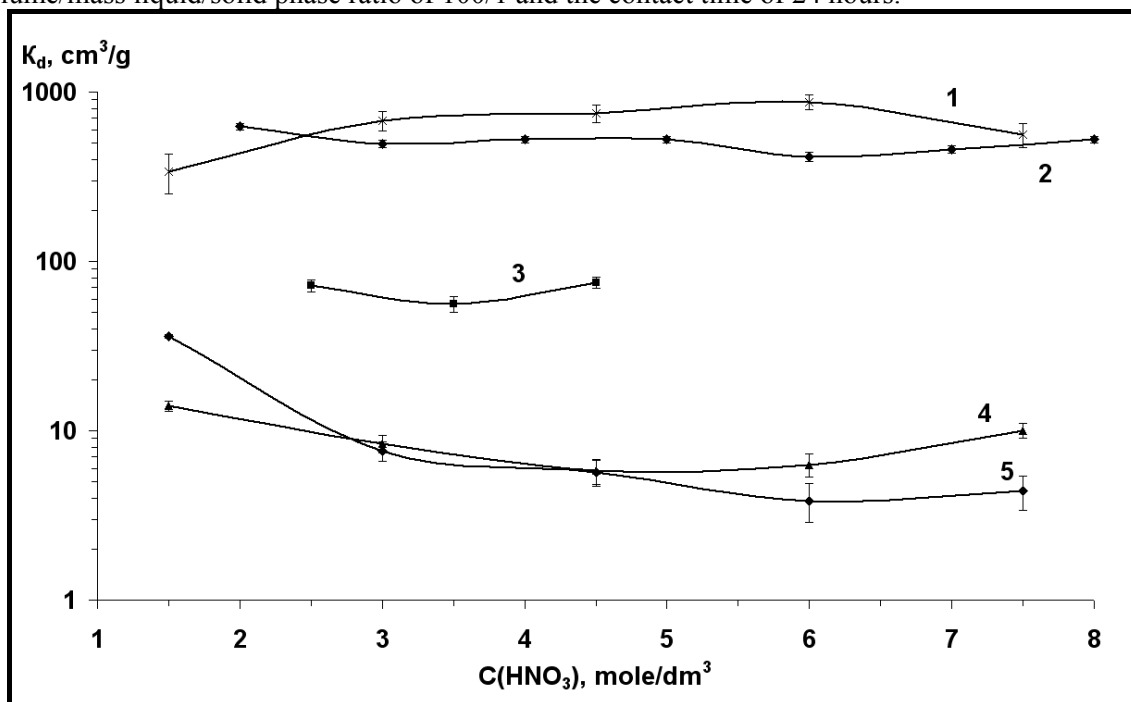

Fig. 1. Mass distribution coefficients of ion micro amounts on S-957 sorbent versus nitric acid concentration. 1 – Pu^{+4}; 2 – UO_2^{+2}; 3 – NpO_2^{+}; 4 – Am^{+3}; 5 – Eu^{+3}.

As it's seen from Fig.1 S-957 sorbent in the investigated acidity range reveals the highest selectivity towards plutonium in the 4+ oxidation state. The oxidation state of plutonium in nitrate solution was stabilized by up to 100 mg/dm^3 hydrazine nitrate additive. Maximum K_d values for Pu^{4+} of ~ 10^3 cm^3/g are observed within the HNO_3 concentration range of 3-6 mole/dm^3. The double charged uranyl nitrate ion UO_2^{2+} also possesses high affinity to S-957; moreover, uranium K_d values are virtually unaffected by the HNO_3 concentration within the range of 2-7 mole/dm^3. K_d values for NpO_2^+ are an order of magnitude less as compared to Pu^{+4} and UO_2^{+2}. Triple charged Am^{+3} and Eu^{+3} ions are adsorbed to far less extent. Hence, given the data obtained, the selectivity series for S-957 sorbent could be written as follows:

$Pu^{4+} > Th^{4+} > UO_2^{2+} >> NpO_2^+ >> Am^{+3} \approx Eu^{+3}$.
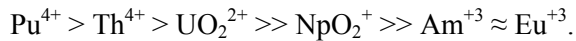
The effect of the nitric acid concentration on the batch S-957 capacity by plutonium was determined in the series of batch experiments. A 0.5 g aliquot weight of air-dry sorbent was contacted by 3 hour shaking with 25 cm^3 of solution containing 500 mg/dm^3 of plutonium and various quantities of nitric acid. The results obtained show the shape of BEC-$C_{[HNO3]}$ dependence to remain unchanged when going to macro quantities. Maximum BEC values are also reached within the acidity range of 3-6 mole/dm^3 where plutonium is present as Pu^{4+} cation species. At a higher nitric acid concentration the developed hexanitrate anion plutonium complexes markedly decrease the S-957 BEC value by plutonium.

Sorption of plutonium macro quantities on S-957 sorbent in the flow mode was conducted according to the following procedure. The feed solution was passed through two glass columns loaded with S-957 sorbent and connected in series. The sorbent bed volume in each column was 7 cm^3, the flow rate was maintained at 2-3 bed volume/hour. The filtrate emerging from the second column was analyzed for the plutonium concentration and the breakthrough capacity of the resin by plutonium was calculated. Concentration of plutonium in the feed was varied within the range on 0.1 – 1.0 g/dm^3, and the nitric acid concentration was varied within the range of 2.5 – 5.5 mole/dm^3. To stabilize plutonium in the oxidation state of 4+ the 50 – 100 mg/dm^3 hydrazine nitrate was added and the mix was kept for 12 hours before sorption.

Results of the performed flow runs show that the effective sorption of plutonium occurs within the entire investigated concentration range of plutonium and nitric acid. The resin capacity prior to the breakthrough amounted 50-60 mg/cm^3. Sorption from solutions with the concentration of plutonium below 1 g/dm^3 gives the content of plutonium in the filtrate not more than 2 mg/dm^3. Sorption from a more concentrated feed results in higher breakthrough of plutonium into the filtrate, which is probably associated with the kinetic characteristics of the investigated sorbent [3]. Half exchange time for quarter charged ions under these conditions is about 1 hour.

In Fig.2 output curves are shown of plutonium and americium during sorption on S-957 sorbent from the solution of the following composition: Pu^{+4} – 0.46 g/dm^3, Am^{+3} – tracer quantity (1×10^5 Bq/dm^3), HNO_3 – 4.5 mole/dm^3. The results show that under those conditions americium is for practical purposes not adsorbed by S-957 resin.
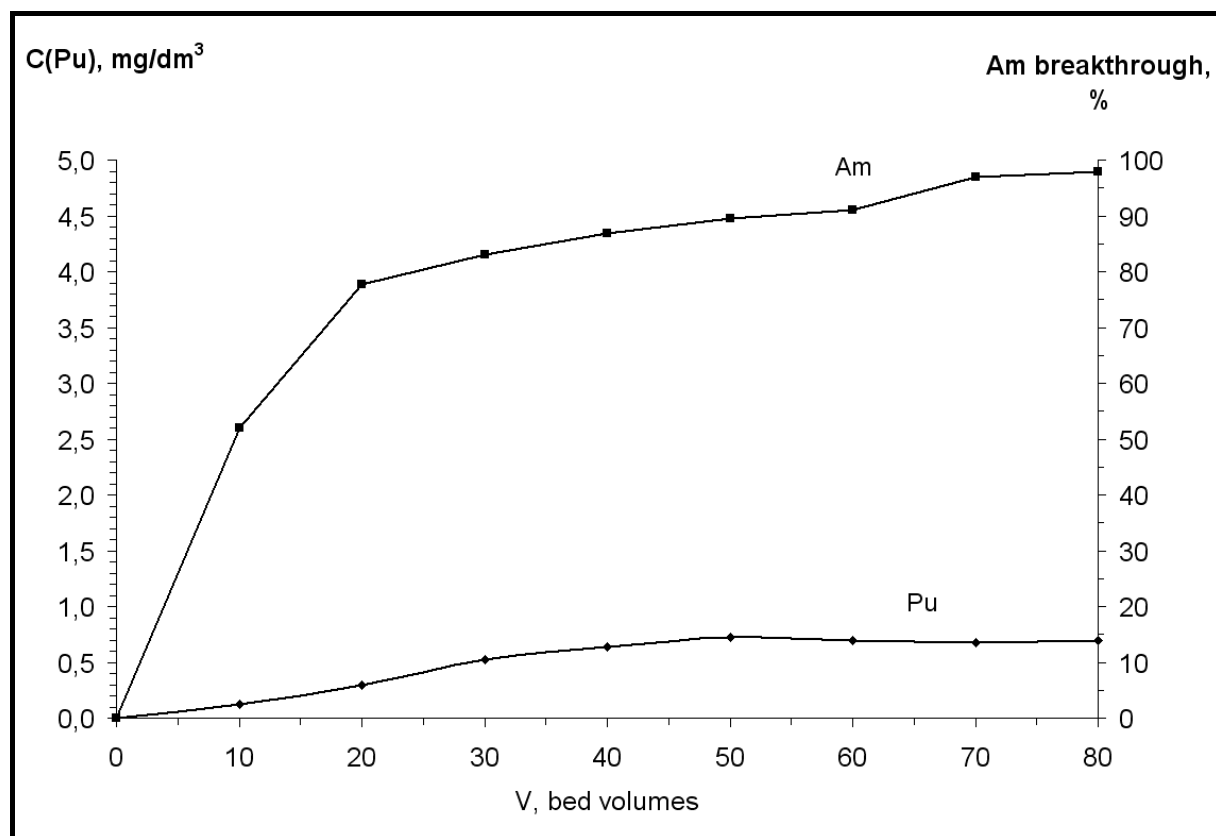
Fig.2. Output curves of plutonium and americium during sorption on S-957 sorbent

For stripping plutonium from the resin we have proposed a reductive desorption technique based on the reduction of Pu^{+4} to Pu^{+3}. Plutonium was stripped from the resin by 2.0-2.5 mole/dm^3 nitric acid solutions in the presence of a reducing agent ascorbic acid and hydrazine nitrate. Complete stripping of plutonium from the sorbent bed occurs into 10-12 bed volumes of the stripping solution.

For the bench-scale study of the plutonium - neptunium pair separation in the column chromatographic mode with S-957 we needed a substitute for plutonium to comply with the radiation safety regulations in the lab. The idea was to use thorium instead; therefore, we needed to prove that plutonium is adequately simulated by thorium under the conditions in question. We checked the possibility by parallel flow sorption runs of plutonium and thorium on S-957 until the 0.5% breakthrough. The experimental conditions and the results obtained are given in Table I.

Table I. Flow Exchange Capacity (FEC) Values by Thorium and Plutonium

Component	C, g/dm^3	C $_{HNO3}$, mole/dm^3	FEC, mg/cm^3
Th^{+4}	0.3	3.5	40
Pu^{+4}	0.4	4.0	40

The results given above prove that thorium may be used as an adequate plutonium simulator within the investigated range of experimental conditions.

A possibility of separating thorium (IV) and neptunium (V) was investigated by passing the feed solution containing 3 mole/dm^3 of nitric acid and 600 mg/dm^3 of the components to be separated through a sorption column loaded by the H-form of S-957 sorbent. The sorbent volume in the column was 1 cm^3; the filtration rate was maintained at 2-3 bed volumes/hour. The emerging filtrate was fractionated and analyzed for the Np and Th content. The results obtained are given in Table II.

Table II. Analysis of the filtrate from the sorption of neptunium and thorium on S-957 sorbent

Total filtrate volume, b.v.	Ion concentration in the filtrate, % of the feed	
	NpO_2^+	Th^{+4}
9.0	100	<1
18.0	100	<1
27.0	100	<1
34.0	100	<1

39.0	100	<1

As it's seen from the data in Table 3, neptunium is not adsorbed under these conditions, whereas thorium is adsorbed completely. Taking into account that plutonium is adequately simulated by thorium, this sorbent offers an option to separate the plutonium-neptunium pair directly. However, the effective separation is not possible unless the appropriate valent states of neptunium and plutonium are stabilized.

Thus, the experiments performed showed a possibility of using the phosphorus-containing S-957 sorbent for concentrating plutonium from solutions as well as separating plutonium (IV)-americium (III) and plutonium (IV) – neptunium (V) pairs.

The recovery of uranium from solutions after the uranium ore digestion by sulfuric acid also presents a challenging task of modern radiochemistry. Average composition of the solutions is given in Table III.

Table III. Average Composition of the Uranium Feed after the Ore Digestion by Sulfuric Acid

Component	Concentration, g/dm^3
UO_2^{+2}	0.1 – 0.2 (counted by uranium)
H_2SO_4	5
NaCl	0.1 – 1.0
pH	1.4-1.6

To study the problem, we looked at a number of sorbents. The sorbents investigated are described in brief in Table IV.

Table IV. Brief Description of Sorbents Studied for the Recovery of Uranium

Sorbent	Type	Functional groups
PFA 600/4740	High basic anionites	Quaternary ammonium bases
PFA 460/4783		
A 500U/4994		
AMΠ[1]		Benzylpyridine group
AM-п[2]		Trimethylammonium groups
Ambersep 920UCl[3]		Quaternary ammonium bases
Amberlite 910UCl[4]		
S-950	Chelating	Aminophosphonic
S-957		Phosphonic and sulfonic groups
A100/2412	Weak basic anionites	Mixed tertiary and quaternary ammonium bases
A 140		-
S 984		-
C 104HC	Weak acidic cationites	Carboxylic groups
C 107/150		

[1, 2] Russian manufacture
[3, 4] Manufactured by the Rohm and Haas Company
All the other sorbents manufactured by the Purolite® Company

Sorption properties of the sorbents under study were studied in batch and flow modes.

The effect of sulfate ion concentration on the sorption characteristics of the sorbents is given in Fig. 3.
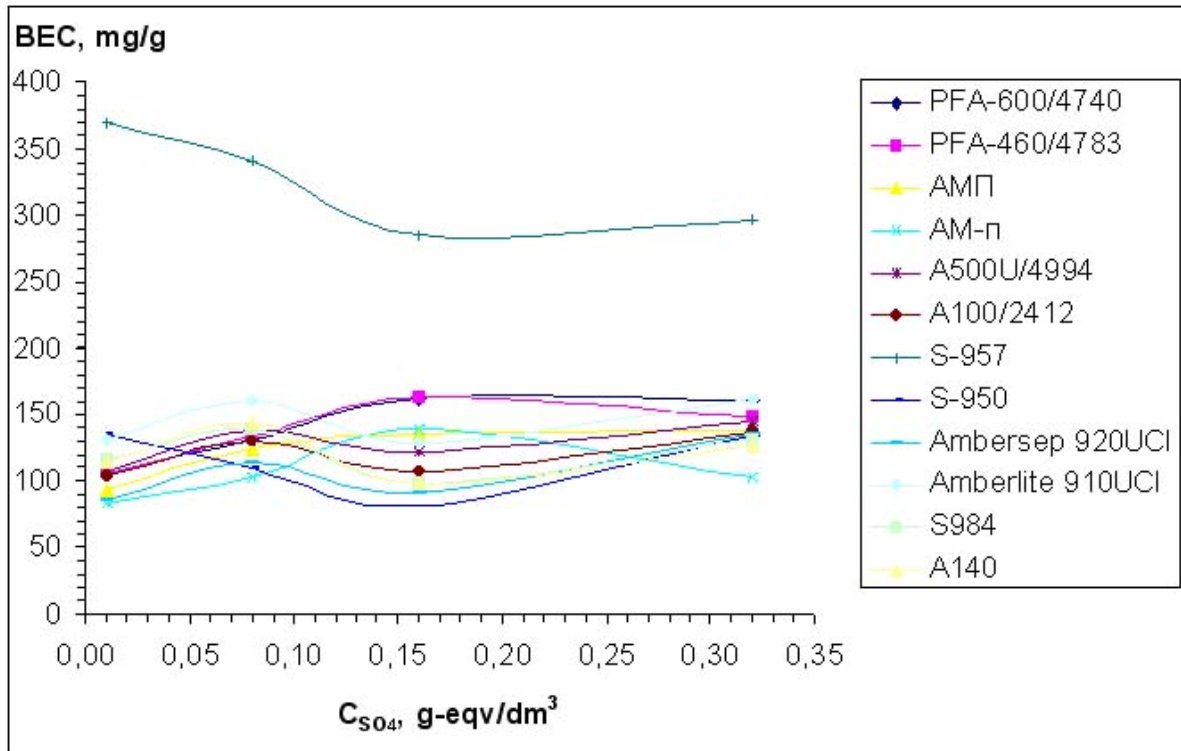
Fig.3. Effect of the sulfate ion concentration in the solution on the BEC value

It's seen from the presented data that for almost all sorbent types their capacity oscillates between 90 and 150 mg/g, and weak acidic cationites do not reveal any sorption properties under these conditions.

BEC value of the chelating sorbent S-957 differs greatly from the others. In the presence of 0.01-0.08 mg-eqv/dm^3 of sulfate ions its capacity amounts about 350 mg/g, and decreases to 280 mg/g in the presence of higher sulfate ion concentration. Under the same conditions the chelating sorbent S-950 shows the BEC value of 100-130 mg/g; similar results are observed for the effect of chloride ions in the solution on the BEC value of the sorbent.

The flow runs showed high efficiency of S-957 sorbent as compared to the anionites used to date in the industry. Full flow capacity of PFA600/4740 anionite under the conditions given was 54 mg/cm^3, and 88 mg/cm^3 for S-957. Thus, the flow capacity of S-957 sorbent is at least 30% as high as the capacity of the other investigated sorbents.

To determine the mechanism of uranium sorption on S-957 sorbent we have recorded the IR-spectra for the resin samples in H$^+$ and UO$_2^{2+}$ forms. IR spectrum of the S-957 sorbent sample in UO$_2^{2+}$ form is shown in Fig.4.
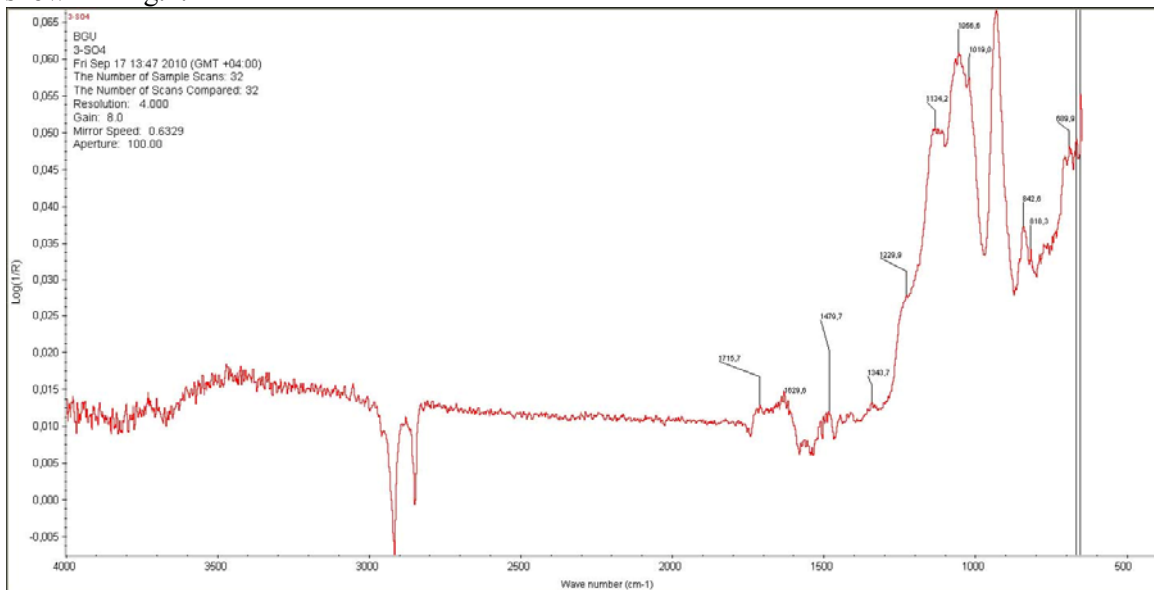

Fig.4. IR-spectrum of the uranyl ion-containing S-957 sorbent

The spectrum obtained shows that as compared to the sorbent in the hydrogen form, the shape of peaks responsible for the valent oscillation of the sulfonic and phosphonic groups is different. Changes in the functional group geometry are also indicated by a significant broadening of the valent oscillation range of the sulfonic and phosphonic groups both into the long wavelength band and short wavelength band of the spectrum. Thus, two functional groups are engaged in the sorption of uranyl ion.

High sorption characteristics of the sorbent under study are directly associated with its structure. Phosphonic groups form very stable complexes with uranium, whereas sulfonic groups promote a better swelling of the sorbent and, hence, the best penetration of the liquid phase into the sorbent matrix.

CONCLUSIONS

A number of radiochemical applications of the S-957 sorbent containing phosphonic and sulfonic functional groups have been investigated. Several basic parameters of the sorbent, namely, the batch exchange capacity, the flow exchange capacity, and the selectivity series have been determined. The data reported allow to assume that S-957 sorbent is a powerful tool for the recovery and separation of transuranic elements and may be effectively used in a number of state-of-the art radiochemical technologies.

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