

## Sorption of Uranium (VI) Ions by a Sorbent Based on a Copolymer of Maleic Anhydride with Styrene Modified by N, N'-diphenylguanidine

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**Summary:** In this paper the results of a study on the extraction and concentration of micro-quantities of uranium (VI) with a polymeric chelating sorbent with fragments of N, N'-diphenylguanidine is discussed. There was studied a static sorption capacity on K<sup>+</sup> ions ((SSC = 9.3 mmol / g) and there were determined the ionization constants of ionogenic groups ( $\overline{pK_1} = 3.97$ ;  $\overline{pK_2} = 8.47$ ) by potentiometric titration. The optimal conditions of the sorption of elements ( $pH_{opt}$ , sorption time -  $\tau$ , the influence of ionic strength -  $\mu$ ) were determined by the dependence of the sorption capacity (SC, mg/g) on the parameter being studied; the sorption capacity of the sorbent (SC) was determined from the saturation curve constructed under optimal sorption conditions. The maximum degree of extraction of uranium by sorbents is achieved from solutions with pH 5. Sorption equilibrium is achieved within 2 hours of contact of the solution with the sorbent. With an increase in the concentration of the uranyl ion in the solution, the amount of the sorbed metal increases, and at a concentration of  $8 \cdot 10^{-3}$  mol/l, it becomes maximal ( $pH = 5, = 8 \cdot 10^{-3}$  mol/l, Vgen = 20 ml, msorb. = 0.05 g, SC = 1258 mg/g). Limits of detection ( $3\sigma, n=20$ ) are 13.9 ng/ml. The effect of various mineral acids (HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl) with the same concentrations on the desorption of uranium (VI) from the sorbent was studied. The developed technique was applied to determine uranium in oil sludge.

**Key words:** Uranium, Sorption, Sorbent, Concentration, Desorption, Oil Sludge.

### Introduction

One of the common methods of preconcentration of micro-quantities of elements is their sorption extraction from solutions with synthetic sorbents. Therefore, obtaining sorbents based on synthetic materials of organic and inorganic origin is one of the main problems of analytical chemistry. And the development on their basis of methods of concentration and the extraction of trace elements are always important. Methods of immobilization of reagents on the surface of various sorbents and their use for the concentration of metals in various objects are devoted to a number of work [1-8].

An important direction in the practice of using synthetic sorbents is the targeted synthesis of new selective sorbents and the improvement of the analytical characteristics of the already known by introducing functional analytic groups into the sorbent matrix that can interact with metal ions to form complexes, chelates, or ionic associates.

This work is devoted to the development of the method of concentration and determination of trace amounts of uranium (VI) on the solid phase using sorbents modified with specific organic reagents.

### Experimental

Reagents used in the work were of analytical grade. A solution of uranium (VI) with a concentration

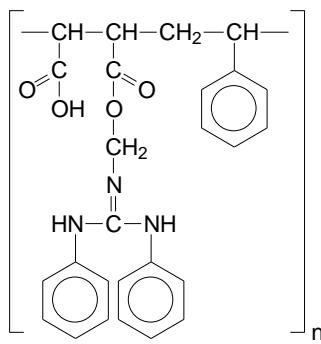
of 0.01 mol/l was prepared by dissolving a UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O sample in distilled water[9]. The exact concentration of the prepared solution was determined complexometrically. Solutions of lower concentration were prepared by diluting stock solutions. To create the necessary acidity in the test solutions, fixanal HCl, ammonium acetate buffer solutions and NaOH were used. The ionic strength was generated by calculated amounts of KCl. For the photometric determination of uranium (VI), 2,2', 3,4-tetrahydroxy-3'-sulpho-5'-chloroazobenzene was used as a reagent. Reagent synthesized according to technique [10]. Compounds used during synthesis of reagents, sorbents, i.e. pirogallo, amines, sodium nitrite, mineral acids, potassium chlorine, maleic anhydride, styrene are of analytical grade (They were bought from "Skeron" firm situated in Moscow). The acidity of the test solutions was controlled with a pH meter "PHS-25" (America). The optical density of the solutions was registered on a photocolorimeter KFK 2 (Russia).

A chelating sorbent based on a copolymer of maleic anhydride with styrene was prepared and identified according to the work [11]. The modification of the copolymer was carried out according to the following scheme: a portion of the copolymer was placed in a round-bottom flask, a water-organic solution of amine - N, N'

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diphenylguanidine and formaldehyde were added to it. The mixture was stirred for one hour while heating. Then it was filtered through a “blue tape” filter and washed with an aqueous solution to remove any formaldehyde residues.

The structure of the sorbent is presented in scheme-1.



Scheme 1. The structure of the sorbent.

Sorption capacity of the sorbent was studied under static conditions. 2 ml of  $10^{-2}$ M solution of uranium (VI) is added to 50 mg of sorbent and left in buffer environment at pH 1-10. The mixture is filtered and the optical density measure at  $\lambda=490$  nm. The amount of uranium (VI) remaining in the solution is found on the basis of the dependence of optical density on concentration and the amount of sorbed metal ions is calculated accordingly.

The IR spectra of the sorbent were registered on a LUMOS FT-IR microscope (BRUKER company Germany) in the wave frequency range of 600–4000  $\text{cm}^{-1}$ .

The ionization constants ( $pK_a$ ) of the functional groups of the sorbent was determined by potentiometric titration of one sample for the sorbent with a solution of potassium hydroxide with a concentration of 0.01 mol/l with the ionic strength of the solution  $\mu=0.1$  mol/l (KCl). It was considered that the equilibrium was established if the pH of the solution over the sorbent did not change with time.

The study of the dependence of sorption of uranium (VI) ions on pH was carried out under static conditions by the method of limited volume from a solution with a concentration of  $1 \times 10^{-3}$  mol/l in the pH range 3.0–9.0 from ammonium acetate buffer solutions.

The sorption isotherm was obtained under static conditions at pH 5.0 (ammonium acetate buffer solution) from solutions of uranium (VI) ions with a concentration of  $1 \cdot 10^{-4}$  to  $2.0 \cdot 10^{-2}$  mol/l.

Oil sludge was selected as the object of study.

## Results and Discussion

*Potentiometric titration.* Acid-base ionization constants of polymeric sorbents are among the main properties. To determine the ionization constant of the sorbent at the beginning, its static sorption capacity for the  $\text{K}^+$  ion ( $\text{SSC} = 9.3$  mmol / g) was studied and potentiometric titration was carried out using a known technique [12].

Based on the results of potentiometric titration, a differential titration curve was constructed in relation  $\frac{\Delta \text{pH}}{\Delta V} - f(V_{\text{KOH}})$  (Fig.1).

From figure 1 it can be seen that the synthesized sorbent contains two different groups. This indicates that the ionization of the sorbent occurs in two stages:

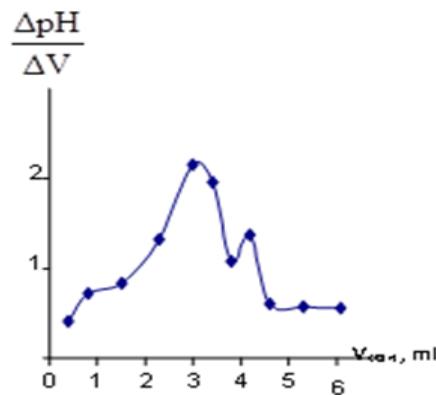
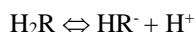


Fig.1. Differential titration curve of the sorbent.

To determine the ionization constants of the sorbent, data from the differential titration curve were used. The results were shown in table 1.

Table-1: Results for calculating the ionization constants of the sorbent ( $C_{KOH}=0.1M$ ,  $m_{sorb}=100$  mg,  $\overline{pK_1}=3.97$ ;  $\overline{pK_2}=8.47$ )

$\alpha$	$\frac{\alpha}{1-\alpha}$	$lg \frac{\alpha}{1-\alpha}$	$V_{KOH}$ , ml	pH	$pK_1$	$\alpha$	$\frac{\alpha}{1-\alpha}$	$lg \frac{\alpha}{1-\alpha}$	$V_{KOH}$ , ml	pH	$pK_2$
0.1	0.(1)	-0.954	0.13	2.87	6.23	0.1	0.(1)	-0.954	1.41	7.78	9.74
0.2	0.25	-0.602	0.26	3.07	5.40	0.2	0.25	-0.602	1.52	7.90	9.27
0.3	0.43	-0.368	0.39	3.29	4.84	0.3	0.43	-0.368	1.63	8.06	8.96
0.4	0.(6)	-0.176	0.52	3.58	4.39	0.4	0.(6)	-0.176	1.74	8.26	8.70
0.5	1.00	0.000	0.65	3.97	3.97	0.5	1.00	0.000	1.85	8.47	8.47
0.6	1.5	0.176	0.78	4.53	3.55	0.6	1.5	0.176	1.96	8.71	8.24
0.7	2.(3)	0.368	0.91	5.21	3.10	0.7	2.(3)	0.368	2.07	8.98	7.98
0.8	4.0	0.602	1.04	6.00	2.54	0.8	4.0	0.602	2.18	9.30	7.67

The ionization constant of the sorbent was calculated by the modified Henderson–Hasselbalch equation. [4].

Measuring the pH value of the solutions above the sorbent for each value of  $\alpha$ , the dependence of pH  $= f\left(lg \frac{\alpha}{1-\alpha}\right)$  was built. The parameters of  $m(tg \alpha = m)$  were calculated from the value of the slope of the straight line. A graphical definition of the ionization constant of the sorbent is shown in Figure 2.

On the IR spectra of the initial sorbent and saturated with uranium (VI), the following absorption bands are observed:

Initial sorbent (fig.1a):  $3600\text{-}3100\text{ cm}^{-1}$  [stretch vibrations of  $-\text{OH}$  group in carboxyl group, also the stretch vibrations of the  $-\text{NH}$  group ( $3300\text{-}3200\text{ cm}^{-1}$ )],  $1750\text{-}1715\text{ cm}^{-1}$  (stretch vibrations of  $-\text{C=O}$  group in carboxyl group),  $1570\text{-}1550\text{ cm}^{-1}$  (stretch vibrations of  $\text{C-N}$  and deformation vibrations of  $\text{N-H}$ ),  $1610\text{-}1510\text{ cm}^{-1}$  (stretch vibrations of  $\text{C=C}$  in benzene ring),  $710\text{-}680\text{ cm}^{-1}$  (deformation vibrations of  $\text{C=C}$  in benzene ring).

Sorbent-U(VI) (fig.1b):  $3640\text{-}3111\text{ cm}^{-1}$  [stretch vibrations of  $-\text{OH}$  group in carboxyl group, also the stretch vibrations of the  $-\text{NH}$  group ( $3342\text{ cm}^{-1}$ )],  $1703\text{-}1689\text{ cm}^{-1}$  stretch vibrations of  $-\text{C=O}$  group in carboxyl group),  $1627\text{ cm}^{-1}$  (stretch vibrations of  $\text{C-N}$ ) and  $1579\text{ cm}^{-1}$  (deformation vibrations of  $\text{N-H}$ ),  $1610\text{-}1510\text{ cm}^{-1}$  (stretch vibrations of  $\text{C-C}$  in benzene ring),  $710\text{-}680\text{ cm}^{-1}$  ((deformation vibrations of  $\text{C-C}$  in benzene ring).

Analysis of the IR spectra showed that the synthesized sorbent is coordinated as a bidentate ligand. Comparison of the IR spectra of the sorbent and the complex formed in the phase of the sorbent shows that with complexation, shifts are observed in the vibration frequencies of the groups in the sorbent

units. Based on the frequency shifts of the stretch vibrations of  $\text{NH}_2$  and  $\text{COO}^-$  compared with the spectra of ligands, it was concluded that in these compounds the metal is coordinated with amino and carboxyl groups.

The optimal conditions of the sorption of elements ( $pH_{opt}$ , sorption time -  $\tau$ , the influence of ionic strength -  $\mu$ ) were determined by the dependence of the sorption capacity (SC, mg/g) on the parameter being studied; the sorption capacity of the sorbent (SC) was determined from the saturation curve constructed under optimal sorption conditions.

The dependence of the degree of extraction of U (VI) on the pH of the solutions with sorbents is shown in figure 3. The maximum degree of extraction of uranium by sorbents is achieved from solutions with pH 5. The dependence of sorption on time was investigated. The results of the study showed that the sorption equilibrium is achieved after 2 hours of contact of the sorbent with the metal. For all further experiments, the time to establish the sorption equilibrium was 2 hours.

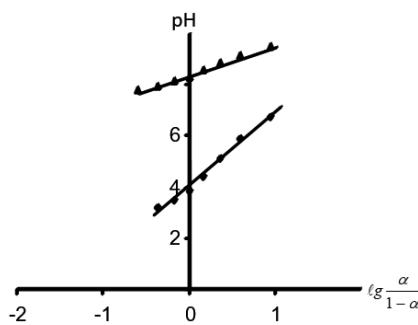


Fig.2: Graphical determination of sorbent ionization constants:  
 $pK_{1(\text{fig})}=3.88$ ,  $pK_{2(\text{fig})}=8.25$ ,  $m_1=2.762$ ;  $m_2=1.070$ ; ( $pK_1$ - characterizes the ionization of carboxyl groups,  $pK_2$ - deprotonization of amine groups).

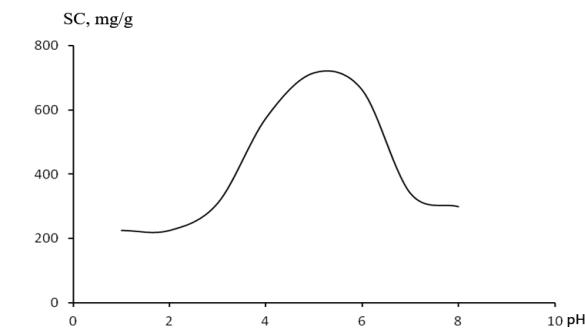


Fig. 3: Dependence of sorption of uranium (VI) on the pH of the medium ( $m_{\text{sorb}} = 30 \text{ mg}$ ,  $V=20 \text{ ml}$ ,  $\text{pH}=5$ ).

The ionic strength of the solution significantly affects the flexibility of the solid-phase matrix and the state of the functional groups of the analytical reagent [13]. Therefore, the dependence of the analytical signal on the concentration of KCl solution in the range of 0.2-1.6 M was investigated. The negative effect of an increase in the ionic strength of the solution on the properties of the sorbent was noted, which is explained by the screening of coordination-active groups by electrolyte ions[13]. The influence of the ionic strength of the solution was studied by the photometric method. The results of the study showed that a significant decrease in metal sorption occurs from KCl solutions with a concentration of more than 0.6 M.

One of the main criteria for assessing sorption equilibria is sorption isotherms, which determine the dependence of the sorption value of a substance on its initial concentration in a solution. In Fig.4. the isotherm of sorption of uranium on the sorbent is given.

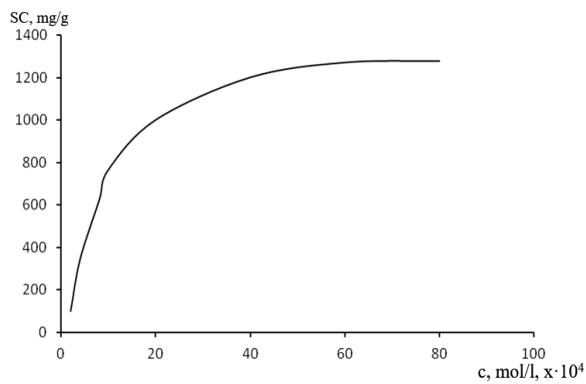


Fig. 4: Sorption isotherm of uranium (VI) with the obtained sorbent:  $m_{\text{sorb}}=30 \text{ mg}$ ,  $V=20 \text{ ml}$ ,  $\text{pH}=5$ .

With an increase in the concentration of the uranyl ion in the solution, the amount of the sorbed metal increases, and at a concentration of  $8 \cdot 10^{-3} \text{ mol/l}$ , it becomes maximal ( $\text{pH} = 5$ ,  $C_{\text{UO}_2^{2+}} = 8 \cdot 10^{-3} \text{ mol/l}$ ,  $V_{\text{gen}} = 20 \text{ ml}$ ,  $m_{\text{sorb}} = 0.05 \text{ g}$ ,  $SC = 1258 \text{ mg/g}$ ).

The possibility of desorption of uranium(VI) with solutions of various mineral acids ( $\text{HCl}$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) was studied. Data were obtained on the degree of elution of uranium depending on the concentration of acids (table 2), volume, transmission rate of the eluent, and conditions for complete desorption(98-100%) were selected: 5 ml of 2M  $\text{HClO}_4$ , transmission rate of 1.0 ml/min (Table 2 ).

Table-2: The effect of the concentration of different acids on the degree of extraction (%) of uranium ( $n = 5$ ).

acid	concentration, mol/l	Degree of desorption, %
Cl	0.5	68
	1.5	77
	2.0	92
	0.5	89
$\text{ClO}_4$	1.0	94
	2.0	98
	0.5	79
$\text{NO}_3$	1.0	82
	2.0	93
	0.5	85
	1.5	92
$\text{SO}_4$	2.0	93

*Detection limit* at  $3\sigma$ ,  $n=20$  [14] is equal to 13.9 ng/ml. It can be improved by increasing the sample volume, if the extraction is quantitative.

The sorption of uranium (VI) ions was studied in a static mode. Quantitative determination of uranium (VI) was performed according to the calibration curve. A method for determining uranium (VI) in oil sludge using synthesized sorbent has been developed.

Sample preparation of oil sludge was carried out according to the following procedure: 0.2 g of oil sludge was evaporated for two days in a graphite bowl at a temperature of 105°C. Then calcined in a muffle furnace at 550-650°C. The resulting ash was dissolved in 8 ml of HF + 3 ml of HCl + 1 ml of  $\text{HNO}_3$ . For complete removal of HF from the resulting mass, it was treated 3-4 times with  $\text{HNO}_3$  at a temperature of 50-60°C. The resulting precipitate was dissolved in distilled water and transferred to a 1000 ml flask,  $\text{HNO}_3$  was added so that the pH reached 6 and diluted to the mark with distilled water. The concentration of U (VI) is determined by the photometric method. The results were calculated under the assumption of 100% extraction of the detected ions (Table-3).

Table-3: Determination of uranium in oil sludge after preliminary concentration by a sorbent ( $R = 0.95$ ;  $n = 5$ ).

Is entered, $\mu\text{g/l}$	Found, $\bar{x} \pm \frac{t_{PS}}{\sqrt{n}}$ , $\mu\text{g/l}$
-	11.200±0.010
5	16.102±0.030
10	21.318±0.050
15	26.107±0.066

\* Sample taken from Azerneftag Oil Refinery.

Table-4: Optimal conditions of concentration of uranium (VI) ions by polymer sorbent at static conditions.

SC	pH <sub>opt</sub>	equilibrium time, h	reusability of the sorbent	note
1258mg/g	5	2	7-8 cycle	our
2.63 mg/g	3	6	2 cycle	[15]
300-350	6	5	1 cycle	[16]
mg/g 0,632	4.3-		5 cycle	[17]
mmol/g	6.9			

The results showed that a chelate sorbent based on a copolymer of maleic anhydride with styrene, synthesized by modifying with N,N'-diphenylguanidine in the presence of formaldehyde, can be used to concentrate uranium. The developed method is more economical, quick and environmentally safe compared to the [15-17] (Tabl. 4). In addition, it is established that it is possible to reuse the regenerated sorbent for the processes of concentration.

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