



## Preconcentration of Uranium (VI) By Chelateforming Sorbent and Its Photometric Determination with 2, 2', 3, 4-tetrahydroxy-3'-sulpho-5'-chlorazobenzol

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Received: 14 April 2016, Revised: 16 May 2016, Accepted: 18 May 2016.

Published online: 1 July, 2016.

**Abstract:** The complex formation of uranium (VI) with 2, 2', 3, 4-tetrahydroxy-3'-sulpho-5'-chlorazobenzol (R) was studied. There is formed a homogenous complex with 1:2 molar ratio of components, maximum light absorption of complex is observed at 490 nm, molar coefficient of absorption is 6250. It was produced a new sorbent. There was a static sorption capacity on K<sup>+</sup> ions and there were determined the constants of ionization of ionogenic groups by potentiometric titration. It was investigated the conditions of concentration of uranium with that sorbent. The degree of extraction of U (VI) ions at optimal conditions is more than 95%. Limits of detection (3σ, n=20) are 14.2 ng/ml. It was worked out a technique of photometric determination of U (VI) in sea water.

**Keywords:** Uranium (VI), preconcentration, photometric determination, sea water.

### 1 Introduction

Main constituents in the nuclear spent fuels are actinides like uranium, thorium and various fission products. Recovery of these metal ions is a challenging task because of high acidic environment associated with them [1–2]. Extraction and preconcentration of these valuable metal ions from other fission products is extremely important not only from the point of view of their limited resource availability, but also to reduce their quantum for disposal as radioactive wastes [3]. Various methods were adopted for separation of actinides, which include precipitation and co-precipitation and ion-exchange chromatography systems. But over the years solvent extraction (SE) has been proved to be promising in this aspect because of simple operation and using this technique several extractants have been developed with various organic. Ligands like phosphonic acid based ligands [4], *N,N*-dialkyl amides, crown ethers, β-diketones, picolinamides, calixarenes. Even though SE technique is the widely adopted process, it suffers from limitations like the third phase formation, disposal of large volumes of extractants and diluents and tedious extraction procedures. More recently, the use of solid phase extraction (SPE) have been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, no disposal of toxic organic solvents as waste and it can be recycled. In SPE, the organic extractants are anchored to an inert polymeric support and several methods have been developed for actinide extractions [5-10].

Concentration and extraction of trace elements by chelating polymer sorbents (CPS) has been widely used [11-14]. Prospects of their use due to the high selectivity and efficiency of action in the concentration of the elements ions from the objects of complex chemical composition. Sorbents are non-toxic, stable under prolonged storage, easy to transport. CPS distinguishing capacity consists in the presence in their structure chemically active functional groups capable of interacting in solution with the ions of elements with the formation of chelate complexes [15]. In this paper the results of studies of the sorption process of uranium (VI) trace by new polymer chelating sorbents containing 2,4-diamin-6-phenil-triazin 1,3,5 fragments has been considered. We have studied the complexation of uranium (VI) with 2, 2', 3, 4-tetrahydroxy -3'-sulfo-5'-chlorazobenzene. A method for the sorption-photometric determination of uranium (VI) in sea water has been elaborated.

### 2 Materials and Methods

**Reagents:** 2,2',3,4-tetrahydroxy-3'-sulpho-5'-chlorazobenzol was received by azocombination of diazotated amine with piragollol in low acid medium on recommended technique [16] and its composition and structure was established. In this work we applied a new polymer chelateforming sorbent with fragments of 2,4-diamin-6-phenil-triazin 1,3,5. Sorbent is synthesized on technique [17]. This sorbent is dried at 50-60°C. Initial solution of uranium (VI)  $1 \cdot 10^{-2}$  M was prepared by

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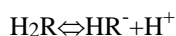
dissolving of precise hinge of  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  in distilled water [18]. Work solutions of U (VI) were prepared by dissolving of an initial solution with distilled water. For making of needed acidity we used physical HCl (pH 1-2) and ammonium-acetate buffer solution (pH 3-11). To create a constant ionic force we used KCl.

**Apparatus:** Solutions pH we measured by ionometr I-130. Optical density of solutions was measured by using of photo colorimeter KFK-2 ( $l=1$  sm). For photometric determination of uranium we used 2, 2', 3, 4-tetrahydroxy-3'-sulpho-5'-chlorazobenzol as a reagent. Concentration of U (VI) was calculated by using of calibration curve and the results were worked up by math statistic methods [19]. The investigation of sorption was made in static and dynamic conditions. In dynamic conditions all solutions were passed through glass mini column (inner diametr is 0.5 sm, length is 5 sm), filled of polymer chelateforming sorbent (100 mg).

### 3 Results and Discussion

**Characteristics of uranium (VI)-R complex:** The study of depending of complex formation on pH showed that the yield of homogeneous complex of U (VI) with TSCAB is maximal at pH 4 ( $\lambda_{\text{max}}=490$  nm), the reagent has a maximal light absorption at 426 nm. The complex is formed right away after the mixing of components. The ratio of reactants in the complexes was established by methods of relative output of Starik-Barbanel, shift of equilibrium and izomolar series [19]. Molar coefficients of absorption of complexes were calculated from curves of saturation. The intervals of concentrations of obeying to Beer's low were established (Table.1). For determination of micro amounts of ions of U (VI) we investigated the conditions of prior concentration of U (VI) by using of a new chelate- forming sorbent on the basis of copolymer of malehine anhydride-styrene, by following determination of ions of U (VI) on aforesaid photometric technique. The optimal conditions of concentration of U (VI) ions by polymer sorbent were established. Acid-base constants of ionization of polymer sorbents are one of the basic properties. To determine the constant of ionization of sorbent we studied its total static sorption capacity on  $\text{K}^+$  ions ( $\text{SSC}_{\text{K}^+} = 11.4$  mmol/g) and the potentiometric titration was done on known technique

[20]. On the base of results of potentiometric titration we made a differential curve of titration between  $\frac{\Delta p\text{H}}{\Delta V} = f(V_{\text{KOH}})$  (Fig.1). Figure 1 shows that the sorbent contains 2 different ionogenic groups. So the ionization of the sorbent goes on in 2 stages:



To determine the contents of ionization of the sorbent, data of differential curve of titration were used. The results in tab1.2 show the constant of ionization of the sorbent is calculated on modified Handerson-Hasselbach equation [20].

After measuring of pH values of solutions under the sorbent for each value of  $\alpha$ , we showed the dependence of  $\text{pH} = f(\alpha)$

$\lg \frac{1}{1-\alpha}$ . There were calculated the parameters  $m$  ( $\text{tg}\alpha = m$ ) on the value of tangent of the straight's inclination's angle.

Graphic determination of the ionization constants of the sorbent is shown in figure 2. The sorption capacity is maximal at pH 8. The sorption capacity of the sorbent increases with increasing of concentration of uranium ions in solution and the sorption capacity is maximal when concentration of uranium ions equals to  $6 \cdot 10^{-3}$  mol/l (pH = 8,  $C_{\text{UO}_2^{2+}} = 6 \cdot 10^{-3}$  mol/l,  $V_{\text{vol.}} = 20$  ml,  $m_{\text{sorb.}} = 0,05$  g,  $\text{SC} = 455$  mg/g). The influence of ionic force on the sorption was studied. Increasing of ionic force till 0.8 mol/l does not influence so much. The following increasing leads to considerable decreasing of sorption. This because with the increasing of ionic surroundings of functional groups, the complex formation of U (VI) decreases. The dependence of sorption on time also was investigated. Complete sorption of U (VI) goes on after 3 hours at static conditions.

The influence of some mineral acids and their concentrations on desorption of U (VI) from the sorbent was studied. The experiment shows that the maximal desorption of U (VI) go on nitric acid. The investigation was made also at dynamic conditions. The dependence of the sorption on the rate of introduction of sample's solutions was also studied. The desorption also was investigated at dynamic conditions; the rate of introduction of an acid and the influence of the concentration. The optimal conditions of concentration of U (VI) ions by polymer sorbent were established. The investigation showed that at optimal conditions the concentration of U (VI) ions quantitatively absorbs and desorbs ( $R > 95\%$ ) (Table.3). The developed method is used for definition of micro amounts U (VI) in sea water with preliminary concentration. Influence of components of a matrix on sorption ions U (VI) is studied by the received polymeric sorbent

(Table.4). Carrying out of analysis and correctness of the results. 1l of filtered sample is brought to the needed value of pH by adding of HNO<sub>3</sub> and then passed through the micro column at the rate of the flow 1.5 ml/min. The concentration of U (VI) in an eluent is determined by photometric method. The results are calculated as 100% of extraction of the determined ions (Table.5). Apparently, from tab. 5 good coincidences of the entered and found quantities of defined ions is received. These results prove correctness of the offered technique.

#### 4 Conclusions

The study revealed the possibility of using synthesized sorbent for sorption-spectrophotometric determination of uranium (VI). The developed method is more economical, quick and environmentally safe as compared to the [16-18] (Table. 6). In addition, it is established that it is possible to reuse the regenerated sorbent for the processes of concentration.

**Table1:** Some analytical characteristics of complex of U (VI) with TSCAB.

pH <sub>opt</sub>	λ <sub>max</sub> , nm	ε <sub>max</sub> · 10 <sup>-4</sup>	Composition of Complex	Constants of stability	Interval of obeying to Beer's law, μg/ml
4	490	0.60±0.02	1:2	5.36±0.03	0.952-9.52

**Table 2:** Results for calculating of the constants of ionization of the sorbent. (C<sub>KOH</sub>=0.1M, m<sub>sorb</sub>=100 mg, pK<sub>1</sub>=5.85; pK<sub>2</sub>=8.85).

α	$\frac{\alpha}{1-\alpha}$	$\lg \frac{\alpha}{1-\alpha}$	V <sub>KOH</sub> , ml	pH	pK <sub>1</sub>	α	$\frac{\alpha}{1-\alpha}$	$\lg \frac{\alpha}{1-\alpha}$	V <sub>KOH</sub> , ml	pH	pK <sub>2</sub>
0.1	0.1	-0.954	0.342	4.5	5.85	0.1	0.1	-0.954	3.762	8.35	8.87
0.2	0.25	-0.602	0.684	5.2	6.05	0.2	0.25	-0.602	4.104	8.45	8.78
0.3	0.43	-0.368	1.026	5.5	6.02	0.3	0.43	-0.368	4.446	8.55	8.75
0.4	0.6	-0.176	1.368	5.6	5.84	0.4	0.6	-0.176	4.788	8.71	8.81
0.45	0.81	-0.087	1.539	5.65	5.77	0.45	0.81	-0.087	4.959	8.8	8.85
0.5	1.00	0.000	1.710	5.7	5.70	0.5	1.00	0.000	5.130	8.9	8.90
0.55	1.2	0.087	1.881	5.85	5.73	0.55	1.2	0.087	5.301	8.98	8.93
0.6	1.50	0.176	2.052	6.05	5.80	0.6	1.50	0.176	5.472	9.0	8.90
0.7	2.3	0.368	2.394	6.5	5.98	0.7	2.3	0.368	5.814	9.1	8.90
0.8	4.00	0.602	2.736	6.7	5.85	0.8	4.00	0.602	6.156	9.2	8.87

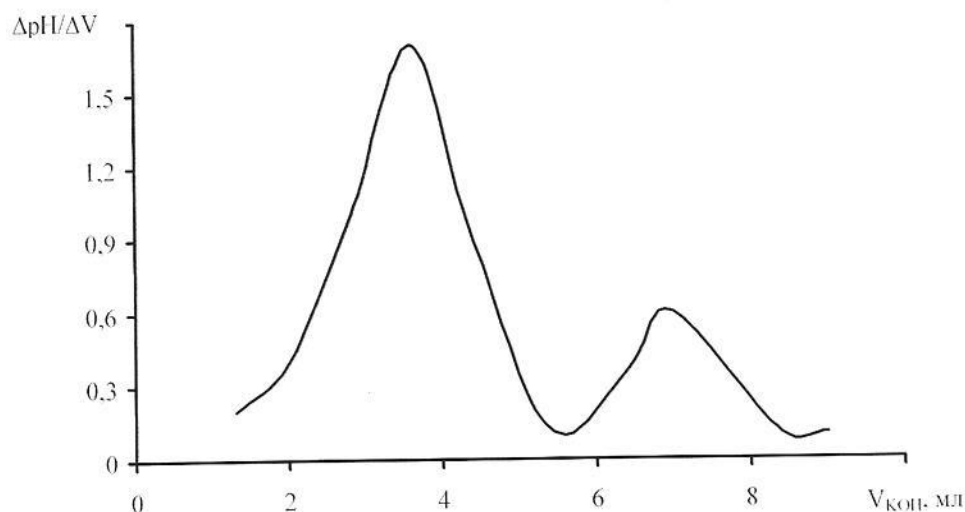


Fig.1. Differential curve of titration of sorbent

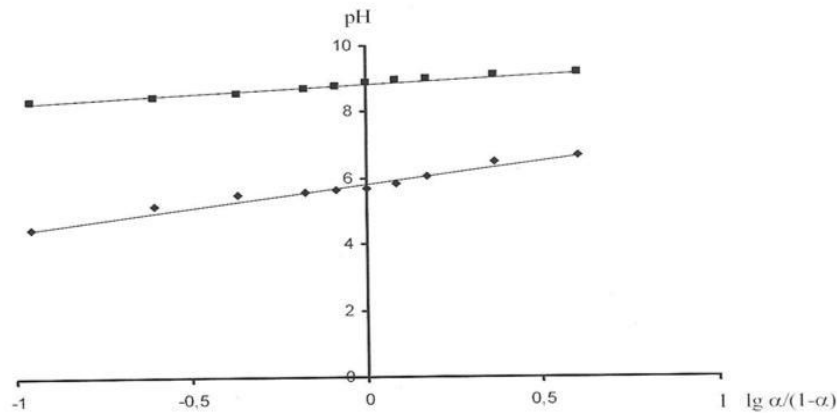


Fig.2. Graphic determination of the ionization constants of the sorbent:  $pK_{1(\text{graph})}=5.80$ ,  $pK_{2(\text{graph})}=9.00$ ,  $m_1=1.419$ ;  $m_2=0.548$ ;

**Table 3:** Optimal conditions of concentration of uranium (VI) ions by polymer sorbent at dynamic conditions

pH <sub>opt.</sub>	Rate of introduction of sample, ml/min	Rate of introduction of eluent, ml/min	Concentration HNO <sub>3</sub> mol/l
8	1.5	1.0	2.5

**Table 4:** Influence of components of a matrix on sorption (speed of a stream of 1,5 ml/mines;  $m_{\text{copб.}} = 100$  mg).

Ion	Concentration, mkq/ml	R, %
Na <sup>+</sup>	22000	97
K <sup>+</sup>	31000	100
Mg <sup>2+</sup>	8000	96
Ca <sup>2+</sup>	6000	96
Cl <sup>-</sup>	30000	98
SO <sub>4</sub> <sup>2-</sup>	10000	99
Fe(III)	20	97
Al(III)	100	99
Mn <sup>2+</sup>	50	96
Cu <sup>2+</sup>	25	96

**Table 5:** Result of analysis of sea water (volume of the sample 1000 ml; volume of eluent 5 ml;  $m_{\text{sorb}} = 100$  mg;  $P = 0.95$ ;  $n = 5$ ).

Sample	Determined element	Introduction, µg/ml	Found, µg/ml
Sea water*	U(VI)	-	5.032 ± 0.125
		10	15.102 ± 0.340
		15	19.925 ± 0.391
		20	25.018 ± 0.482

\* Samples are taken on coast of Caspian Sea, the item Seaside.

**Table.6:** 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
455 mg/g	8	3	7-8 cycle	Our
2.63 mg/g	3	6	2 cycle	[21]
300-350 mg/g	6	5	1 cycle	[22]
0,632 mmol/g	4.3-6.9		5 cycle	[23]

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