

## CONCENTRATION OF URANIUM(VI) WITH A CHELATE-FORMING SORBENT

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### ABSTRACT

The sorption properties of a modified sorbent based on a maleic anhydride-styrene copolymer with respect to uranium(VI) have been studied. The main quantitative characteristics of metal ion sorption are determined. A sorbent containing fragments of molon acid hydrazide for the selective extraction of uranium(VI) from solutions is proposed. The optimal sorption conditions were determined. The degree of extraction of uranium(VI) under optimal conditions exceeds 95%. A technique for the sorption-photometric determination of uranium(VI) in sea water has been developed.

**Keywords:** uranium (VI), concentration, copolymer, sorbent, sorption, determination.

### Introduction

Sorption methods have found wide application for the preconcentration of radionuclides. Chelating sorbents are of particular interest as sorption material. More efficient is the use of modified forms of the copolymer of maleic anhydride with styrene. For example, chelating sorbents, which are matrices on which organic compounds are fixed [1–18]. Recent publications indicate that the copolymer of maleic anhydride with styrene is a promising matrix for the preparation of chelating sorbents [19–28].

The main goal in the present work is to study the conditions for the preconcentration of uranium(VI) with a new chelating sorbent containing molon acid hydrazide fragments, followed by the determination of these ions by photometric spectrometry to extract uranium(VI) from sea water.

### Method

**Sorbent.** To study the sorption of uranium, a chelating sorbent containing fragments of molon acid hydrazide was used.

*Synthesis of sorbents based on copolymer of maleic anhydride with styrene.*

Radical copolymerization of maleic anhydride with styrene was carried out in a benzene solution in a water bath (75–80°C) for 140 minutes. Azobisisobutyronitrile recrystallized in ethanol was used as an initiator. The resulting copolymer was washed with benzene and dried in an oven at 50°C until a constant weight was obtained. The output of the copolymer is 95–97%. From the literature it is known that maleic anhydride forms with styrene a linear sequential copolymer with a molar ratio of 1:1. The calculated amount of formaldehyde and the

corresponding amine was added to the obtained copolymer. The reaction was carried out in a sand bath with continuous stirring. Due to the fact that the reaction was carried out in an aqueous medium, the anhydride groups in the composition of the copolymer undergo hydrolysis [29].

As a result of the interaction of formaldehyde and amine, an unstable carbonylamine is formed in the system. The resulting carbonylamine interacts with the carboxyl groups of the macromolecule, and the introduced amine fragment enters the macromolecule [29]. For use in the analysis, the sorbent granules were ground in an agate mortar and sieved through a sieve (0.14 mm). The sorbents were identified by IR spectroscopy. IR spectra were recorded on a LUMOS IR Fourier microscope (BRUKER, Germany) in the wave frequency range 600–4000 cm<sup>-1</sup>.

**Solutions.** The initial solution (2.38 g/l) of uranium (VI) was prepared by dissolving an accurate weight of the metal salt UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (chemically pure) in distilled water [30]. Al(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), Sr(II) solutions, Zn(II) was prepared by dissolving accurate weights of metal chlorides in 1 M hydrochloric acid. Working solutions were obtained by appropriate dilution of the stock solutions.

To create the required acidity, fixanal HCl (pH 1–2) and ammonium acetate buffer solutions (pH 3–11) were used. In order to create a constant ionic strength, KCl (analytical grade) was used. The determination of uranium in solutions was carried out by the spectrophotometric method using the reagent - 2,2',3,4-tetrahydroxy-3'-sulfo-5'-chloroazobenzene.

**Study of metal sorption.** Metal sorption isotherms were obtained under static conditions at 20°C. The sorption value and the degree of metal extraction were calculated from their equilibrium concentration in the solution by the spectrophotometric method [31]. Spectrophotometric measurements were performed using a Lambda Perkin Elmer spectrophotometer and a KFK-2 photoelectric colorimeter.

The degree of extraction (R, %) and the value of sorption (a<sub>s</sub>, mg/g) for the studied component were calculated using the formulas:

$$R = \frac{(C - [C])}{C} \cdot 100$$
$$a_s = \frac{(C - [C]) \cdot V}{m}$$

where C and [C] are the initial and residual (equilibrium) concentrations of the adsorbate, respectively, mg/l; V is the volume of the solution, l; m is the mass of the sorbent, g.

When studying sorption in a static mode, 4.76 mg of U(VI) metal aqueous solution was introduced into a test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the required acidity to a total volume of 20 ml. 0.05 g of the sorbent was added to a test tube, closed with a cork, and intensively stirred for 1–240 min, depending on the task. The solution was separated from the sorbent by filtration.

To study the effect of the amount of sorbent on the amount of sorption of uranium(VI) ions at pH 5, different amounts of sorbent (10, 20, 30, 40, and 50 mg) and the same volume of solution (20 ml) containing 4.76 mg of metal ions were added.

The dependence of metal desorption from the modified sorbent surface on acidity and eluent concentration was studied under static conditions. A portion of the modified sorbent weighing 0.05 g was placed in a 50 ml beaker with a metal solution and left for three hours with occasional stirring. After three hours, the sorbent was separated by filtration. The concentration of desorbed

uranium (VI) was determined in the obtained filtrate.

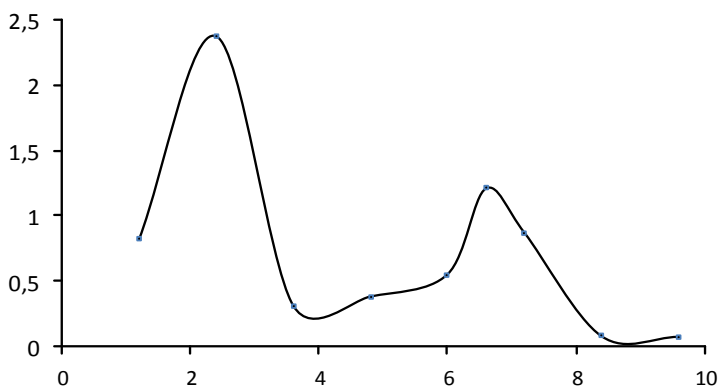
**Performing the analysis.** 100 ml of the filtered analyzed sample was adjusted to the required pH by adding HNO<sub>3</sub> and passed through a minicolumn with a sorbent at a flow rate of 1.0 ml/min. The sorbed metal ions were eluted with 5 ml of 2 M HClO<sub>4</sub> at a rate of 1.0 ml/min. The uranium concentration in the eluate was determined by the photometric method. The results were calculated assuming 100% uranium recovery.

## Results and discussions

**Potentiometric titration.** The acid–base ionization constants of functional analytical groups (FAGs) of polymeric sorbents are important characteristics that are directly related to the pH of element sorption [32]. Since the process of sorption on chelate sorbents is a complexation with the FAG of the sorbent, it can be assumed that similar correlations should also take place in the case of sorbents. To establish them, data on the pK of the FAG sorbents are required.

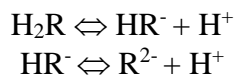
To determine the pK values, we used the Henderson-Hasselbach method, which allows us to determine the conditional constants of acid-base ionization of FAG. The determination was carried out by the potentiometric method after establishing the static capacity of the sorbent for the K<sup>+</sup> ion (SCSK<sup>+</sup> = 11.32 mmol/g) [32].

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



**Fig.1.** Differential titration curve of the sorbent.

From fig. 1 it can be seen that the resulting sorbent contains two different ionogenic groups. So the ionization of the sorbent occurs in two stages:

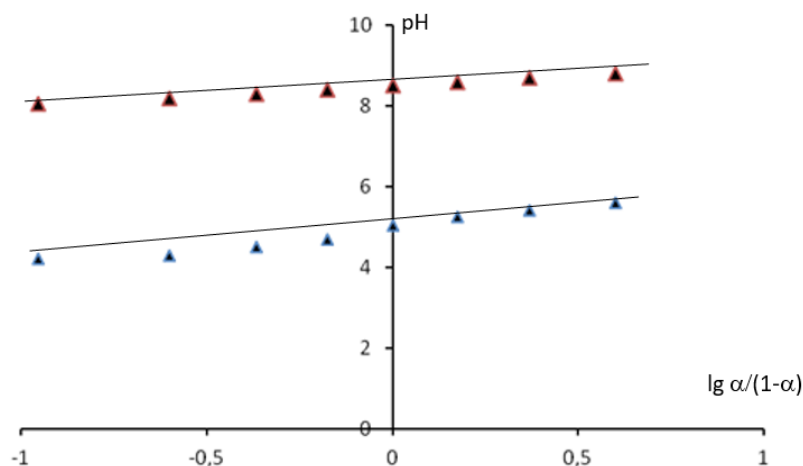


The ionization constant of the sorbent was calculated by the modified Henderson-Hasselbach equation [32].

By measuring the pH value of the solutions over the sorbent for each value of  $\alpha$ , we plotted

the dependence  $\text{pH} = f\left(\lg \frac{\alpha}{1-\alpha}\right)$ . The parameters  $m(\text{tg } \alpha = m)$  were calculated from the value of the tangent of the slope of the straight line.

The graphical definition of the ionization constant of the sorbent is shown in Figure 2.



**Fig.2.** Graphical determination of the sorbent ionization constant:  $\text{pK}_1(\text{graph})=4.90$ ,  $\text{pK}_2(\text{graph})=8.60$ ,  $m_1=0.995$ ;  $m_2=0.488$ ; ( $\text{pK}_1$ - characterizes the ionization of carboxyl groups,  $\text{pK}_2$ -deprotonization of amine groups)

**Influence of pH on sorption.** The study of the effect of pH (in the range of 1-8) on the preconcentration of uranium(VI) ions under static conditions showed that the quantitative extraction of metal ions is achieved at pH 4.

At low pH values (1–3) of the liquid phase, the low degree of extraction can be associated with the protonization of the functional groups present in the sorbent phase and the low degree of polymer swelling.

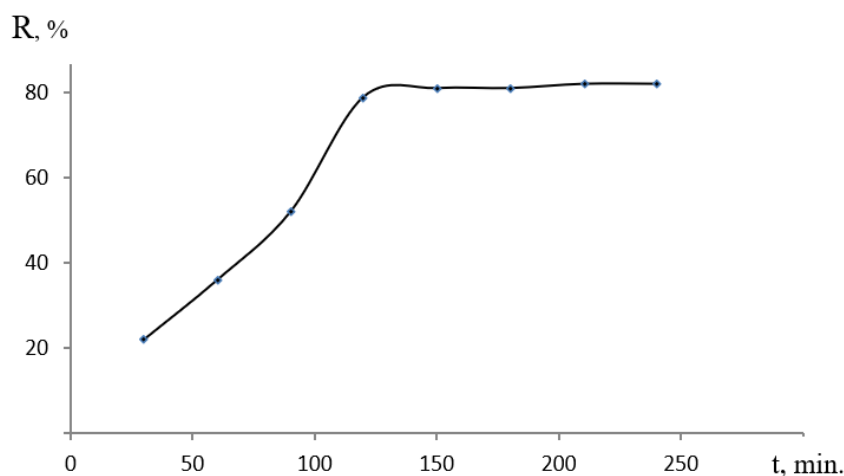
At such pH values, U(VI) ions are in the form  $\text{UO}_2^{2+}$  [33]. With an increase in the pH of the liquid phase, the degree of swelling of such polymeric sorbents increases. The maximum degree of uranium extraction by sorbents is achieved from solutions with pH 4. It was also found that at pH 4, the maximum metal sorption is achieved using 30 mg of the sorbent (Table 1).

**Table 1.** Influence of the amount of sorbent on the degree of extraction of uranium(VI):  $C_{\text{UO}_2^{2+}}=238 \text{ mg/l}$ ,  $V=20 \text{ ml}$ ,  $\text{pH}=4$

m, mg	10	20	30	40	50
R, %	23	49	80	80	80

All further studies were carried out at pH 5.

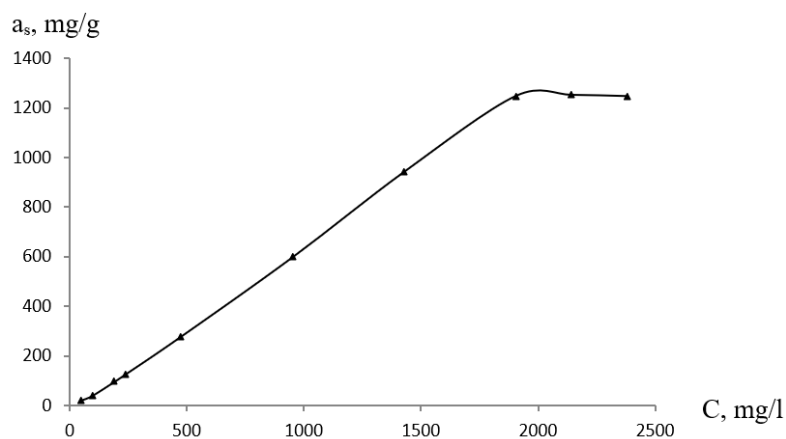
**Effect of time on sorption.** It was found that the sorption equilibrium in the "sorbent - liquid phase" system is achieved after 2 hours of contact (Fig. 3). For all further experiments, the time to establish the sorption equilibrium was 2 hours.



**Fig. 3.** Dependence of the degree of extraction of uranium(VI) on time.

**Influence of ionic strength on sorption.** It is known [34] that 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, in connection with this, the dependence of the analytical signal on the ionic strength was studied. An increase in ionic strength to 0.6 does not affect sorption. Its subsequent increase from 0.6 to 1.4 leads to a significant decrease in the sorption value. All further experiments were carried out in solutions with an ionic strength of 0.8.

**Influence of uranium (VI) concentration.** The study of the dependence of the sorption capacity on the concentration of uranium (VI) showed that the sorption value changes with the concentration of the uranyl ion. The sorption isotherm of uranium (VI) shows a steep rise in the initial linear section, the convexity of the isotherm curve, which indicates a high sorption (Fig. 4).



**Figure 4.** Isotherm of sorption of uranium(VI) by the obtained sorbent:  $m_{\text{sorb}}=30$  mg,  $V=20$  ml,  $\text{pH}=4$

So, with an increase in the concentration of the uranyl ion in the solution, the amount of sorbed metal increases, and at a concentration of 1252 mg/l it becomes maximum ( $\text{pH}=5$ ,  $V_{\text{tot.}}=20$  ml,  $m_{\text{sorb.}}=0.05$  g)

**Study of the desorption of the absorbed uranyl ion from a polymeric sorbent.** To select a suitable eluent, various acids were tested -  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ . It was found that the desorption capacity of  $\text{HClO}_4$  is higher than that of other acids; this may be due to the fact that perchlorate ions do not form complexes with metals, including uranium. A study of the influence of the  $\text{HClO}_4$  concentration showed that U(VI) ions are maximally desorbed at a volume of 5 ml and a concentration of 2 M perchloric acid (Table 2).

**Table 2.** Effect of concentration and volume of eluent on the degree of desorption (%) of uranium

Concentration and volume $\text{HClO}_4$	Degree of desorption , %
0,5 M 5 ml	84
10 ml	86
1,0 M 5 ml	91
10 ml	93
1,5 M 5 ml	93
10 ml	96
2,0 5 ml	97
10 ml	97

Note:  $n=5$ ,  $p=0,95$

After determining the optimal preconcentration conditions, the developed method was successfully applied to determine the microquantities of uranium(VI) in sea water (the coast of the Govsan settlement, the Caspian Sea, Azerbaijan) with preliminary preconcentration (Table 3). The table shows that sea water contains  $7.306 \pm 0.101 \mu\text{g/ml}$  of uranyl ion. The correctness of the technique was checked by the "introduced - found" method (Table 3).

**Table 3.** Seawater analysis results.

introduced, mkq/ml	found $\bar{X} \pm \frac{t_{pS}}{\sqrt{n}}$ , mkq/ml
-	$7,306 \pm 0,101$
10	$16,489 \pm 0,127$
20	$27,299 \pm 0,318$

Note: sample volume 100 ml; eluent volume 5 ml;  $m_{\text{copo}}=100 \text{ mg}$ ;  $\lambda=490 \text{ nm}$ ,  $l=1 \text{ sm}$ ,  $p=0,95$ ;  $n=6$

## Conclusion

A new sorbent based on a copolymer of maleic anhydride with styrene was synthesized by modification with molon acid hydrazide in the presence of formalin. The resulting sorbent was used to extract uranium from sea water. The optimal conditions for the sorption of uranium on the sorbent are determined. The sorbent used to determine trace amounts of radioactive metal has higher sorption properties (sorption capacity, analysis time, concentration temperature, influence of foreign ions on sorption) compared to those known in the literature [1–18]. The data obtained showed that the proposed sorbent can be used to preconcentrate uranium from solutions such as natural waters. It is possible to reuse the regenerated sorbent for preconcentration.

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## References

1. Akl Z.F. A comparative investigation of uranium and thorium adsorption behavior on amidoximated copolymeric hydrogel. *J Radioanal Nucl Chem* 331, 1859–1867 (2022). <https://doi.org/10.1007/s10967-022-08250-z>
2. Jiang X., Yan J., Xingquan W., Ying Y., Yongzhong J. Preconcentration of Uranium(VI) from Aqueous Solution by Amidoxime-Functionalized Microspheres Silica Material: Kinetics, Isotherm and Mechanism Study // *Chemistry select.* 2018. Volume3. Issue 43. Pages 12346-12356. <https://doi.org/10.1002/slct.201802472>
3. Li X., Hu H.Y., Yu J.Y., Zhao W.Y. Selection of Suitable Microalgal Species for Sorption of Uranium in Radioactive Wastewater Treatment // *Huan jing ke xue= Huanjing kexue*, 2016, V. 37, No 5, p.1858-63
4. Zhang J., Guo Z., Li Y., Pan S., Chen X., Xu J. Effect of environmental conditions on the sorption of uranium on Fe<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub> hollow spheres // *Journal of Molecular Liquids*, 2016, No 223, p. 534-540
5. Elhefnawy O. A., *Radiochimica Acta*, 2017, V. 105, No 12, pp. 1-12.
6. Vijayabhaskara R.B., Saritha B., Giri A., Sreenivasulu R.T., *Inter. Journal of advances in pharmacy, biology and chemistry*, 2014, Vol. 3, No 3, pp. 667-672.
7. Hisham K. F., Saeyda A.T., Randa M.E., Shaimaa S.A., *International Journal of Advanced Research*, 2015, Vol. 3, No 7, pp. 326-336.
8. Muhammad H.K., Muhammad H., Syed M.H., Akbar A., *J Radioanal Nucl Chem*, 2014, No 301, pp. 703–709.
9. Afrin A., Manirul I.M., Jamaluddin A.M., *International Journal of Current Research*, 2019, Vol. 11, No 09, pp.7281-7291.
10. Dolak Ī., Hacettepe *J. Biol. & Chem*, 2018, Vol. 46, No 2, pp. 187–197.
11. Aslam M.M., Khuhawar M.Y., Arain R., Aziz Ch.M., *Arabian Journal of Chemistry*, 2018, No 11, pp. 305–312.
12. Abhijit S., Sadhan B. D., Arnab S., Manoj K. S., Tomar B. S. Simultaneous preconcentration of uranium and thorium in aqueous samples using cloud point extraction // *RSC Advances*. 2016. Vol. 6. p. 20109-20119. <https://doi.org/10.1039/C5RA23734C>.
13. Ito S., Takaku Y., Ikeda M., Kishimoto Y., *Prog. Theor. Exp. Phys.*, 2017, 113H01 (11 pages). DOI: 10.1093/ptep/ptx145.
14. Yulong Y., Amir M.P., Zdenek S., Stanislava M., Martin P. Radioactive Uranium Preconcentration via Self-Propelled Autonomous Microrobots Based on Metal–Organic Frameworks // *ACS Nano*. 2019. 13. 10. 11477–11487. <https://doi.org/10.1021/acsnano.9b04960>
15. Ahmed O., Mohamed A., Hend S. Selective preconcentration of uranium on chitosan stearyl thiourea prior to its spectrophotometric determination // *Separation Science and Technology*. 2018. Volume 53. Issue 14. Pages 2267-2283. <https://doi.org/10.1080/01496395.2018.1445113>
16. Habacuc P.T., Taryn L.N., Ashley T.T., Andrew R.B., Zanna C. Pre-concentration of thorium and neodymium isotopes using Nobias chelating resin: Method development and application to chromatographic separation // *Talanta*. 2019. Volume 202. P. 600-609. doi:10.1016/j.talanta.2019.03.086
17. . Susan S., Abdolbaset D., *Journal of Molecular Liquids*, 2019, Vol. 291, 111242.
18. Srivastava B., Barman M.K., Chatterjee M., Roy D., Mandal B., *Journal of*

- chromatography A, 2016, Vol. 1451, pp. 1-14. DOI: 10.1016/j.chroma.2016.04.079
19. Bahmanova, F.N. Concentration and Determination of Uranium(VI) by a Sorbent Containing Fragments of p-Aminobenzoic Acid. *Radiochemistry* 64, 375–378 (2022). <https://doi.org/10.1134/S1066362222030158>
  20. Magerramov A.M., Alieva R.A., Alieva Z.M. and etc. Concentration of thorium (IV) with a chelating sorbent. *Zavodskaya laboratoriya. Diagnostika materialov*. 2018, vol. 84, no. 3, pp. 21–24. [in Russian]. DOI: 10.26896/1028-6861-2018-84-3-021-024.
  21. Hajiyeva S.R., Bahmanova F.N., Alirzaeva E.N., Shamilov N.T., Chiragov F.M. // *Radiochemistry*. 2018. V. 60. No. 2. S. 175
  22. Basargyn N.N., Maharramov A.M., Hajiyeva S.R. and etc. Determination of uranium (VI) in natural waters after preliminary concentration with a sorbent containing fragments of m-amino phenol / *Russ. J. An. Chem.* 2013. V. 68. N 2. P. (136-139). [in Russian].
  23. Aliyev E.H., Bahmanova F.N., Hamidov S.Z., Chyragov F.M. Lead (II) concentration by a chelating sorbent containing meta-phenylenediamine fragments. *Proceedings of Universities. Applied Chemistry and Biotechnology*. 2020. Vol. 10. № 1. P.107.
  24. Bahmanova F.N., Hajiyeva S.R., Chyragov F.M. // *Proceedings of Universities. Applied Chemistry and Biotechnology*. 2019. Vol. 9. №2. P. 194.
  25. Maharramov A.M., Hajiyeva S.R., Bahmanova F. N., Gamidov S. Z., Chyragov F. M. // *Journal of Analytical Chemistry*. 2011. Vol. 66. No. 5. p. 465.
  26. Bahmanova F.N., Hajiyeva S.R., Chyragov F.M. Determination of Th(IV) in natural waters after preconcentration with a chelating sorbent // *Radiochemistry*. 2019. T. 61. № 5. C. 604-606.
  27. Bahmanova F.N. // *Journal of Analytical chemistry*. 2020. Vol. 75. № 9. P. 1116.
  28. Bahmanova F.N., Hajiyeva S.R., Alirzaeva E.N., Shamilov N.T., Chyragov F.M. // *Journal of the Chemical Society of Pakistan*. 2020. Vol. 42. № 3. P. 413-417.
  29. Алиева Р.А., Велиев В.Н., Гамидов С.З., Чырагов Ф.М. // *Химические проблемы*. -2006. -№ 3. -С. 496
  30. Коростелев П.П. Приготовление растворов для химико-аналитических работ. - М.: Наука, 1964. -261 с
  31. Булатов М.И., Калинин И.П. Практическое руководство по фотометрическим и спектрофотометрическим методом анализу. - Л.: Химия, 1972. -407 с.
  32. Корреляции и прогнозирование аналитических свойств органических реагентов и хелатных сорбентов / Под ред. д.х.н. Н.Н. Басаргин, д.х.н. Э.И. Исаев. - М.: Наука, 1986. -199 с.
  33. В.А.Назаренко, В.П. Антонович, Е.М.Навская Гидролиз ионов металлов в разбавленных растворах М.: Атомиздат, 1979, 192 с.
  34. Мельник Т.А. Дисс. канд. хим. наук. Воронеж: УГЛТУ, 2005. 114 С.



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## КОНЦЕНТРИРОВАНИЕ УРАНА(VI) ХЕЛАТООБРАЗУЮЩИМ СОРБЕНТОМ

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### Резюме

Изучены сорбционные свойства модифицированного сорбента на основе сополимера малеинового ангидрида и стирола по отношению к урану(VI). Определены основные количественные характеристики сорбции ионов металлов. Предложен сорбент, содержащий фрагменты гидразида молонной кислоты, для селективного извлечения урана(VI) из растворов. Определены оптимальные условия сорбции. Степень извлечения урана(VI) в оптимальных условиях превышает 95%. Разработана методика сорбционно-фотометрического определения урана(VI) в морской воде.

**Ключевые слова:** уран (VI), концентрирование, сополимер, сорбент, сорбция, определение.

## URANIN(VI) XELAT ƏMƏLƏ GƏTİRƏN SORBENTLƏ QATILAŞDIRILMASI

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### XÜLASƏ

Malein anhidrid-stirol sopolimeri əsasında modifikasiya olunmuş sorbentin urana (VI) münasibətdə sorbsiya xassələri tədqiq edilmişdir. Metal ionlarının sorbsiyasının əsas kəmiyyət xüsusiyyətləri müəyyən edilir. Məhlullardan uranın (VI) seçilərək çıxarılması üçün tərkibində molon turşusunun hidrazidi fraqmentləri olan sorbent təklif edilmişdir. Optimal sorbsiya şərtləri müəyyən edilmişdir. Optimal şəraitdə uranın (VI) çıxarılması dərəcəsi 95%-i ötür. Dəniz suyunda uranın (VI) sorbsiya-fotometrik təyini üçün texnika işlənib hazırlanmışdır.

**Açar sözlər:** uran (VI), konsentrasiya, sopolimer, sorbent, sorbsiya, təyin.