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DETERMINATION OF IONIZATION CONSTANTS OF NEW CHELATING SORBENTS AND CONCENTRATION OF U(VI) AND Th(IV) IONS BY THE PROPOSED SORBENTS

Fidan Bahmanova, Elnara Alirzayeva, Hamida Huseynova,
Nazim Shamilov & Famil Chyragov
Baku State University, Baku, Azerbaijan

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One of the important tasks of analytical chemistry at the present time is the development of reliable methods for environmental quality monitoring. To solve this problem, the determination of trace amounts of various ions is widely used among the main analytical methods. On the basis of a copolymer of maleic anhydride with styrene, eight chelating sorbents containing the following fragments were synthesized: dithizone-1 (M1); 2-aminophenol-4,6-disulfonic acid (M2); o-acetylaminophenoxyacetic acid (M3); N,N′,N′-triphenylguanidine (M4); m-phenylenediamine (M5); 3-nitro-4-sulfoaminobenzene (M6); p-acetylamidobenzoic acid (M7); and norsulfazole (M8). The sorbents were synthesized using a known procedure, and their composition and structure were determined by IR spectroscopy. The physicochemical properties of the synthesized sorbents were studied. To determine the ionization constants of the sorbents, the total static sorption capacity (P) with respect to K^+ ions was investigated according to a known method. In determining P, the amount of consumed K^+ ions was equivalent to the amount of carboxyl groups in the sorbent unit. The ionization constants of the obtained sorbents were determined by potentiometric titration. The conditions for the sorption of U(VI) and Th(IV) by the synthesized sorbents were studied. The developed methods were applied to the preconcentration of U(VI) and Th(IV) in various natural objects.

Keywords: sorbent, physicochemical properties, potentiometric titration, concentration, uranium(VI), thorium(IV)

INTRODUCTION

One of the priority tasks of analytical chemistry at the present time is the development of reliable methods for environmental quality monitoring. Among the main approaches to solving this problem, the determination of trace amounts of various ions is widely used. The use of polymeric sorbents makes it possible to isolate and preconcentrate trace amounts of ions from environmental objects [1–3].

It is known from the literature [4,5] that the acid–base properties of chelating sorbents are an important characteristic. These properties largely determine the selectivity of the sorbents. The selectivity of chelating sorbents depends on the sorption conditions (solution pH, concentration and speciation of metal ions in solution, ionic strength, and the presence of

E-mail address: fidan_chem@rambler.ru

ligands in the solution) [6]. In general, the selectivity of chelating sorbents reflects differences in the stability of complexes formed in the sorbent phase. The analytical application of chelating sorbents is based on these differences.

The analysis of natural objects aimed at the determination of individual components is carried out using various chemical and physicochemical methods [7–10]. However, the capabilities of the latter do not always allow the determination of trace amounts of toxic and radioactive elements in objects of complex composition. All these sorbents possess certain drawbacks. Some of them have low sorption capacity [7]; some sorbents absorb thorium maximally upon heating to 45–60 °C, whereas at room temperature metal sorption does not occur [8]; for some sorbents, thorium sorption decreases in the presence of K^+, Na^+, and Li^+ ions [9]; and for others, optimal sorption is achieved only after prolonged contact (20–78 hours) [10].

In this regard, studies aimed at increasing the sensitivity and selectivity of sorption–spectrophotometric analytical methods are promising. Successful solution of such problems can be achieved by combining preliminary selective separation and preconcentration of elements using polymeric complex-forming sorbents.

For the determination and separation of thorium(IV) and uranium(VI) from natural and industrial objects by preconcentration, natural and synthetic sorbents are often used [11–24]. At present, chelating sorbents are mainly employed as synthetic sorbents for the preconcentration and determination of thorium(IV) and uranium(VI). The efficiency, simplicity, and selectivity of this method ensure its wide application in analytical chemistry.

In the present work, in order to select sorbents with optimal physicochemical and sorption properties for the preconcentration of U(VI) and Th(IV) ions, the ionization constants of new chelating sorbents were determined by potentiometric titration, and their sorption properties toward U(VI) and Th(IV) ions were studied.

EXPERIMENTAL

The sorbents were synthesized according to a known procedure, and their composition and structure were determined by IR spectroscopy. Stock solutions with a concentration of 1 × 10^{-1} mol/L $UO_2SO_4\ 3H_2O$ (analytical grade) and $Th(NO_3)_4$ (analytical grade) were prepared using a known method. Working solutions were obtained by diluting the stock solutions.

The ionization constants (pK_a) of the functional groups of the sorbents were determined by potentiometric titration of individual weighed portions with a 0.1 mol/L potassium hydroxide solution at an ionic strength of $\mu = 1$. Equilibrium was considered to be established when the pH of the solution above the sorbent did not change with time. The titration was carried out at 25 °C. The ionic strength of the solutions was maintained constant by adding a calculated amount of KCl. The solutions were stirred using a magnetic stirrer.

The pH of the solutions was measured using a PHS-25 pH meter. A glass electrode, previously conditioned in a mixed solvent for 24 hours and calibrated using standard buffer solutions, was used as the indicator electrode. Quartz cuvettes with an optical path length of 1 cm were used for the measurements.

RESULTS AND DISCUSSION

To determine the ionization constants of the sorbents, the total static sorption capacity (P) with respect to K^+ ions was studied according to a known procedure (Table 1). When determining P, the amount of consumed K^+ ions was equivalent to the number of –COOH groups in the sorbent unit.

Table 1. Values of the static sorption capacity of the sorbents

Sorbent	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8
$TSSC_{K^+}$, mmol/g	12.26	13.68	14.34	13.40	12.80	13.66	13.54	6.80

The sorbents under study are polyampholites, which affects the shape of their titration curves. Figure 1 shows the titration curve of sorbent M2.

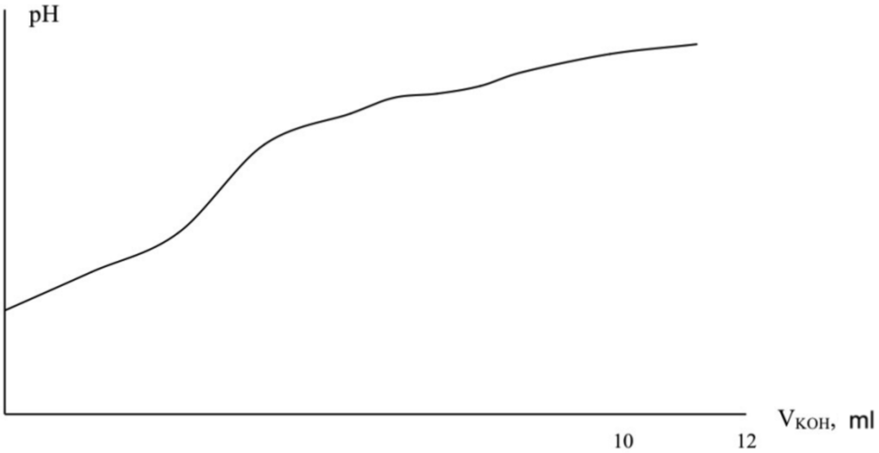

Figure 1. Potentiometric titration curve of sorbent M2. C_{KOH} = 0.1 mol//

The curve is shallow, and the jumps are not clearly visible. By potentiometrically titrating the obtained sorbents, differential curves were constructed in the coordinates $\frac{\Delta pH}{\Delta V} - V_{KOH}$ (Fig. 2). On the differential curve, the jumps are clearly seen, making it possible to determine that the studied sorbents contain two distinct ionogenic groups, each character-ized by its own pK_a.

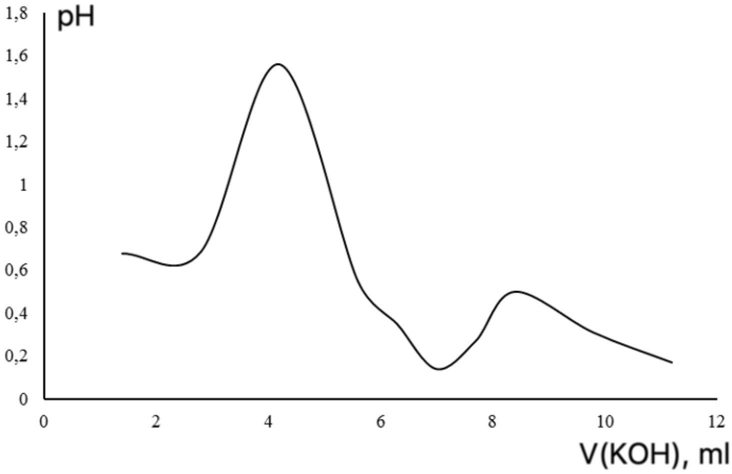

Figure 2. Differencial titration curves of sorbent M2

The ionization constants of these groups were determined graphically from the linear dependence. The obtained results are presented in Table 2.

Table 2. Ionization constants of the sorbents.

Sorbent	$pK_{1(\text{граф.})}$	Titrated group	$pK_{2(\text{граф.})}$	Titrated group
M_1	5.00	$-COOH$	8.50	$-\overset{+}{N}H_2-$
M_2	3.90	$-COOH$	7.75	$-\overset{+}{N}H_2-$
M_3	4.15	$-COOH$	7.80	$-\overset{+}{N}H_2-$

M_4	5.70	$-COOH$	9.80	$-\overset{+}{N}H_2-$
M_5	4.20	$-COOH$	8.45	$-\overset{+}{N}H_2-$
M_6	3.90	$-COOH$	7.50	$-\overset{+}{N}H_2-$
M_7	4.60	$-COOH$	6.75	$-\overset{+}{N}H_2-$
M_8	4.40	$-COOH$	6.90	$-\overset{+}{N}H_2-$

As can be seen from Table 2, the ionization constants of the synthesized sorbents differ slightly. This difference is due to the various inductive effects created by the fragments introduced into the macromolecule.

The sorption of U(VI) and Th(IV) by the synthesized sorbents was studied, including the influence of medium acidity, metal concentration, and ionic strength on sorption.

Effect of pH on the sorption of thorium(IV) and uranium(VI). The influence of pH on the complexation of metals with chelating sorbents was studied in the pH range of 1–10. The results showed that quantitative extraction is achieved within the pH interval of 4–6.

Effect of thorium(IV) and uranium(VI) concentration on the sorption process. To determine the optimal conditions for the sorption of thorium(IV) and uranium(VI) with the obtained sorbent, a study of the dependence of the sorption capacity (SC) on the metal concentration was carried out.

As the concentration of metal ions increases, the sorption capacity of the sorbents initially rises and then becomes constant after reaching a certain metal ion concentration. With increasing thorium(IV) and uranium(VI) concentration in the solution, the amount of sorbed metal increases, reaching a maximum at a concentration of 8×10^{-3} mol/L. This is due to the complete binding of the reactive functional groups of the macromolecules by the metal ions.

Effect of solution ionic strength on the sorption of thorium(IV) and uranium(VI). It is known that the ionic strength of the solution significantly affects the flexibility of the sol-id-phase matrix and the state of the functional groups of the analytical reagent. Therefore, the dependence of the analytical signal on the KCl concentration in the range of 0.1–1.2 was studied. An adverse effect of increasing the solution's ionic strength on the sorption properties of the sorbent was observed, which can be explained by the screening of the coordination-active groups by the electrolyte ions.

Effect of contact time on the sorption of thorium(IV) and uranium(VI). Full sorp-tion of metal ions onto the solid phase requires a certain contact time. It was found that sorp-tion equilibrium is achieved within 2 hours of contact between the solution and the sorbent.

Desorption. The effect of different mineral acids ($HClO_4$, H_2SO_4, HNO_3, HCl) at the same concentrations on the desorption of metals from the sorbent was also studied. Experi-mental results showed that the maximum desorption of metal ions occurs in hydrochloric acid.

CONCLUSION

The results of both groups were collected, and each student's performance was evaluated on a 100-point scale. The results for each area were aggregated, and overall results were derived. The collected data underwent statistical analysis. To determine the differences between the groups, the t-test method was employed. This enhances the reliability of the results and allows for a more accurate assessment of differences between the groups. In the group using integrative approaches, analytical thinking skills were rated with a success indicator of 85%. In the traditional group, this indicator was 70%, demonstrating that integrative approaches enhance students' analytical thinking skills. In the integrative group, 90% of the questions related to establishing interdisciplinary connections were answered correctly. In contrast, the traditional group achieved only 70%, indicating that students in the integrative group have a better understanding of the connections between different scientific disciplines. The ability to explain the application of chemistry in real life was assessed at 80% accuracy in the group utilizing integrative approaches. In the traditional group, this figure was only 55%, confirming that integrative methods increase students' understanding of the application of chemistry in their daily lives.

The results of the experiment have proven that the implementation of integrative approaches positively affects students' analytical thinking skills, their ability to establish interdisciplinary connections, and their understanding of the application of chemistry in real life. These results highlight the importance of expanding the use of integrative approaches in chemistry education. It is essential to further develop these approaches within the educational system to ensure that students grasp scientific concepts in a deeper and broader context. The findings also reveal potential opportunities for more effective application of modern methods in future chemistry classes, enhancing the dynamism of the teaching process.

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