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Sorption–Spectroscopy and Test Determination of Uranium(VI) and Iron(III) from a Single Sample on the Solid Phase of Fiber Materials Filled with an AB-17 Ion Exchanger

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Received July 4, 2012; in final form, December 3, 2012

Abstract—Diffuse reflectance spectroscopy has been used for the study of the sorption of malonate and glycolate complexes of uranium(VI) and iron(III), present simultaneously in solution, onto the solid phase of fiber materials filled with an AB-17 anion exchanger. In the form of malonate complexes uranium(VI) is determined in 0.5 M HCl on substrate discs with immobilized Arsenazo III, while iron(III) is determined on substrate discs with potassium thiocyanate in 0.5 M HCl. The dependence of the analytical signals on the concentrations of U(VI) and Fe(III) is linear in the ranges $0.02-0.16$ μg/mL; the detection limit is 0.01 μg/mL. The possibility of analysis of U(VI) and Fe(III) mixtures in ratio from 1 : 5 to 5 : 1 in the presence of 2-fold concentrations of Zr(IV), Th(IV), and Ti(IV), 5-fold concentrations of Bi(III), 10-fold concentrations of Cu(II), 20-fold concentrations of La(III), 100-fold concentrations of Ni(II) and Zn(II), and 200-fold concentrations of Co(II) and Ca(II) has been demonstrated. Standard color scales in the concentration range from 0.02 to 0.2 μg/mL have been used for the visual determination of uranium(VI) and iron(III).

*Keyword*s: diffuse reflectance spectroscopy, PANF-AB-17 fiber material, uranium(VI), iron(III), KSCN, Arsenazo III

Photometric and fluorometric determination of uranium is often affected by iron, which should be separated. In the analysis of rocks, it may be precipitated by carbonate, cupferron, and others. Uranium is separated by extraction with iron nitrate as one of salting-out agents. It has been found that the dissolution of iron(III) nitrate in weakly acidic solutions provides the quantitative transfer of uranium from spent nuclear fuel into a solution and its separation from Mo, Tc, Ru and, partially, from Nd, Zr, Pd. An efficient method of uranium separation from iron, thorium, cerium, calcium is based on the formation of anionic acetate complexes of uranium and their sorption onto anion-exchange resins. The other metals form cation complexes and are not adsorbed. Many metal ions, including iron, quench uranium fluorescence at certain ratios of elements in the rock. The determination of iron(III) is affected by many elements [1–4].

Recently inorganic ions have been determined using complexation with organic reagents on the solid phase. Usually, such an approach leads to the improvement of the selectivity and sensitivity of determination [5–8].

Fiber ion exchangers are very convenient, mechanically and chemically stable material as a solid phase in sorption spectroscopy and test methods of determination. Filled fiber materials are produced industrially and the required finely dispersed ion exchanger is introduced into polyacrylonitrile fiber in the process of its formation. The process results in colorless or slightly colored fine polyacrylonitrile non-woven fabric filled with an ion exchanger (Research Institute of Synthetic Fibers, Tver). The filling degree can be varied in the range 80–50 wt %; the fiber thread diameter is 30–40 μm; the ion exchanger particle diameter is 5–10 μm. The materials are stable in the range from strongly acidic media to weakly alkaline, have good kinetic and ion exchange parameters, and are convenient for use. They can be used for preconcentration and determination both under dynamic and batch conditions. They can be easily transferred with tweezers and are not deformed when moved, heated in solution, dried, and as a result of other operations. Fiber materials filled with different ion exchangers can be superposed over each other in a flow cell and stirred in a test solution for the simultaneous sorption of different elements. Thereby, the rapidity of determination can be significantly improved. On the other hand, 2–3 elements can be preconcentrated on a single substrate disc for the further subsequent determination of each of them by a solid-phase reaction with an appropriate organic reagent. Fiber materials filled with an anion exchanger can be used for metal ion sorption as

anionic complexes. This can be used for the improvement of analysis selectivity by separating the cations that do not form such anionic complexes. This property of fiber ion exchangers was used in the present study.

The study is devoted to the investigation of the possibility of the individual determination of uranium(VI) and iron(III) in case of their simultaneous presence using a fiber material filled with an AB-17 anion exchanger, complexation with Arsenazo III and potassium thiocyanate.

EXPERIMENTAL

Solutions, reagents, adsorbents. All reagents were chemically pure or analytical grade. Metal salt solutions (0.01 M) were prepared using well-known procedures by dissolving corresponding nitrates or chlorides. Solutions of the necessary concentration were obtained by dilution. Working solutions containing 25 µg/mL were prepared by diluting more concentrated solutions of $FeCl_3$ and $UO_2(NO_3)_2$. Solutions of thioglycolic and malonic acid (0.5 M) were prepared by dissolving weighted portions in water; 1 and 0.1 M solutions of HCl and NaOH were prepared using ampoules with their precise concentrations; 10% solution of KSCN was prepared by dissolving a 10-g portion of KSCN in a 90-mL portion of water, while a 0.05% solution of Arsenazo III was prepared by dissolving a 0.05-g portion of the reagent in a 100-mL portion of water. A 0.0005% solution of Arsenazo III further used for immobilization on a substrate was prepared by diluting a 0.05% solution.

The solid phase was polyacrylonitrile fiber filled with a strong anion exchanger AB-17 (**PANF-AB-17**). The filling degree was ~50 wt %. Preliminarily after swelling the substrates were washed from the cations with 1 M HCl to ensure negative reaction towards iron(III) with thiocyanate ions and then with water to ensure negative reaction towards chloride ions with silver(I). Adsorbents were used as discs 20 mm in diameter and weighted ~20 mg in the swelled state. For this purpose the discs were kept in distilled water for a day and then stored there.

Arsenazo III was immobilized as follows. A 500-mL portion of a 0.0005% solution Arsenazo III, 25 discs of swelled polyacrylonitrile fiber filled with an AB-17 anion exchanger were placed into a 1000-mL beaker and the mixture was stirred for 10 min. As a result, the solution discolored and the substrate discs became violet. The solution was decanted, the discs were once washed with distilled water. Thereby, polyacrylonitrile fiber filled with AB-17 containing immobilized Arsenazo III was obtained (**PANF-AB-17-ARS**).

The influence of sorption and complexation conditions, the concentrations of metal ions, the duration of substrate stirring with the solution, and selectivity was studied in the batch mode from a 25-mL portion of solution.

Apparatus. Diffuse reflectance parameters were registered using a Pulsar colorimeter (Khimavtomatika, Chirchik, Uzbekistan). The analytical signal was the difference of the diffuse reflectance coefficients of the discs (ΔR) after the sorption and reaction of ions adsorbed from the blank and test solutions with the reagent. The blank solution contained all the reaction components except from the component the effect of which was studied; it was subjected to the same operations as the test solution. The solution acidity was controlled with a glass electrode using a pH-673 potentiometer. The solutions were stirred using a LAB-PU-02 device.

Procedure. A 25-mL portion of a test solution was placed into a 100-mL conical flask and one disc of PANF-AB-17 and of PANF-AB-17-ARS were added and stirred for a certain time. The solutions were decanted, the white disc was transferred into a 50-mL beaker for the determination of Fe(III) by the reaction with KSCN; the analytical signal was measured at 550 nm. Five drops of 0.5 M HCl were applied onto the colored disc on the flask bottom and the concentration of uranium(VI) was determined by the reaction with immobilized Arsenazo III; the analytical signal was measured at 670 nm.

The color scales for the visual determination of uranium and iron were prepared similarly for the concentrations 0, 0.5, 1.5, 3.5, 5.0 µg in a 25-mL portion. The color changed from red-violet to violet-blue for uranium and from white to red-brown for iron.

RESULTS AND DISCUSSION

Uranium(VI) and iron(III) form complexes with organic oxyacids. Earlier we have demonstrated that uranium as its malonate complex [9] and iron as its malonate and glycolate complex [10] are adsorbed on the solid phase of a fiber material filled with an AB-17 anion exchanger. These properties of uranium and iron were studied for their simultaneous sorption from a single solution followed by determination on the solid phase.

Sorption conditions. The dependence of the analytical signals of uranium complexes with Arsenazo III and iron with KSCN on the concentrations of malonic and glycolic acids in the sorption was studied. The concentration of malonic acid solution was chosen to be 2×10^{-3} M on the basis of the results presented in Fig. 1 for the sorption of uranium and iron.

The influence of the acidity of a 2×10^{-3} M solution of malonic acid on uranium and iron sorption was studied in the pH range of 1–6. Figure 2 shows that the optimal value is pH 4.5 ± 0.5.

The duration of disc stirring in the test solution appeared to be 10 min. An increase in the duration of
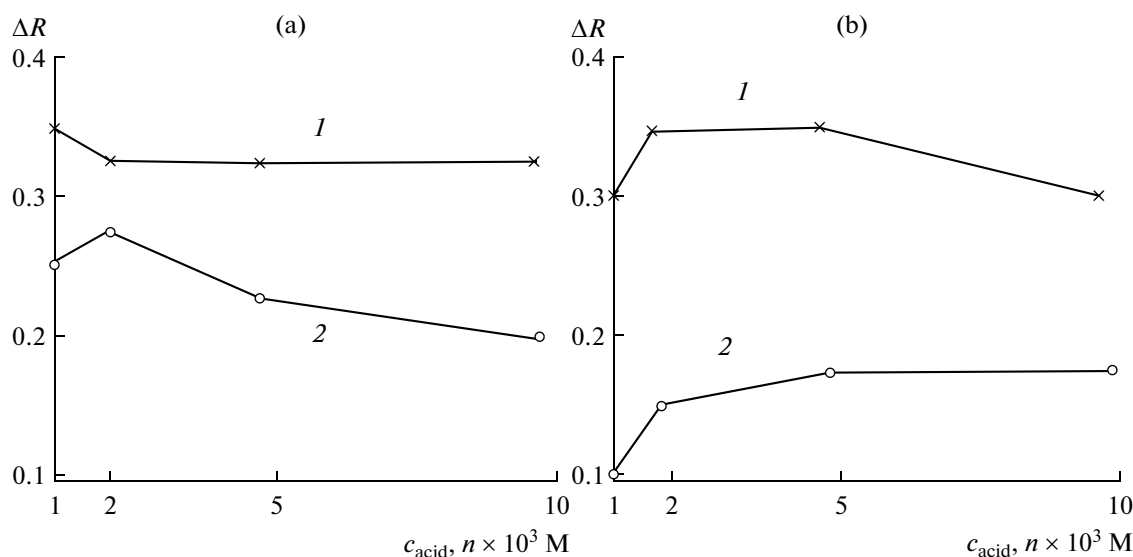
Fig. 1. Dependence of the analytical signals of uranium (*1*) at 670 nm on PANF-AB-17-ARS and iron (*2*) at 550 nm on PANF-AB-17 on the concentration of $(1-10) \times 10^3$ M solutions of (a) malonic and (b) glycolic acids. Sorption was carried out at pH 4, Me concentration was 0.1 µg/mL.

stirring did not cause significant growth of the analytical signals:

Time, min	3	5	10	15
$\Delta R_{U(VI)}$	0.28	0.31	0.31	0.35
$\Delta R_{Fe(III)}$	0.19	0.23	0.28	0.30

It should be noted that uranium malonate complexes were adsorbed both onto PANF-AB-17 and the substrate with immobilized Arsenazo III. Obviously, in the case of PANF-AB-17-ARS, sorption proceeded predominantly due to the complexation of uranium with the functional groups of Arsenazo III, while conventional ion exchange took place on PANF-AB-17. Iron malonate complexes are adsorbed on PANF-AB-17 discs.

Complexation conditions. The color of Arsenazo III solutions depended on the medium pH. At medium acidity from pH 4 to 10 M of HCl, the reagent solutions were pink and, at pH 5 and below, they were violet or blue [11]. When uranium malonate complexes were adsorbed onto PANF-AB-17-ARS from solutions with pH 4, the disc color changed from red-violet to blue-violet. When HCl was further applied onto the disc, the disc color in the blank experiment became redder and the color of discs with the uranium complex changed from red-violet into violet-blue, depending on the uranium concentration. The difference in the colors of the test and blank solutions became more obvious. The analytical signal was maximal at 670 nm. The dependence of the analytical signals on the acid concentration in the complexation on the solid phase is presented in Fig. 3. The 0.5 M HCl solution was chosen for disc treatment after sorption.

Five drops of a 10% solution of KSCN in 0.5 M HCl were applied for iron determination after its sorption on PANF-AB-1 discs. The discs acquired brown-red color and the analytical signal was maximal at 550 nm.

Dependence of analytical signals on metal concentrations. The influence of uranium and iron concentrations was studied in the range 0.02–0.2 µg/mL; the elements were adsorbed from 25-mL portions and their weight ratio was 1 : 1.

When uranium concentration was increased, the color of PANF-AB-17-ARS discs changed from red-violet to violet-blue. Visually disc color was estimated by the color scale corresponding to uranium concentration of 0.02, 0.06, and 0.2 µg/mL. The calibration curve equation for the signal measured using a Pulsar colorimeter looked as follows:

$$c(U), \text{µg/mL} = (\Delta R - 0.08)/2.12,$$

where $\Delta R = (R_0 - R_{Me})$ was the difference in diffuse reflectance coefficients obtained for the blank and test solutions.

The dependence of analytical signals on the uranium concentration was linear in the range 0.02–0.16 µg/mL; the detection limit for U(VI) calculated by the 3s-test was 0.01 µg/mL.

With increasing iron concentration, the color of PANF-AV-17 disks changes from white to brown-red. The disk color is visually estimted by the color scale, corresponding to Fe(III) concentrations 0.02; 0.06; 0.2 µg/mL. The calibration graph equation in measuring signals on the pulsar colorimeter at 550 nm is
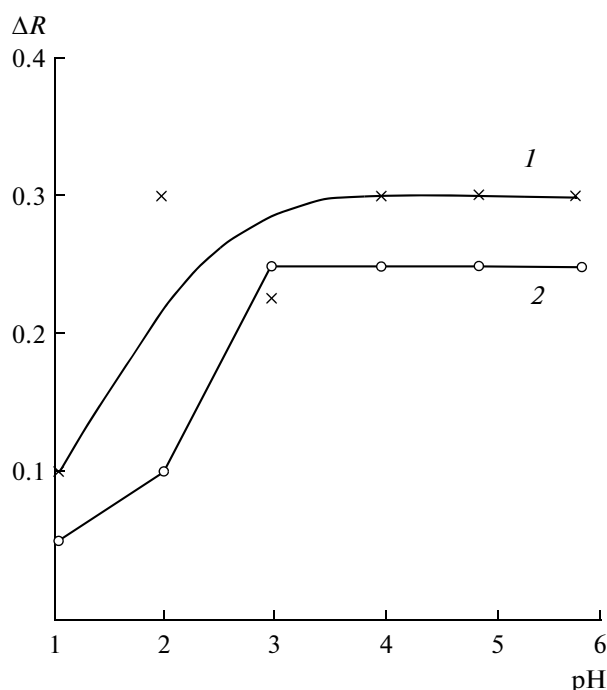
$$c(Fe), \text{µg/mL} = (\Delta R - 0.02)/1.93.$$

Fig. 2. Influence of the pH of a 2×10^{-3} M solution of malonic acid in sorption on the analytical signals of (*1*) uranium on PANF-AB-17-ARS at 670 nm and (*2*) iron on PANF-AB-17 at 550 nm. Metal concentration was 0.1 μg/mL.

The dependence of the analytical signals of the concentration of Fe(III) is linear in the range 0.02–0.16 μg/mL; the detection limit for Fe(III) calculated by the 3*s*-test is 0.01 μg/mL.

Procedure for the individual determination of uranium and iron present simultaneously. Three drops of a 0.5 M solution of malonic acid neutralized to pH 4.5 ± 0.5 are added into 100-mL conic flasks with 25-mL portions of a solution containing 0.02–0.2 μg/mL uranium and iron and PANF-AB-17 and PANF-AB-17-ARS discs are introduced into the solution and stirred there. The solution is decanted, white the
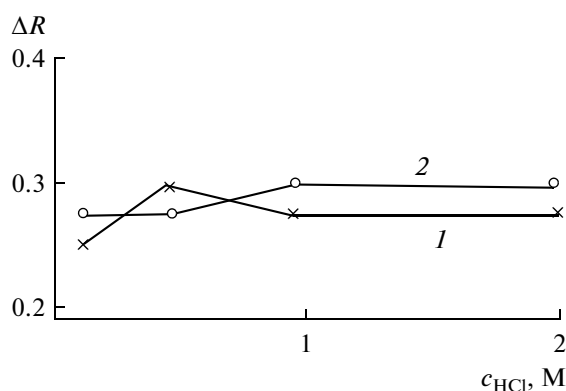

Fig. 3. Dependence of the analytical signals of (*1*) uranium and (*2*) iron on HCl concentration in complexation on PANF-AB-17-ARS (*1*) at 670 nm and PANF-AB-17 (*2*). Metal concentration was 0.1 μg/mL.

PANF-AB-17 disc is transferred into a 50-mL beaker and 5 drops of a 1% solution of KSCN in 0.5 M HCl are applied onto the disc; the color is visually compared with the color scale or R_{550} is measured instrumentally. Five drops of 0.5 M HCl are applied onto the colored PANF-AB-17-ARS disc on the flask bottom and the color is visually compared with the color scale or the analytical signal R_{670} is measured instrumentally.

The blank experiment is carried out similarly and R_0 is found. The concentrations of U(VI) and Fe(III) are found by the calibration curve or the equations above.

To perform the visual estimation of U(VI) and Fe(III) concentration, one should use standard color scales in the concentration range 0.02–0.2 μg/mL.

Analysis of a mixture of uranium and iron. We studied the possibility of determining uranium and iron at different ratios of their concentrations in solution. The results are presented in Table 1. The studied ratios from 1 : 5 to 5 : 1 were associated with the linear dependence of the analytical signals in the concentration range 0.02–0.16 μg/mL of uranium and iron. The

Table 1. Results of sorption–spectroscopy determination of uranium(VI) and iron(III) in their simultaneous presence ($n = 3$, $P = 0.95$)

Ratio U : Fe	Added, μg/mL		Found, μg/mL			
	uranium	iron	uranium	RSD, %	iron	RSD, %
1 : 1	0.080	0.080	0.09 ± 0,01	5	0.10 ± 0.01	4
1 : 2	0.050	0.100	0.05 ± 0.01	9	0.12 ± 0.02	8
1 : 3	0.040	0.120	0.04 ± 0.01	11	0.14 ± 0.03	10
1 : 5	0.030	0.150	0.03 ± 0.01	15	0.15 ± 0.02	6
2 : 1	0.100	0.050	0.11 ± 0.01	4	0.06 ± 0.02	15
3 : 1	0.120	0.040	0.12 ± 0.01	4	0.04 ± 0.01	11
5 : 1	0.150	0.030	0.14 ± 0.01	3	0.03 ± 0.01	15

Table 2. Selectivity factors for uranium and iron determination in the presence of interfering ions. Mixture U(VI) : Fe(III) = = 1 : 1. $c_U = c_{Fe} = 0.04$ μg/mL

Interfering ion	U(VI)	Fe(III)
U(VI)	–	5
Fe(III)	10	–
Zr(IV)	2	20
Th(IV)	2	20
Ti(IV)	2	10
Bi(III)	5	5
La(III)	20	20
Cu(II)	10	10
Ni(II)	100	100
Zn(II)	100	100
Co(II)	500	200
Ca(II)	500	200

relative standard deviation of uranium and iron determination did not exceed 15%.

Selectivity of uranium(VI) and iron(III) determination in the presence of interfering ions is shown in Table 2. The selectivity factor was the weight ratios of the interfering ion and the analyte provided the error ±10% or less. As it follows from Table 2, uranium could be determined in the presence of elements that form complex compounds with Arsenazo III, 2-fold concentrations of Zr, Th, Ti; 5-fold concentrations of Bi, 10-fold concentrations of Cu, Fe; 20-fold concentrations of La and more than 100-fold concentrations of the other elements. The determination of Fe(III) was not affected by 5-fold concentrations of U, Bi, 10-fold concentrations of Ti and Cu, 20-fold concentrations of La, Zr, Th and more than 100-fold concentrations of other elements.

The described study allowed us to propose a sorption–spectroscopy and a test method for the individual determination of uranium(VI) and iron(III) in their simultaneous presence on the solid phase of PANF-AB-17, a fiber material filled with a strongly basic anion exchanger AB-17 using complexation with Arsenazo III and KSCN.

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Translated by L. Malinina