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ARTICLES

Organic Reagents and Double-Layer Supports in the Sequential Sorption-Spectroscopic Determination of Ti(IV), V(V), Mo(VI), and Ni(II) from One Sample

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Abstract—The conditions of the simultaneous preconcentration of Ti(IV), V(V), Mo(VI), and Ni(II) on a double-layer support and their sequential determination using organic reagents are studied by diffuse reflectance spectroscopy. Disks of polyacrylonitrile fiber filled with an anion exchanger (**PANV–AV-17**) or a cation exchanger (**PANV–KU-2**) are used as supports. The determination of titanium and nickel on PANV–KU-2 disks is based on the successive interaction of nickel with dimethylglyoxime (**DMG**) and titanium with 2,7-dichlorochromotropic acid (**DCCA**). The determination of vanadium and molybdenum on PANV–AV-17 disks is based on the interaction of vanadium with 8-hydroxyquinoline-5-sulfonic acid (**HOS**) and 0.1 M HCl and molybdenum with phenylfluorone (**PF**). The dependences of the analytical signals of Ti–DCCA and Ni–DMG complexes on PANV–KU-2 and V–HOS and Mo–PF complexes on PANV–AV-17 on the pH of solutions in sorption in the dynamic mode are studied. The optimal pH value of the solutions for the simultaneous sorption of four elements is 3.5 ± 0.1. The influence of accompanying elements in the mixture on the determination of Ti, V, Mo, and Ni is studied. Characteristics of the sorption-spectroscopic determination of elements are given, i.e., the sequence of the treatment of support disks with reagent solutions, the conditions for eliminating the signal of the previous element, the coefficients of calibration equations and the linearity ranges of the calibration curves, and the limits of detection of elements. Selectivity factors are determined and a procedure for the sorption-spectroscopic determination of Ti, V, Mo, and Ni on their simultaneous presence is developed. The results of analysis of model solutions with different ratios of elements are presented; RSD < 15%.

Keywords: diffuse reflectance spectroscopy, PANV–KU-2, PANV–AV-17, 2,7-dichlorochromotropic acid, dimethylglyoxime, 8-hydroxyquinoline-5-sulfonic acid, phenylfluorone, Ti(IV), V(V), Mo(VI), Ni(II)

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Methods for determining element ions on a solid support in recent years have gained advantage over conventional photometric methods, because they are usually more sensitive and selective. Reactions in the solid phase are used for sorption spectroscopy and test determinations of elements [1–3]. Iron(III) and molybdenum(VI) are bound into a colored complex with pyrocatechol at pH 6.2, the complexes are sorbed on a strongly basic anion exchanger and the absorbance of the complexes is measured in the sorbent phase at 520 and 400 nm, respectively [4]. Trioxyfluorones immobilized on cellulose matrices are used for test-determinations of rare elements. Phenylfluorone on cellulose papers ensures the determination of Ti, Ge, Zr, Mo, V, and Nb [5]. Usually, when several elements are sorbed simultaneously from the solution, their desorption and subsequent determination by atomic absorption spectrometry (**AAS**), inductively coupled plasma mass spectrometry , etc. are used. Thus, silica modified with tyrone was used in [6] to extract Fe, Cu, and Al at pH 4 and Pb, Zn, Mn, Fe, Al, and Cu at pH 7 from natural waters, followed by the determination by inductively coupled plasma atomic emission spectrometry. To determine trace amounts of Co, Ni, and Cu, their sorption without a chelating agent was used [7] using magnetic Fe_3O_4 nanoparticles at pH 10–12, which were then separated by an external magnetic field; Co, Ni, and Cu were then desorbed with 1 M HNO_3 and determined by flame AAS with the limits of detection of 0.9, 0.7, and 0.3 ng/mL, respectively.

Among many supports proposed as solid phases, fibrous polyacrylonitrile materials filled with ion exchangers are also used. A thin fibrous fabric filled with an ion exchanger combines all good properties of ion exchangers with a convenient form, which ensures their use for the separation and preconcentration of elements in both dynamic and batch sorption conditions.

Fibrous ion exchangers provide a very convenient, mechanically and chemically resistant material for use as a solid phase in sorption spectroscopy and test methods of determination. Filled fibrous materials are produced in the industry: during the molding process, a necessary fine-dispersed ion exchanger is introduced into the polyacrylonitrile fiber. A weakly colored thin polyacrylonitrile non-woven fabric filled with an ion exchanger (Research Institute of Synthetic Fibers, Tver) is obtained. The degree of filling can be varied within the range 50–80 wt %, the filament diameter of the fiber is 30–40 μm, the diameter of the ion exchanger particles is 5–10 μm. The materials are stable in the range from strongly acid to slightly alkaline media, have good kinetic and ion-exchange characteristics, and are convenient in use. They are easily transferred by forceps and are not deformed in stirring, heating in solution, drying, and other operations. Fibrous materials filled with various ion exchangers can be superimposed on each other in a flow cell or mixed in the solution under analysis, with performing the simultaneous sorption of various elements. Thus, it is possible to significantly increase the rate of determination. On the other hand, two or three elements can be preconcentrated on one disk of the support, followed by the successive determination of each element by a reaction on a solid phase with a suitable organic reagent. Sorption of two or more elements from a single sample significantly reduces the time of analysis and the consumption of the analyte. We previously proposed procedures for determining V(V) and Mo(VI) [8], V(V) and Cr(VI) [9], and sorption spectroscopic and test determination of Cr(VI), Cu(II), and Ni(II) [10, 11], Hg(II), Cd(II), and Pb(II) [12], Cr(VI), V(V), Ni(II), and Cu(II) [13] in one sample.

This work is devoted to the study of a possibility of the separate determination of Ti(IV), V(V), Mo(VI), and Ni(II) after their simultaneous sorption from a single solution. The possibility of the presence of these ions in various ionic forms, i.e., titanium and nickel in the cationic form, and vanadium and molybdenum in the anionic form, is used. In aqueous solutions, tetravalent cations, including titanium, occur as M^{4+} or MO^{2+}. Because of the high liability to hydrolysis and polymerization, all operations with them are carried out in acidic media. From dilute hydrochloric acid solutions titanium ions are not adsorbed by strongly basic anion exchangers. Nickel is not adsorbed on the anion exchanger in the entire concentration range of hydrochloric acid. The elements of the fifth group of the Periodic Table (including vanadium) are present in the solution in the anionic form; therefore anion exchangers are the most widely used in their separation. Molybdenum in weakly acid and neutral solutions also occurs predominantly in the anionic form and the separation of molybdenum from cations, especially multiply charged and sorbed on cation exchangers, is based on this property [14].

EXPERIMENTAL

Solutions, reagents, and sorbents. Reagents of reagent or analytical grade were used. Solutions of metal salts (0.01 M) were prepared according to known procedures by dissolving sodium vanadate, nickel chloride, and sodium molybdate. Dilution yielded solutions of the necessary ($n \times 10^{-4}$ M) concentration. The stock solution of titanium(IV) (1 mg/mL) was prepared by diluting 0.23 mL of a titanium chloride preparation ("Merck," density 1.73 g/mL) to 100 mL with 6 M HCl. A working solution of titanium(IV) (20 μg/mL) was prepared by diluting 1 mL of the stock solution to 50 mL with 0.1 M HCl. A dimethylglyoxime (0.1% solution) was prepared by dissolving 0.1 g of the preparation in 10 mL of ethanol, 8 mL of conc. NH_3 was added, and the solution was diluted with water to 100 mL. A solution of 8-hydroxyquinoline-5-sulfonic acid (0.05%) was prepared by dissolving 50 mg of the reagent in 50 mL of water with adding 0.2 mL of a 1 M NaOH solution and heating in a water bath; after cooling to room temperature, the solution was diluted to 100 mL with water. The stock solution of phenylfluorone (0.5%) was prepared by dissolving 50 mg of the preparation in ~ 80 mL of ethanol containing 1 mL of 6 M HCl on heating in a water bath; after cooling to room temperature, the solution was diluted to 100 mL with ethanol. A solution of 2.7-dichlorochromotropic acid (3%) was prepared by dissolving 0.60 g of the preparation in 20 mL of water. A solution of ascorbic acid (2%) was prepared by dissolving 1 g of the preparation in 50 mL of water. The reagent solutions were stored in a refrigerator. The necessary acidity of the solutions prior to sorption was created by adding 0.1 and 1 M solutions of NaOH or HCl.

A polyacrylonitrile fiber filled with a fine-dispersed strongly acidic cation exchanger KU-2 (PANV–KU-2) or anion exchanger AB-17 (PANV–AV-17) was used as a solid phase. The degree of filling was 50 wt %. Sorbents in the form of disks with the diameter 20 mm and weight ~ 15 mg (PANV–KU-2) and ~20 mg (PANV–AV-17) were used in the swollen state, for which the disks were kept for 24 h and then stored in distilled water. A double-layer support was composed of PANV–KU-2 and PANV–AV-17 disks.

Equipment. The parameters of diffuse reflectance were determined on a Pulsar colorimeter (OKBA Khimavtomatika, Chirchik, Uzbekistan). The analytical signal was the difference between the coefficients of diffuse reflectance of disks ($\Delta R = R_0 - R_{Me}$) after the sorption and reaction of ions adsorbed from the blank and test solutions with the reagent. The blank solution contained all reaction components, except for the component whose effect was studied; it was passed through all operations as the test solution. The acidity of solutions was controlled with a glass electrode (pH-673 potentiometer). The effect of sorption conditions

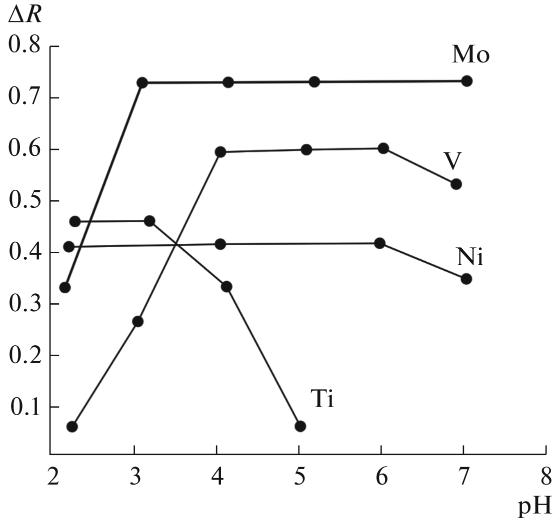

Fig. 1. Dependences of analytical signals of Ti–DCCA and Ni–DMG complexes on PANV–KU-2 and V–HOS and Mo–PF on PANV–AV-17 on the pH of test solutions during sorption. $c_{\text{Me}} = 0.1$ μg/mL.

and concentrations of metal ions on the selectivity of the determination was studied at room temperature in the dynamic mode from a volume of 100 mL at a flow rate of 5 mL/min. The solutions were pumped through cells using a PP-2-15 peristaltic pump.

Procedure. In the dynamic mode, the PANV–KU-2 and PANV–AV-17 disks were placed layer-by-layer in the flow cell and 100 mL of a test solution was pumped through them at a rate of 5 mL/min using a peristaltic pump. After completion of sorption, the disks are divided into two cells and organic reagents were pumped followed by the measurement of the analytical signals.

RESULTS AND DISCUSSION

To determine elements by diffuse reflectance spectroscopy, organic reagents forming colored complex compounds with V(V), Mo(VI), Ni(II), and Ti(IV) on the solid phase were chosen. These were 8-hydroxyquinoline-5-sulfonic acid, phenylfluorone, dimethylglyoxime, and 2,7-dichloro-chromotropic acid, respectively [15]. Polyacrylonitrile fiber, the upper layer of which was filled with the PANV–AV-17 anion exchanger and the lower layer, with the PANV–KU-2 cation exchanger, was used as a support. Depending on the acidity of the solution, the speciation of the ions studied was different.

Dependences of the analytical signals on the acidity of test solutions are shown in Fig. 1. The complexity of choosing the optimal pH for the simultaneous sorption of four elements is due to the fact that titanium is sorbed well on PANV–KU-2 in acid media, and vanadium and molybdenum on PANV–AV-17 at pH > 4. The pH value of 3.5 ± 0.1 in solutions in sorption ensures obtaining of analytical signals of all four elements with an error of < 5%.

Influence of the concentration of accompanying elements on the analytical signals of Ti–DCCA, V–HOS, Mo–PF, and Ni–DMG complexes is illustrated in Fig. 2. The sorption of the elements was carried out on double-layer PANV–KU-2 and PANV–AV-17 disks from 100 mL of a solution of pH 3.5. The determination of all three elements was not affected by a 5-fold weight excess of nickel. The strongest influence was exerted by vanadium on the determination of titanium.

Dependences of the analytical signals of complexes on various factors were studied after the sorption of elements in the dynamic mode at a flow rate of 5 mL/min on a double-layer support with the lower layer of PANV–KU-2 and the upper layer of PANV–AV-17. After sorption, the layers were separated and nickel and titanium were determined on PANV–KU-2, whereas vanadium and molybdenum were determined on PANV–AV-17. The PANV–KU-2 disk was treated with solutions of DMG and DCCA reagents, and the PANV–AV-17 disk, with solutions of HOS and 0.1 M HCl and a solution of PF.

The sequence and mode (dynamic or batch) of the processing of disks with reagent solutions, the time of the development of complex coloring on disks, and methods of eliminating the analytical signal of the previous element were found. The dependences of analytical signals on the concentrations of elements were studied and the coefficients of equations of calibration curves, linearity ranges, and the limits of detection of the elements were determined. The results of studying the sorption conditions and determining four elements are presented in Table 1.

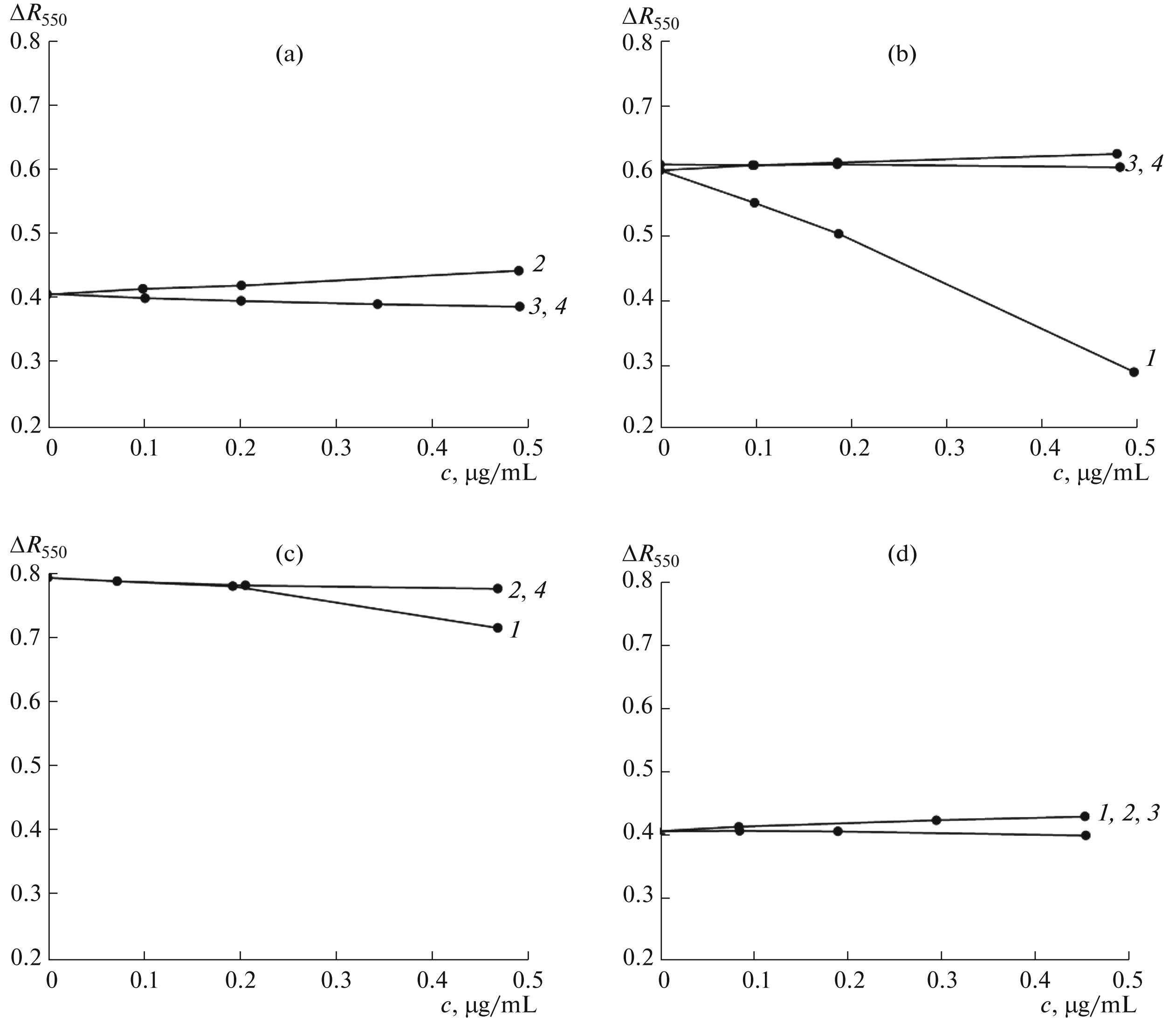

Fig. 2. Influence of accompanying elements on the determination of (a) Ti with DCCA, (b) V with HOS, (c) Mo with PF, and (d) Ni with DMG at simultaneous sorption from 100 mL of solutions with pH 3.5 on PANV–AV-17 (V, Mo) and PANV–KU-2 (Ti, Ni). *c* of the analyte determined – 0.1 μg/mL; *c* of accompanying element 0.1–0.5 μg/mL. (*1*) Ti, (*2*) V, (*3*) Mo, and (*4*) Ni.

The selectivity of sorption-spectroscopic determination of Ti(IV), Ni(II), V(V), and Mo(VI) in the presence of extraneous ions is characterized in Table 2. The highest selectivity was observed in the determination of titanium in the presence of copper and in the determination of vanadium in the presence of cobalt and copper. The least selective determination of elements was in the presence of iron(III).

Based on the results obtained, a procedure for the sorption-spectroscopic determination of Ti(IV), V(V), Ni(II), and Mo(VI) from a single sample was developed, based on the simultaneous sorption of elements on a double-layer support and their subsequent determination by organic reagents.

Determination procedure. PANV–KU-2 and PANV–AV-17 disks are layer-by-layer placed in the flow cell, and 100 mL of a test solution of pH 3.5 are pumped through them at a rate of 5 mL/min. Then the PANV–AV-17 disk is transferred to another cell, 2 mL of a 0.005% HOS solution and 0.5 mL of 0.1 M HCl are pumped through it, and, after 3 min, an analytical signal is measured at 600 nm (R_V). The disk is placed in the same cell, 1 mL of a 2% solution of ascorbic acid and 1 mL of a 0.01% solution of PF are pumped, and, after 5 min, the analytical signal is measured at 550 nm (R_{Mo}).

One milliliter of a 0.1% DMG solution is pumped through a PANV–KU-2 disk in the first cell and, after 3 min, an analytical signal is measured at 550 nm

Table 1. Characteristics of procedures for the sorption-spectroscopic determination of titanium, nickel, vanadium, and molybdenum from one sample ($V = 100$ mL, sorption at pH 3.5, pumping rate of the solution 5 mL/min)

Characteristic	PANV–KU-2		PANV–AV-17	
	Ni(II)	Ti(IV)	V(V)	Mo(VI)
Sequence of disk treatment with reagents	1	2	1	2
Reagent for determination	DMG (pH 1)	DCCA (pH 1)	HOS (pH 1)	PF (pH ~ 0.3)
Wavelength, nm	550	530	600	550
Elimination of the signal of the 1st element	0.1 M HCl	–	2% ascorbic acid solution	–
Coefficients of the *CC equation	$a = 0.01$ $b = 5.15$ $r = 0.999$	$a = 0.04$ $b = 9.17$ $r = 0.993$	$a = 0.01$ $b = 6.83$ $r = 0.999$	$a = 0.09$** $b = 16.34$ $r = 0.996$
The linearity range of CC, μg/mL	0.01–0.07	0.005–0.035	0.01–0.08	0.003–0.03
Limit of detection, ng/mL	5	5	5	3

* CC – calibration curve.

** Calibration curve using the treatment of disks with HOS, HCl, ascorbic acid, and PF.

Table 2. Characteristics of selectivity of the determination of Ti(IV), Ni(II), V(V), and Mo(VI) in the presence of extraneous ions (c_{Me}, μg/mL: Ti, Mo—0.01, V—0.05, Ni—0.07)

Extraneous ion	Selectivity factor			
	Ti(IV)	V(V)	Ni(II)	Mo(VI)
Fe(III)	10	2	10	2
Zn(II)	10	20	100	20
CdII)	10	10	100	50
Mn(II)	20	20	5	50
Co(II)	20	250	20	50
Cu(II)	200	500	10	50
Cr(VI)	20	2	100	5

(R_{Ni}). After the measurement, the disk is wetted with a filter, placed in a Petri dish, 3 drops of 0.1 M HCl are applied, after ~0.5 min 3 drops of a 3% solution of DCCA are applied, and, after 5 min, the analytical signal is measured at 530 nm (R_{Ti}).

Similarly, a blank experiment with no metal ions to be determined is performed, and R_0 is measured at the appropriate wavelengths. From the values found, $\Delta R = R_0 - R_{\mathrm{Me}}$ is calculated and metal concentrations in μg/mL are found from the equations of calibration curves: $c_{\mathrm{V}} = (\Delta R_{\mathrm{V}} - 0.01)/6.83$, $c_{\mathrm{Mo}} = (\Delta R_{\mathrm{Mo}} - 0.09)/16.34$, $c_{\mathrm{Ni}} = (\Delta R_{\mathrm{Ni}} - 0.01)/5.15$, and $c_{\mathrm{Ti}} = (\Delta R_{\mathrm{Ti}} - 0.04)/9.17$. The limits of detection for Ni, Ti, V, and Mo estimated by the 3*s*-test are 5, 5, 5, and 3 ng/mL, respectively. Satisfactory results of analysis of model solutions with different ratios of Ti, V, Ni, and Mo were obtained (Table 3), RSD < 15%.

Table 3. Sorption-spectroscopic determination of Ti(IV), V(V), Ni(II), and Mo(VI) from one sample on their simultaneous presence ($n = 3$, $P = 0.95$)

Weight ratio Ti : V : Ni : Mo	Added				Found (RSD, %)			
	Ti	V	Ni	Mo	Ti	V	Ni	Mo
1 : 1 : 1 : 1	0.025	0.025	0.025	0.025	0.021 ± 0.006 (14)	0.022 ± 0.004 (3)	0.023 ± 0.005 (10)	0.026 ± 0.003 (5)
2 : 3 : 4 : 1	0.016	0.024	0.032	0.008	0.016 ± 0.001(4)	0.022 ± 0.004 (8)	0.030 ± 0.004 (6)	0.010 ± 0.002 (9)
3 : 2 : 5 : 2	0.033	0.022	0.055	0.022	0.032 ± 0.006 (9)	0.018 ± 0.005 (13)	0.052 ± 0.006 (5)	0.022 ± 0.008 (13)

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