

ARTICLES

Method of Two Reagents on a Solid Phase for the Determination of Simultaneously Present Vanadium(V) and Molybdenum(VI)

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Abstract—The possibility of the use of two reagents for the determination of two elements from one sample on one disk of fibrous sorbent was studied. Vanadium(V) and molybdenum(VI) are sorbed on a disk of an anion-exchange fibrous material and, next, sequentially detected by diffuse reflection spectrometry with 8-hydroxyquinoline-5-sulfonic acid and phenylfluorone. It was demonstrated that vanadium and molybdenum can be determined when present simultaneously in ratios from 1 : 10 to 10 : 1 in the concentration range 0.01–0.15 µg/mL (RSD < 15%). The detection limit is 0.005 and 0.003 µg/mL for vanadium and molybdenum, respectively.

Fibrous materials filled with finely dispersed ion exchangers are used in sorption–spectrometric and test methods for the determination of metal ions [1–3]. These materials have wide potentialities because of favorable kinetic and sorption properties, the possibility of their use with and without modification with organic reagents, chemical and mechanical stability, and other properties. Limits of their application are under study and being extended.

This work is devoted to the determination of two simultaneously present metal ions from one sample on the same support disk using vanadium(V) and molybdenum(VI) as examples.

It is known that vanadium can be separated from concomitant elements by cation or anion exchange. Vanadium is preconcentrated using chemically modified silicas, fibrous sorbents, cellulose filters with conformationally flexible groups, etc. Hydrogen peroxide, Xylenol Orange, 4-(2-pyridylazo)resorcinol, 1-(2-pyridylazo)-2-naphthol, 8-hydroxyquinoline and other reagents are used for the spectrophotometric determination of vanadium [4].

8-Hydroxyquinoline (HQ) is one of the most widely used organic reagents [5]. It interacts with many elements, and its selectivity is low. Selectivity can be significantly improved by the control of pH and with the use of masking agents. A cellulose sorbent with immobilized HQ was used for the on-line preconcentration of titanium and vanadium in their determination in natural waters by mass spectrometry [6]. Fibrous materials filled with HQ were used for the preconcentration of lead, copper, and cadmium in the analysis of water [7]. Sorption cartridges DIAPAK-C₁₆ modified with HQ were used for the preconcentration of cadmium and lead [8].

Previously, we studied the use of a fibrous material filled with the AV-17 anion exchanger and modified with HQ and 8-hydroxyquinoline-5-sulfonic acid (HQ-SFA) as the support for conducting the reaction of the determination of vanadium with 4-(2-pyridylazo)resorcinol. It was found that HQ-SFA is more strongly retained on the anion exchanger than HQ, and sorption occurs via sulfo groups of the reagent, leaving the –nitrogen–hydroxy– functional analytical group free for complexation with vanadium. Therefore, we used HQ-SFA in this work.

It is known from the literature that anion exchangers weakly adsorb molybdenum(VI) from dilute solutions of HNO₃ or HCl. The maximum absorption of molybdenum was observed from 5 M HCl, from more than 7 M HF, and, in the presence of thioglycolates, from 0.1 M H₃PO₄ [9]. There are no selective photometric reagents for the determination of molybdenum. Commonly, molybdenum is determined using thiocyanates, dithiol, and trihydroxyfluorone derivatives, particularly phenylfluorone (PF) [10, 11]. In our investigations, it was found that molybdenum is sorbed at pH 4 from a 0.2% solution of ascorbic acid on a fibrous material filled with the AV-17 anion exchanger and is determined with PF in the presence of sevenfold amounts of vanadium.

Obtained results were used in the study of the possibility of the determination of vanadium(V) and molybdenum(VI) in the presence of each other on one support disk.

EXPERIMENTAL

Stock 0.01 M solutions of sodium molybdate and vanadate were prepared by the dissolution of weighed

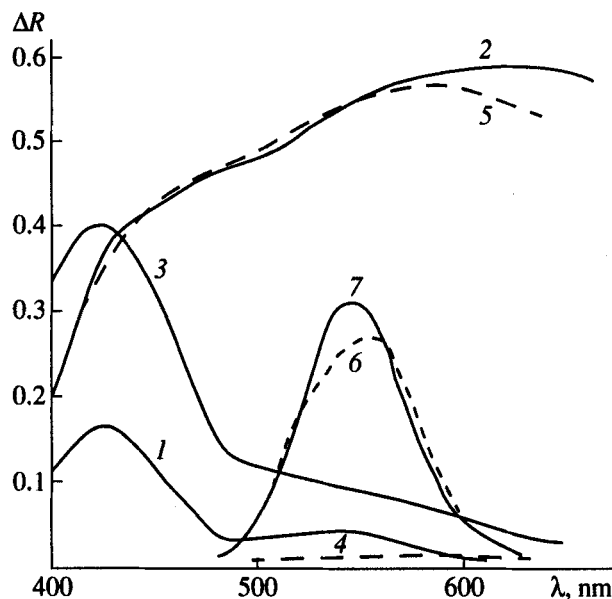


Fig. 1. Diffuse reflection spectra of HQ-SFA and PF complexes of vanadium(V) and molybdenum(VI) on a solid phase of fibrous sorbent filled with AV-17; (1) V-HQ-SFA, (2) V-HQ-SFA-HCl, (3) V-HQ-SFA-HCl-ascorbic acid, (4) Mo-HQ-SFA-HCl, (5) V-Mo-HQ-SFA-HCl, (6) Mo-PF, and (7) V-Mo-PF.

portions of $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in water. Working $n \times 10^{-4}$ M solutions were prepared by the dilution of stock solutions. A 0.05% solution of HQ-SFA was prepared by the dissolution of 50 mg of the reagent in 50 mL of water with the addition of 0.2 mL of 1 M NaOH on heating in a water bath; after cooling to room temperature, the solution was diluted with water to 100 mL. A stock 0.05% solution of PF was prepared by the dissolution of 50 mg of the compound in ~ 80 mL of ethanol containing 1 mL of 6 M HCl on heating in a water bath; after cooling, the solution was diluted with ethanol 100 mL. A working solution containing 0.005% PF, 30% ethanol and 0.5 M HCl was prepared by mixing 4 mL of the stock solution of PF, 8 mL of ethanol, and 3.3 mL of 6 M HCl and dilution with water to 40 mL. A 5% solution of ascorbic acid was prepared daily. A 0.1 M aqueous solution of glycolic acid was used. Acidity was adjusted using 0.1 M solutions of HCl and NaOH.

As the solid phase, we used a fibrous material of polyacrylonitrile fiber, which was filled in with the strongly basic anion exchanger AV-17 in the course of formation; the degree of filling was 50%. Disks with the diameter 2 cm and mass 22–24 mg were punched out from this material. The disks were washed with 1 M HCl and, next, with water to neutral reaction; disks were used in the swollen state.

Test solutions with a volume of 25–100 mL were passed through disks placed in flow cells at a flow rate of 10 mL/min using a PP-2-15 peristaltic pump. Diffuse reflection spectra and diffuse reflection coeffi-

cients were measured on a Spectroton colorimeter. Acidity was measured on a pH-673 potentiometer with a glass electrode.

The difference between diffuse reflection coefficients after passing the blank (R_0) and test (R_t) solutions was taken as the analytical signal (ΔR). The blank solution contained all components of the reaction except metal ions and passed through all operations as well as the test solution.

RESULTS AND DISCUSSION

At pH 3–5, 8-hydroxyquinoline forms a dark-blue complex of vanadium, which is extracted with chloroform, benzene, and other solvents. In neutral and acetic acid solutions, a blue-black or yellow precipitate of different compositions is formed [4, 5]. Probably, HQ-SFA reacts analogously yielding complexes of different colors and compositions. We found that, when vanadium(V) sorbed on disks of a fibrous material filled with AV-17 is treated with a solution of HQ-SFA, it yields a yellow-green complex, which changes its color to nearly black on the treatment of the disk with a dilute HCl solution. Figure 1 presents the diffuse reflection spectra of the HQ-SFA complex of vanadium and the PF complex of molybdenum(VI). As seen in the figure, the maximum analytical signal of vanadium on the interaction with HQ-SFA in an acidic solution was observed at 600 nm. Under these conditions, the analytical signal of molybdenum is virtually absent. The maximum analytical signal of the PF complex of molybdenum on the solid phase was observed at 550 nm.

On the treatment of the HQ-SFA complex of vanadium with ascorbic acid, the color turns from black to green-yellow, and, as seen in Fig. 1, vanadium does not interfere with the subsequent determination of molybdenum with PF. Possibly, this effect of ascorbic acid is due to both the reduction of V(V) to V(IV) and a change in the composition of the complex. The composition of the complex and the degree of oxidation of vanadium on the solid phase have not been studied.

The effect of ascorbic acid was studied in the range of 0.5–2 mL of a 5% solution. It was found that 0.5 mL of this solution was sufficient for the decomposition of the HQ-SFA complex of vanadium, and this amount of ascorbic acid does not interfere with the determination of molybdenum with PF.

We studied the effect of acidity on the development of the black color of the HQ-SFA complex of vanadium. From Fig. 2, it is seen that the analytical signal is nearly independent of the concentration of HCl in the range 0.05–0.25 M. In the further work, acidification was performed by passing 0.5 mL of 0.1 M HCl.

The study of the effect of the amount of HQ-SFA and PF on the analytical signals of vanadium and molybdenum demonstrated that the use of 2 mL of a 0.05% HQ-SFA solution and 1 mL of a 0.005% PF

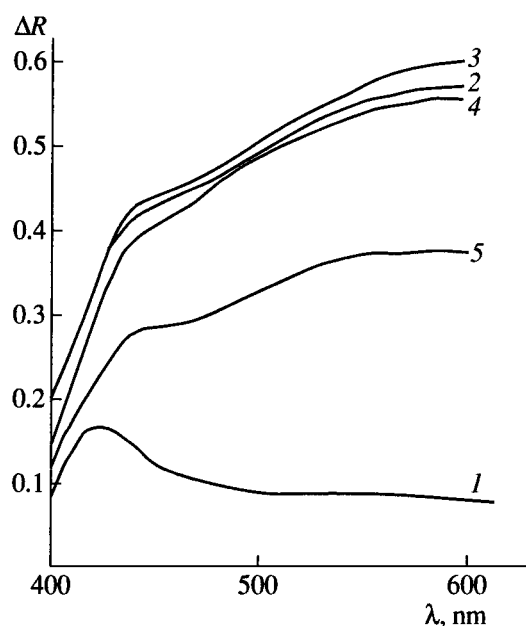


Fig. 2. Effect of HCl on the development of color of the HQ-SFA complex of vanadium; $c_V = 0.4 \mu\text{g/mL}$; $c_{\text{HCl}} = (1) 0.01$, (2) 0.05, (3) 0.1, (4) 0.25, and (5) 0.5 M; $V_{\text{HCl}} = 0.5 \text{ mL}$.

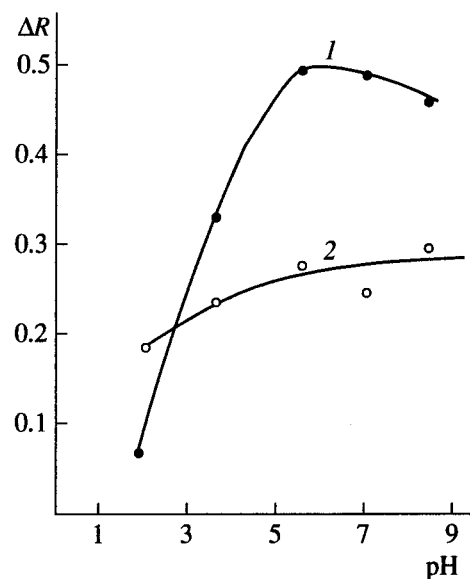


Fig. 3. Analytical signal on the solid phase (1) for the HQ-SFA complex of vanadium at 600 nm and (2) for the PF complex of molybdenum at 550 nm as a function of the pH of the analyzed solution of a mixture of two elements.

solution is optimal for the full development of the color of vanadium and molybdenum complexes, respectively.

Figure 3 presents the analytical signals of the HQ-SFA complex of vanadium and PF complex of molybdenum on the solid phase as functions of the acidity of the initial solution of a mixture of vanadium and molybdenum. As seen in the figure, the optimal value of pH is 6.0 ± 0.5 .

For samples containing vanadium and molybdenum simultaneously in the ratio 2 : 1, we studied the dependences of analytical signals on the concentrations of vanadium and molybdenum. Sorption was performed from the volumes of 25 and 100 mL. For this purpose, test solutions with volumes of 25 or 100 mL containing 1–5 μg of vanadium and 0.5–2.5 μg of molybdenum in distilled water (pH 5.5) were passed through fibrous sorbent disks with AV-17 at the flow rate 10 mL/min, next, 2 mL of an HQ-SFA solution and 0.5 mL of 0.1 M HCl were successively passed, and, within 3 min, the diffuse reflection coefficient (analytical signal of vanadium) was measured at 600 nm. Next, 0.5 mL of a 5% solution of ascorbic acid and 1 mL of a PF solution were successively passed through the same disks, and, within 5 min, the diffuse reflection coefficient (analytical signal of molybdenum) was measured at 550 nm. In this process, the color of disks changed from white to light-yellow, gray-black, yellow, and pink. Calibration plots are described by the following equations corresponding to the volumes 25 and 100 mL: $\Delta R_{600} = 2.46c + 0.002$ and $\Delta R_{600} = 8.8c + 0.024$, respectively, for vanadium(V) and $\Delta R_{550} = 2.07c + 0.084$ and $\Delta R_{550} = 9.16c + 0.074$, respectively, for molybdenum(VI), where $\Delta R = R_0 - R_t$ and c is the concentration of ele-

ments ($\mu\text{g/mL}$). The blank experiment was performed analogously without addition of vanadium and molybdenum ions. Calibration plots are linear in the concentration range 0.01–0.05 $\mu\text{g/mL}$ of V(V) and 0.005–0.025 $\mu\text{g/mL}$ of Mo(VI) for sorption from a volume of 100 mL. Detection limits were estimated from 3s-values at 0.005 and 0.003 $\mu\text{g/mL}$ for vanadium and molybdenum, respectively. Vanadium and molybdenum, which were present simultaneously in the ratios from 1 : 10 to 10 : 1, were determined in the total concentration range 0.01–0.15 $\mu\text{g/mL}$. Points of the calibration plot for sorption from 25 or 100 mL lie nearly in one straight line, which indicates that a change of volume in this range does not affect the results of the determination. The correlation coefficient is 0.994.

Results of the determination of vanadium and molybdenum in the presence of each other in 100 mL of distilled water containing different amounts of molybdenum and vanadium are presented in the table. As seen from the results, the determination of these two elements from one sample on one support disk is possible for the ratios between vanadium and molybdenum from 1 : 10 to 10 : 1.

As is known, HQ and HQ-SFA are group reagents [5]. The photometric reactions are most sensitive for vanadium and iron. The selectivity of the determination of vanadium and molybdenum in the presence of each other on a solid phase was studied in the presence of aluminum, iron, copper, zinc, and chromium(VI). Preliminary tests demonstrated that foreign ions more strongly interfere with the reaction of vanadium with HQ-SFA than with the reaction of molybdenum with PF. Therefore, we first determined the permissible excess of foreign ions with respect to vanadium and

Results of the determination of vanadium and molybdenum in the presence of each other on one support disk ($P = 0.95$; $n = 3$)

Ratio V : Mo	Added, $\mu\text{g/mL}$		Found, $\mu\text{g/mL}$			
	vanadium	molybdenum	vanadium	RSD, %	molybdenum	RSD, %
1 : 0	0.050	–	0.051 ± 0.005	4		
1 : 1	0.050	0.050	0.054 ± 0.007	6	0.046 ± 0.008	8
1 : 2	0.050	0.100	0.040 ± 0.010	11	0.108 ± 0.015	6
1 : 5	0.010	0.050	0.012 ± 0.003	11	0.047 ± 0.006	6
1 : 10	0.010	0.100	0.009 ± 0.003	15	0.095 ± 0.010	5
2 : 1	0.050	0.025	0.046 ± 0.005	5	0.021 ± 0.005	11
5 : 1	0.050	0.010	0.044 ± 0.008	8	0.010 ± 0.002	9
10 : 1	0.050	0.005	0.049 ± 0.003	3	0.004 ± 0.001	11
0 : 1	–	0.010	–		0.011 ± 0.002	8

then checked its effect on the determination of molybdenum. It was found that the reaction of iron(III) with HQ-SFA develops with time. The detrimental effect of aluminum ions is decreased when sorption is performed in the presence of 0.1 M glycolic acid. Under these conditions, the determination of molybdenum and vanadium is not affected by the interference from 20-fold amounts of Cu(II), 10-fold amounts of Al(III), fivefold amounts of Zn(II), twofold amounts of Fe(III), and equal amounts of Cr(VI).

Thus, this study revealed the possibility of the successive sorption–spectrometric determination of two elements in the presence of each other on one support disk using two reagents.

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