

Determination of Titanium(IV) and Chromium(VI) with 2,7-Dichlorochromotropic Acid and 1,5-Diphenylcarbazide on the Solid Phase

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Abstract—Possibility of the selective determination of Ti(IV) and Cr(VI) by diffuse reflection spectroscopy after their simultaneous adsorption from one sample on a two-layer substrate is studied. Titanium(IV) is adsorbed on a fiber filled with a cation exchanger (PANV-KU-2) and determined with 2,7-dichlorochromotropic acid; chromium(VI) is adsorbed on a fiber filled with an anion exchanger (PANV-AV-17) and determined with 1,5-diphenylcarbazide. Conditions are selected for the simultaneous adsorption of titanium and chromium in the batch and dynamic modes. Conditions are optimized for the determination of titanium with 2,7-dichlorochromotropic acid on PANV-KU-2. The selectivity of titanium and chromium determination in the presence of foreign ions is studied. Calibration graphs are linear in the ranges 5–40 and 2–20 ng/mL for Ti(IV) and Cr(VI), respectively; the detection limits are 4 and 2 ng/mL. The possibility of determining Ti(IV) and Cr(VI) in one sample at their ratios from 5 : 1 to 1 : 4 is shown.

Keywords: Ti(IV), Cr(VI), diffuse reflection spectroscopy, PANV-KU-2, PANV-AV-17, 2,7-dichlorochromotropic acid, 1,5-diphenylcarbazide

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Titanium and chromium are determined in rocks, ores, minerals, waters, experimental solutions, and industrial products by X-ray spectrochemical analysis and X-ray fluorescence, atomic absorption spectrometry, photometry, etc. Doping titanium with chromium gives alloys with better mechanical properties compared to titanium. A composite hard-alloy material containing 2.8% of chromium obtained on the basis of titanium is used for the production of cutting tools. In the analysis of biological fluids, the concentrations of chromium and titanium are referred to ultratrace amounts, and chromium is a vitally important element, whereas titanium is a potentially toxic one [1].

Titanium is determined by photometry with hydrogen peroxide in the concentration range 0.04–5.0 µg/mL, with diantipyrylmethane with c_{\min} 0.06 µg/mL, and with chromotropic acid at a level of 0.01 µg/mL [2–4]. One of the best sensitive reagents for the determination of titanium is chromotropic acid; however, it is unstable in storage. Its analogue, 2,7-dichlorochromotropic acid (DCCA) is more stable to oxidation [4]. It reacts with titanium at pH 1–2 with the formation of a crimson compound. Chromium reacts with DCCA with the formation of a pink-

violet compound in the medium of highly concentrated H₂SO₄. At pH 1, Fe(III), Cr(VI), V(V), Mo(VI), and W(VI) strongly interfere with the determination of titanium. Their interference is eliminated by adding masking substances. The lower limit of quantitation (LOQ) for titanium is 0.1 µg/mL and that with preliminary extraction, 0.01 µg/mL.

The reaction of chromium with 1,5-diphenylcarbazide (DPC) was used as a basis for the best method for the determination of chromium(VI). W(VI), Mo(VI), Fe(III), V(V), and Hg ions interfere with the determination. A procedure for the determination of chromium in titanium was proposed based on the application of DPC after the oxidation of chromium by potassium permanganate [5]. In the analysis of steels, chromium is oxidized with perchloric acid. The method gives good results at the concentrations of Cr 0.01–0.1%; Co and V, 1%; and Mo and Ti, 1.5% [2].

Inorganic components in water and soils were determined by test methods [6]. For the semiquantitative estimation of the concentration of titanium in waters, tablets based on polyurethane foams were proposed for the adsorption of yellow thiocyanate complexes of titanium. The determination of 0.03–0.5 mg/L of titanium was performed visually by comparing the color of a tablet with a color scale. Chromium was most often determined with DPC on vari-

[†]Deceased.

ous substrates; c_{\min} for chromium(VI) was as follows: 0.5 mg/L on paper; 0.05 mg/L by diffuse reflection spectroscopy on polyurethane foams; 0.001 mg/L on a polyacrylonitrile fiber filled with an anion exchanger; and in the range 0.1–500 mg/L with a RIB-chromate test. Chromium(III) was determined with DPC after oxidation with ammonium peroxydisulfate; the lower boundary of the analytical range was 0.01 mg/L of CrO_4^{2-} [6].

In this work we studied the possibility of the selective determination of Ti(IV) with DCCA and Cr(VI) with DPC after their simultaneous adsorption from one test sample on two disks of polyacrylonitrile fiber filled a cation and an anion exchanger.

EXPERIMENTAL

Solutions, reagents, adsorbents. We used reagents of chemically pure or analytical grade. Solutions of metal salts (0.01 M) were prepared by the known procedures using the dissolution of corresponding nitrates or chlorides. A stock solution of titanium(IV) (1 mg/mL) was prepared by the dilution of 0.23 mL titanium(IV) chloride from Merk ($d = 1.73 \text{ g/mL}$) to 100 mL using 6 M HCl. The working solution (20 $\mu\text{g/mL}$) of titanium(IV) was obtained by the dilution of 1 mL of the stock solution to 50 mL with 0.1 M HCl. A solution of chromium(VI) was prepared from $\text{K}_2\text{Cr}_2\text{O}_7$; a 0.025% solution of DPC (containing 5% of acetone and 0.5 M H_2SO_4) was prepared by the dissolution of 25 mg of a preparation in 5 mL of acetone, addition of 10 mL of 5 M H_2SO_4 , and dilution to 100 mL with water; a 3% solution of DCCA was prepared by the dissolution of 0.60 g of a preparation in 20 mL of water. Solutions of DCCA and DPC were stored in a refrigerator. The necessary acidity of solutions before adsorption was created by adding 0.1 and 1 M HCl and NaOH.

The solid phase was polyacrylonitrile fiber filled with a finely dispersed strongly acid KU-2 cation exchanger (PANV-KU-2) or an AV-17 anion exchanger (PANV-AV-17, Research Institute of Synthetic Fibers, Tver'). The degree of filling was 50 wt %. The sorbents shaped as disks of the diameter 20 mm and weight ~15 mg (PANV-KU-2) and ~20 mg (PANV-AV-17) were used swelled, for which the disks were kept in distilled water within a day and then stored in it. We assembled two-layer substrates of PANV-KU-2 and PANV-AV-17 disks. For the easier separation of layers, we placed a disk of polyvinylchloride mesh between the layers.

Instruments. The parameters of diffuse reflection were determined on a Pulsar colorimeter (OKBA Khimavtomatika, Chirchik, Uzbekistan). The difference in the coefficients of diffuse reflection from disks after the adsorption and the reaction of ions adsorbed from the reference and test solutions with the reagent ($\Delta R = R_0 - R_{\text{Me}}$) was taken as the analytical signal. The refer-

ence solution contained all components of the reaction except for the component whose action was studied; it was passed through all operations as the studied solution. The acidity of solutions was controlled with a glass electrode (potentiometer pH-673). The influence of adsorption conditions and the concentration of metal ions and the selectivity of determination were 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 the cells using a PP-2-15 peristaltic pump.

Experimental procedure. In the batch mode, 25 mL of analyzed Ti(IV) and Cr(VI) solutions were stirred with PANV-KU-2 or PANV-AV-17 disks within 10 min. In the dynamic mode, a disk of PANV-AV-17, a disk of polyvinylchloride mesh, and a disk of PANV-KU-2 were placed layer-by-layer in a 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 the completion of adsorption, the disks were placed in 50-mL beakers, 3 drops of DCCA (PANV-KU-2) and DPC (PANV-AV-17) solutions were applied onto them and the coefficients of diffuse reflection were measured in 5 and 10 min at 530 and 560 nm, respectively.

RESULTS AND DISCUSSION

Choice of conditions of complex formation. 2,7-Dichlorochromotropic acid in solutions forms a complex compound with titanium with a molar absorption coefficient of 1.12×10^4 at pH 2 and 490 nm [4]. We studied the conditions of formation of the Ti–DCCA complex on PANV-KU-2 disks. When a DCCA solution was applied onto a disk after the adsorption of titanium, a brownish–crimson color developed. A change in the concentration of the reagent in the range 1–5% had virtually no effect on the value of the analytical signal. For the determination of titanium we selected the application of three drops of a 3% DCCA solution with pH 2.3. The reaction of titanium with DCCA on the solid phase developed in time, the analytical signal attained a maximum within 5 min (Fig. 1).

The conditions of complex formation between chromium(VI) and DPC on the solid phase of PANV-AV-17 were selected by us earlier [7]. The effect of the time of color development for the reaction of chromium with DPC on a disk PANV-AV-17 of after adsorption from a mixed solution of chromium(VI) and titanium(IV) was studied. The time of disk storage before the measurement of the analytical signal equal to 10 min was selected by the results presented in Fig. 1.

Choice of conditions for the simultaneous adsorption of chromium(VI) and titanium(IV). In aqueous solutions, titanium forms quadruply charged cations with a strong trend to hydrolysis: the pH of the hydrolysis of titanium(IV) is equal to 4. In the presence of

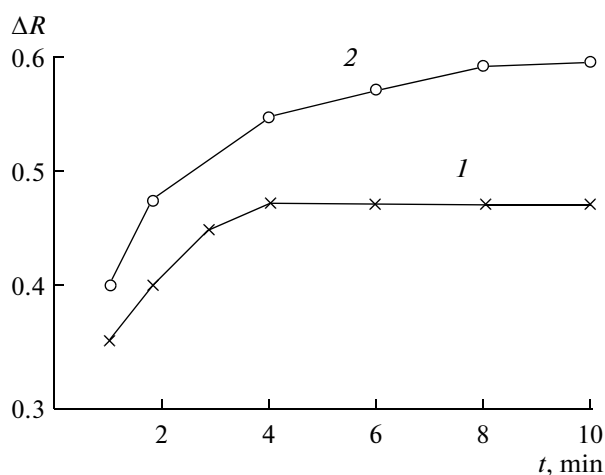


Fig. 1. Analytical signals of (1) PANV-KU-2-Ti-DCCA disks at 510 nm and (2) PANV-AV-17-Cr-DPC disks at 560 nm as functions of the time of storage of disks before the measurement; 0.05 $\mu\text{g/mL}$ of titanium or chromium, pH 3.

strong mineral acids, the adsorption of titanium on organic cation exchangers strongly depends on the nature and concentration of the acid [8]. Organic anion exchangers do not adsorb titanium(IV) ions from dilute HCl, but easily adsorb titanium(IV) complexes with various oxyacids. Thus, at pH 4, a complex of titanium(IV) with malonic acid was adsorbed on PANV-AV-17 and could be determined by the reaction of complex formation with DCCA.

To select the conditions of the simultaneous pre-concentration of titanium(IV) and chromium(VI), we used a two-layer substrate of PANV-KU-2 for the adsorption of titanium and of PANV-AV-17 for the adsorption chromium. The dependences of the analytical signals of complexes on the solid phase of PANV-KU-2 and PANV-AV-17 on the pH of the analyzed solutions were studied. As can be seen in Fig. 2, the optimum pH region for adsorption from one solution was 3.0 ± 0.2 .

Diffuse reflection spectra of disks after the sorption of titanium, chromium, and their mixture from solutions of pH 3 and treatment of PANV-KU-2 with a DCCA solution and PANV-AV-17 with a DPC solution are shown in Fig. 3. As can be seen in Fig. 3a, on disks of PANV-KU-2, the analytical signals of titanium(IV) complexes from solutions of titanium and a mixture of titanium and chromium were almost identical and exhibited a maximum at 530 nm; no analytical signal from chromium was observed. On disks of PANV-AV-17 (Fig. 3b), the analytical signals of complexes from solutions of chromium and a mixture of titanium and chromium differed slightly and exhibited a maximum in the wavelength region 530–570 nm. For the determination of chromium we selected the wavelength 560 nm.

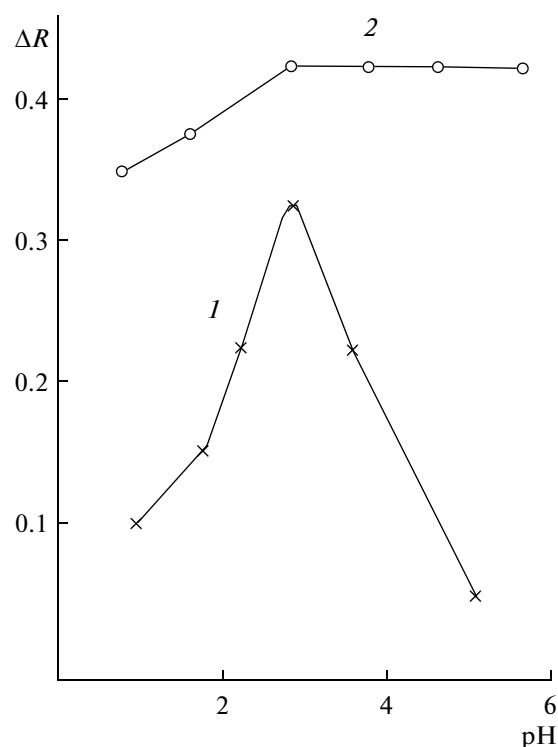


Fig. 2. Analytical signals of (1) Ti-DCCA complexes on PANV-KU-2 and (2) Cr-DPC complexes on PANV-AV-17 as functions of the pH of test solutions; 0.2 $\mu\text{g/mL}$ of titanium, 0.1 $\mu\text{g/mL}$ of chromium.

The dependences of analytical signals on the concentration of analytes were studied at the ratio Ti : Cr = 2 : 1 after adsorption from 100 mL of solutions of pH 3 in the dynamic mode. The calibration graphs were linear in the concentration ranges 5–40 ng/mL for titanium(IV) and 2–20 ng/mL for chromium(VI) and could be described by the equations

$$c_{\text{Ti}} (\mu\text{g/mL}) = (\Delta R - 0.02)/8.51 \text{ and}$$

$$c_{\text{Cr}} (\mu\text{g/mL}) = (R - 0.06)/16.62.$$

The detection limits estimated by the 3s-test were equal to 4 and 2 ng/mL for titanium and chromium, respectively.

Visually, under these conditions, the color of PANV-KU-2 disks with the Ti-DCCA complex changed with an increase in the concentration of metal ions from pale yellow to brownish crimson and the color of PANV-AV-17 disks with the Cr-DPC complex changed from white to pink.

Mutual effects of titanium and chromium on their simultaneous presence in one sample was studied at the ratios from 5 : 1 to 1 : 4 in the concentration range 8–40 ng/mL. The results presented in Table 1 confirm the possibility of the determination of titanium(IV) and chromium(VI) in one sample; RSD did not exceed 20%.

Characteristics of the selectivity of determination of titanium and chromium in the presence of foreign ions

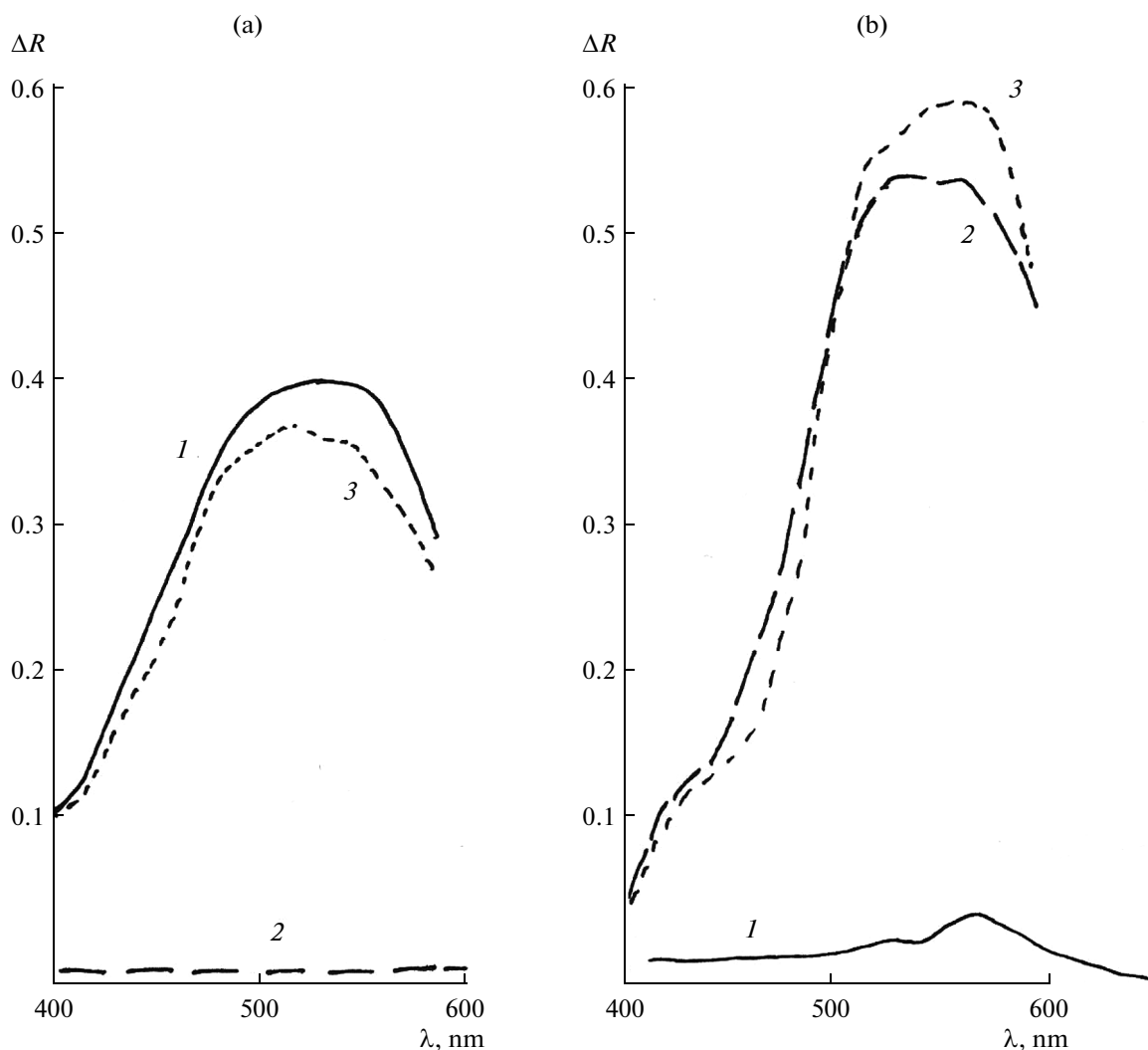


Fig. 3. Diffuse reflection spectra of (1) titanium, (2) chromium complexes and (3) their mixture (a) with DCCA on PANV-KU-2 and (b) with DPC on PANV-AV-17; $c_{\text{met}} = 0.05 \mu\text{g/mL}$, adsorption from solutions of pH 3.

Table 1. Determination of titanium ($\mu\text{g/mL}$) on PANV-KU-2 disks with DCCA and of chromium on PANV-AV-17 disks with DPC after their simultaneous adsorption on a two-layer substrate ($n = 3$, $P = 0.95$)

Weight ratio Ti : Cr	Added		Found			
	Ti(IV)	Cr(VI)	Ti(IV)	RSD, %	Cr(VI)	RSD, %
1 : 1	0.020	0.020	0.020 ± 0.003	6	0.021 ± 0.003	6
2 : 1	0.010	0.005	0.010 ± 0.003	12	0.005 ± 0.001	12
5 : 1	0.040	0.008	0.038 ± 0.014	17	0.011 ± 0.003	11
1 : 2	0.008	0.016	0.011 ± 0.003	11	0.020 ± 0.005	12
1 : 4	0.005	0.020	0.007 ± 0.003	17	0.022 ± 0.003	5

Table 2. Selectivities of determination of titanium(IV) and chromium(VI) (10 ng/mL titanium, 5 ng/mL chromium)

Foreign ion	Selectivity factor	
	Ti(IV)	Cr(VI)
Ti(IV)	—	50
Cr(VI)	20	—
Fe(III)	10	100
Mo(VI)	10	100
Zn(II)	10	100
Co(II)	20	200
Cr(III)	50	100
Ca(II)	100	400
Al(III)	100	400
Ni(II)	200	200
Cu(II)	200	200

are presented in Table 2. The selectivity factor was taken equal to the ratio of weight amounts of a foreign ion to an analyte at which the error of determination did not exceed $\pm 10\%$. The following multiple weight amounts did not interfere with the determination: Ni and Cu, 200; Ca and Al, 100; Cr(III), 50; Co, 20; and Fe(III), Zn, and Mo(VI), 10.

The study performed shows the possibility of the simultaneous adsorption and determination of tita-

nium(IV) and chromium(VI) in one sample by diffuse reflection spectroscopy or by a visual test.

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