

Spectrophotometric Determination of Simultaneously Present Niobium and Tantalum

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Abstract—The formation of niobium(V) and tantalum(V) complexes of 2,3,4-trioxyphenylazo-5-sulfonaphthalene in the presence of cetyltrimethylammonium bromide was studied by spectrophotometry. The effect of surfactants on the chemical and analytical properties of niobium(V) and tantalum(V) complexes of this reagent was studied. Procedures were developed for the spectrophotometric determination of niobium and tantalum present simultaneously as mixed-ligand complexes. The procedures were tested on model solutions.

The determination of elements with similar chemical properties (Zr and Hf, Nb and Ta, Mo and W) on their simultaneous presence is an interesting and complex analytical problem; major differences arise in the determination of one of the two elements in the presence of large amounts of the other element [1–3]. Procedures are known for the spectrophotometric determination of niobium and tantalum with organic reagents from different classes that bear donor oxygen atoms. Among these reagents are polyatomic phenols and their derivatives, fluorones, azo compounds and basic triphenylmethane dyes, as well as some inorganic reagents [1, 4, 5]. The procedure for determining both elements with pyrogallol [1, 4] proved to be a relatively good procedure among the known methods. Several works were reported on the spectrophotometric determination of the elements of interest both separately and on their simultaneous presence [6–8]. However, these methods are characterized by certain drawbacks, most of which relate their low selectivity, in particular with respect to Mo(VI), W(VI), Cr(III), and Ti(IV) ions and also to one of the ions in the presence of another ion. Therefore, the determination of niobium and tantalum using the known procedures requires their preliminary separation and the separation of almost all concomitant elements present in natural and industrial samples.

The aim of this work was to develop highly selective procedures for the spectrophotometric determination of simultaneously present niobium and tantalum based on the use of their mixed-ligand complexes with 2,3,4-trioxyphenylazo-5'-sulfonaphthalene and cetyltrimethylammonium bromide.

EXPERIMENTAL

Instruments. Spectrophotometric measurements in the UV and visible spectral regions were performed on a Perkin Elmer Lambda-40 spectrophotometer with special software and on a KFK-2 photocolormeter

with 1-cm cells. The pH of the solutions was measured using a pH-121 pH meter with a glass electrode.

Reagents. The stock 1×10^{-2} M solutions of niobium and tantalum were prepared from niobium and tantalum metals according to the procedure reported in [9]. Metals were dissolved in a mixture of H_2F_2 and HNO_3 , and H_2SO_4 was added to the solution. After the liberation of nitrogen oxides was completed, the solutions were diluted with a 5% aqueous solution of sodium oxalate. Niobium and tantalum in oxalate solutions form complexes of the composition $\text{Na}_3[\text{MeO}(\text{C}_2\text{O}_4)_3]$ (Me = Nb, Ta). Working 1×10^{-3} M solutions were obtained by diluting the stock solutions with distilled water.

The third component was cetyltrimethylammonium bromide (CTAB), a cationic surfactant. Stock 2×10^{-3} and 1×10^{-2} M solutions of 2,3,4-thioxyphenylazo-5'-sulfonaphthalene (R) in CTAB were prepared by dissolving corresponding reagent portions in water. The reagents were of no worse than analytical grade. The required acidity of the solutions was adjusted using ammonia–acetate buffer solutions (pH 3–11) and HCl (pH 0–2).

Procedure. Different amounts of a niobium solution to adjust niobium concentrations of 0.19–2.98 $\mu\text{g/mL}$ were placed in 25-mL volumetric flasks, 2.5 mL of a 1×10^{-3} M reagent solution and 0.8 mL of a 1×10^{-2} M CTAB solution were added, and the mixture was diluted to mark with an ammonia–acetate buffer solution of pH 4.0. The blank solution was prepared similarly. The absorbance of the test solution was measured on KFK-2 at 490 nm against the blank solution using optical cells $l = 1$ cm. Tantalum was determined using a similar procedure.

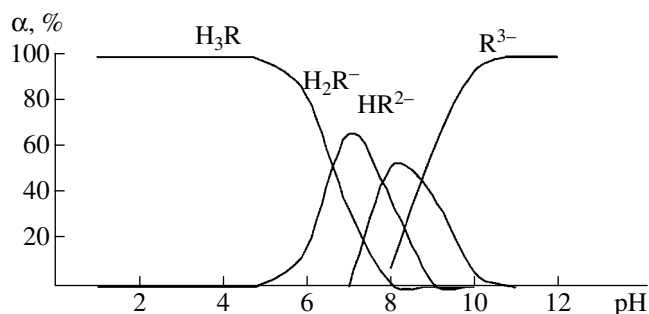


Fig. 1. Molar fractions of different forms of 2,3,4-trioxo-phenylazo-5'-sulfonaphthalene as a function of pH of the solution.

RESULTS AND DISCUSSION

2,3,4-Trioxo-phenylazo-5'-sulfonaphthalene was synthesized according to the procedure reported in [10]. The synthesized reagent was identified by the data of elemental analysis and IR spectrometry. Absorption spectra were recorded at different pH values (Lambda-40 spectrophotometer). It was found that the reagent was a tribasic acid. It can occur as molecular (H_3R) and anionic (H_2R^- , HR^{2-} , R^{3-}) species, depending on the acidity of the solution. The speciation diagram of the reagent is shown in Fig. 1.

It can be seen that, in acid solutions (pH 5.0), the reagent occurs mainly as molecular H_3R species. The acidity constants of the reagent were found by potentiometric titration [11]. Titration was performed with a standard 1×10^{-3} M solution of KOH at 25°C. The volume of the titrated solution was 50 mL. The ionic strength of the solution was kept constant (0.1) by adding calculated amounts of KCl. The following stepwise dissociation constants were found for the reagent:

$$K_{a(1)} = (5.75 \pm 0.21) \times 10^{-7}, K_{a(2)} = (3.55 \pm 0.13) \times 10^{-8}, \text{ and } K_{a(3)} = (2.34 \pm 0.08) \times 10^{-9}.$$

The reactions of niobium(V) and tantalum(V) with the reagent give colored complexes. The absorption spectra of the molecular reagent species H_3R and its complexes with niobium(V) and tantalum(V) are shown in Fig. 2.

The absorbance of H_3R exhibits a maximum at 377 nm (curve 1), and the absorbances of niobium(V) and tantalum(V) complexes exhibit maxima at 434 and 432 nm (curves 2 and 4), respectively. The study of the pH dependence of the absorbance of solutions indicated that the complexes form in the pH range 0–8 (Fig. 3), and that the yield of the complexes attains a maximum at pH 5.0–5.5 and 1.0–1.6, respectively.

The color of the reagent and complexes depends on the pH of the solution; therefore, absorption spectra in the course of complex formation were studied with reference to the reagent spectra. It was found that, for both complexes, the maximum absorbance relative to the

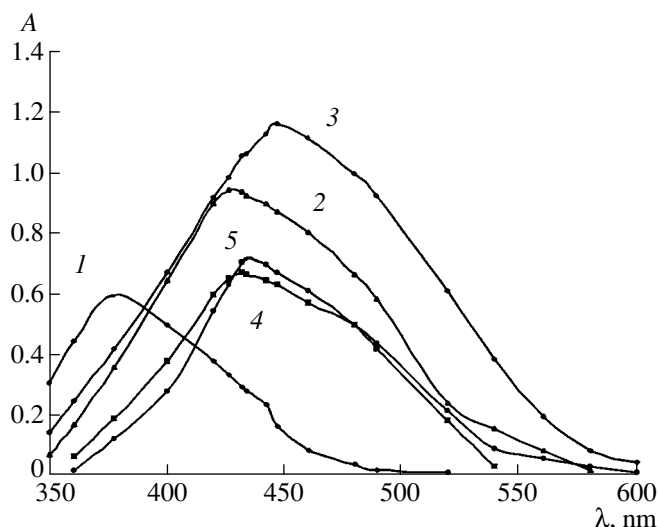


Fig. 2. Absorption spectra of niobium(V) and tantalum(V) complexes: 1, R; 2, Nb(V)-R; 3, Nb(V)-R-CTAB; 4, Ta(V)-R; 5, Ta(V)-R-CTAB.

reagent is observed at 490 nm. To completely bind the ions into complexes, a 1.6×10^{-4} M reagent solution is necessary. Its two- to twelvefold molar excess do not affect the absorbance of the complexes (Table 1).

Effect of CTAB. In the presence of CTAB, mixed-ligand Me(V)-R-CTAB complexes formed, and the maxima in the absorption spectra shifted. As can be seen in Fig. 2, the formation of the Nb(V)-R-CTAB complex is accompanied by a bathochromic shift (curve 3), whereas the formation of the Ta(V)-R-

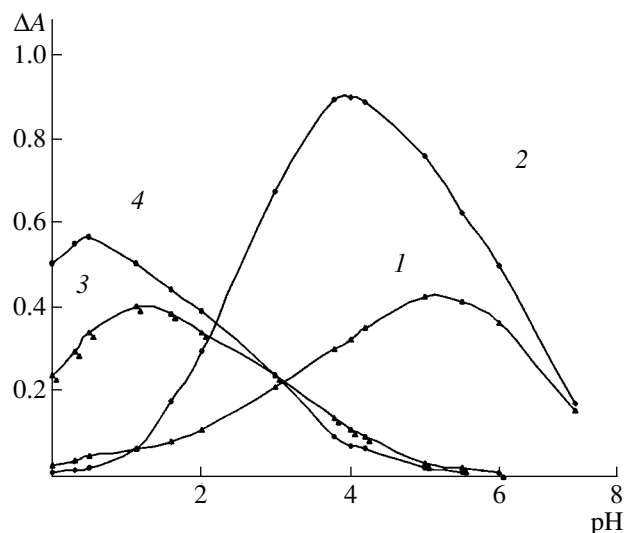


Fig. 3. Effect of pH on the absorbency of niobium(V) and tantalum(V) complexes at λ_{opt} of the blank experiment: 1, Nb(V)-R; 2, Nb(V)-R-CTAB; 3, Ta(V)-R; 4, Ta(V)-R-CTAB. $c_{Nb} = c_{Ta} = 4 \times 10^{-5}$ M; $c_R = 2 \times 10^{-4}$ M; $c_{CTAB} = 3.2 \times 10^{-4}$ M; Lambda-40, $l = 1$ cm.

Table 1. Chemical and analytical properties of niobium(V) and tantalum(V) complexes of 2,3,4-trioxyphenylazo-5'-sulfonaphthalene in the presence of CTAB

Complex	pH _{opt}	λ_{\max} , nm	$\epsilon \times 10^4$ (at λ_{opt})	c_R/c_{Me}	$c_{\text{CTAB}}/c_{\text{Me}}$	Ratio of components	Linearity range of the calibration graph (μg per 25 mL of solution)
Nb(V)-R	5.0-5.5	434	1.06 ± 0.03	2-12		1 : 2	9.3-93
Nb(V)-R-CTAB	3.7-4.3	447	2.25 ± 0.11	2.5-18	8-20	1 : 2 : 2	4.65-93
Ta(V)-R	1.0-1.6	432	1.00 ± 0.05	2-12		1 : 2	18.1-181
Ta(V)-R-CTAB	0.3-0.6	426	1.40 ± 0.08	2.5-15	8-20	1 : 2 : 2	9.05-217.2

Table 2. Effect of concomitant ions on the results of determining niobium(V) and tantalum(V) (added 50 μg niobium and tantalum per 25 mL of solution)

Concomitant ion	Allowable amount of concomitant ion, mg			
	Nb(V)-R	Nb(V)-R-CTAB	Ta(V)-R	Ta(V)-R-CTAB
Ca(II)	10	34	2.3	138
Ba(II)	0.6	11.5	40	95
Mg(II)	10	20.2	7	50
Cu(II)	0.16	0.33	1.13	4.5
Co(II)	2.5	50	17	40.8
Ni(II)	5	50	17	40
Mn(II)	14	46	6.4	34
Zn(II)	0.3	34	18.8	45
Cd(II)	0.3	94	32.3	78
Pb(II)	2.9	11.5	5.8	29
Al(III)	0.13	0.15	7.8	20
Fe(III)	0.03	48	0.06	0.13
Bi(III)	0.02	0.08	0.01	0.03
Ga(III)	0.3	0.35	17.5	70
In(III)	0.4	0.4	24	75
Sc(III)	0.38	1.5	0.2	2.13
Cr(III)	22	26.3	15	36.3
Zr(IV)	0.7	0.5	0.3	0.3
Hf(IV)	1.5	3.13	0.002	0.04
Nb(V)	-	-	0.16	0.65
Ta(V)	0.22	0.94	-	-
V(V)	0.06	0.17	0.14	0.7
Mo(VI)	0.08	0.17	0.01	0.02
W(VI)	0.16	0.16	0.01	0.03
F ⁻	9.4	31.3	10.7	15.4
HPO ₄ ²⁻	15	150	51.3	125
C ₂ O ₄ ²⁻	1.6	113	3.9	93
SCN ⁻	6.4	38.4	2.6	26.5
Citrate	0.1	0.7	33	83
Tartrate	0.7	126	26	104

CTAB complex is accompanied with a hypsochromic shift (curve 5) relative to the spectra of the monoligand complexes.

The absorbances of the Nb(V)–R–CTAB and Ta(V)–R–CTAB complexes exhibited maxima at 447 and 426 nm, respectively. The optimum conditions for the formation of mixed-ligand complexes shift to more acid solutions compared to those for the formation of corresponding monoligand complexes (Fig. 3): pH_{opt} for Nb(V)–R–CTAB (curve 2) and Ta(V)–R–CTAB (curve 4) are 3.7–4.3 and 0.3–0.6, respectively. The absorbance of mixed-ligand complexes relative to the blank solution (R + CTAB) attains a maximum at 490 nm.

The yields of both mixed-ligand complexes attained maxima at R and CMAB concentrations of 2×10^{-4} M and 3.2×10^{-4} M, respectively; the absorbances of the complex solutions remained constant in the presence of an eight- to twenty-fold molar excess of CTAB.

Effect of time and temperature. The complexes form immediately after the components were mixed and differed in stability. Thus, the monoligand complexes were stable within 1 h and when being heated to 60°C; the mixed-ligand complexes were stable within one day and when being heated to 80°C.

Stoichiometry and stability constants. We used the Starik–Barbanel' relative yield method and also the slope and isomolar series methods [12]. The component ratios in the monoligand M(V) : R and mixed-ligand M(V) : R : CTAB complexes were 1 : 2 and 1 : 2 : 2, respectively.

It is known that CTAB in acid solutions is protonated and electrostatically interacts with the reagent by the sulfo group. The resulting mixed-ligand complexes belong to ion associates.

The stoichiometry and stability constants of the monoligand complexes were determined by the curve intersection method. The results obtained substantiated the stoichiometry found by the above methods; it was found that $\log \beta (\text{Nb-R}) = 8.67 \pm 0.17$ and $\log \beta (\text{Ta-R}) = 9.83 \pm 0.10$. The stability constants of the mixed-ligand complexes were determined taking into account molar ratios of components.

It was found that the stability of niobium and tantalum compounds in the presence of CTAB enhanced by about nine and seven orders of magnitude, respectively:

$$\log \beta (\text{Nb-R-CTAB}) = 18.17 \pm 0.27;$$

$$\log \beta (\text{Ta-R-CTAB}) = 16.94 \pm 0.32.$$

Calibration graph. The calibration graphs were linear in the range of niobium concentrations 9.3–93 μg and 4.65–93 μg per 25 mL of solution for Nb(V)–R and Nb(V)–R–CTAB complexes and in the range of tantalum concentrations 18.1–181 and 9.05–217.2 μg per 25 mL of solution for Ta(V)–R and Ta(V)–R–CTAB complexes, respectively. The molar absorption coefficients of the complexes are given in Table 1. It can be

Table 3. Determination of niobium(V) in an artificial mixture containing 30 mg Ca and Zn, 50 mg Co and Ni, 10 mg Ba and Pb, 90 mg Cd, 45 mg Mn and Fe, 0.93 mg Ta, and 0.165 mg V ($n = 5$, $P = 0.95$)

Added Nb, μg	Found Nb, μg	RSD, %
50.0	51.7 ± 4.3	3.2
55.8	56.3 ± 2.3	1.6
65.1	66.1 ± 2.9	1.7
74.4	74.2 ± 2.3	1.2
83.7	82.9 ± 2.1	1.0

Table 4. Determination of tantalum(V) in an artificial mixture containing 135 mg Ca, 95 mg Ba, 50 mg Mg, 45 mg Zn, 35 mg Co and Ni, 25 mg Pb, 75 mg Cd, 30 mg Mn, 18 mg Al, 0.650 mg Nb, and 0.700 mg V ($n = 5$, $P = 0.95$)

Added Ta, μg	Found Ta, μg	RSD, %
54.3	52.1 ± 4.3	3
72.4	71.4 ± 4.6	2.5
90.5	91.4 ± 5.3	2.2
108.6	109.4 ± 5.0	1.8
126.7	127.7 ± 4.2	1.3

seen that the introduction of CTAB increases the molar absorption coefficient.

Effect of foreign ions. The selectivities of the proposed methods using monoligand and mixed-ligand complexes are compared in Table 2. Tantalum(V) in an amount of 940 μg does not interfere with the determination of niobium(V), and 700 μg niobium(V) does not interfere with the determination of tantalum(V). This ensures the spectrophotometric determination of both elements on their simultaneous presence in complex samples.

The developed procedures were tested on model solutions. Niobium and tantalum were determined in artificial mixtures using the above procedure; their concentrations were found from calibration graphs (Tables 3 and 4).

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