

Spectrophotometric Study of Scandium(III) Complexation with 2,2',3,4-Tetrahydroxy-3'-sulfo-5'-nitroazobenzene in the Presence of Papaverine, Dibazole, and Urotropine

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Abstract—Complexes of scandium(III) with 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene were studied in the absence and presence of a third component, papaverine, dibazole, or urotropine. Optimal conditions for their formation were found, and their spectrophotometric parameters were determined. It was found that binary compounds ScR and mixed-ligand compounds formed at pH 2 exhibited absorption maxima at 477, 482, 479, and 478 nm. The stability constants of the complexes were calculated. The determination of scandium(III) with 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene in the presence of papaverine, dibazole, and urotropine was found to be selective in comparison to the other known reagents. A procedure was developed for the photometric determination of scandium in hard rocks.

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Many reagents have been proposed for the photometric determination of scandium. Among them are Aluminon, Murexide, Cochineal, Alizarin C, propylfluorone, 1-(2-pyridylazo)-2-naphthol and its analogues, Xylenorange, Methylthymol blue, Sulfonazo, Arsenazo, Thoron, and other reagents [1]. However, the contrast, sensitivity, and selectivity of determination are not quite satisfactory for most reagents.

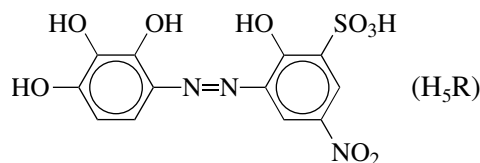
Color reactions of scandium with *o,o'*-tetrahydroxyazo compounds still are unknown. These pyrogallol-based reagents were proven to be candidates for the photometric determination of many elements [2, 3]. Therefore, the study of reactions of these reagents with scandium(III) to reveal and compare their analytical potentials is of undoubted interest. In this work, the color reaction of scandium with 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene (H_5R) was studied with the aim of increasing the sensitivity and selectivity of determining scandium. Mixed-ligand complexes were used to improve the analytical parameters. The effect of papaverine (Pap), dibazole (Dib), and urotropine (Ur) on scandium(III) complexation with H_5R was studied.

EXPERIMENTAL

Apparatus. The absorbance of solutions was measured on a Lambda-40 spectrophotometer with Perkin-Elmer software and a KFK-2 photocalorimeter using 1-cm cells. The acidity of test solutions was measured with a pH-121 pH meter with a glass electrode. The specific electroconductivity of the solutions was measured with a KEL-1M2 conductometer.

Reagents and solutions. The reagent was synthesized according to the procedure described in [2]; its

composition and structure were determined by elemental analysis and IR spectroscopy.



IR (cm^{-1}): 1578 ($-N=N-$);
1042, 1046, 1050, 1054 (Ar-OH)

Anal. calc. (%): C 38.81; H 2.43; N 11.32; S 8.63.

Found (%): C 38.79; H 2.39; N 11.30; S 8.60.

The reagent is highly soluble in water. A 1×10^{-1} M stock scandium solution was prepared by dissolving a calculated amount of metallic scandium in HCl according to [4]. Solutions with lower concentrations were prepared by diluting the stock solution. A 1×10^{-3} M scandium(III) solution and a 1×10^{-3} M aqueous solution of 2,2',3,4-tetrahydroxy-3'-sulfo-5'-nitroazobenzene were used. A 1×10^{-2} M urotropine solution in a water-ethanol mixture, a 0.2% papaverine solution, or a 0.1% dibazole solution was used as the third component. A standard HCl solution (pH 1–2) and ammonia acetate buffer solutions (pH 3–11) were used to adjust specified pH values.

RESULTS AND DISCUSSION

The study of complexation as a function of pH showed that the highest yield of the ScR complex was obtained at pH 2 ($\lambda_{max} = 477$ nm); reagent absorption attained a maximum at 397 nm. Ternary compounds

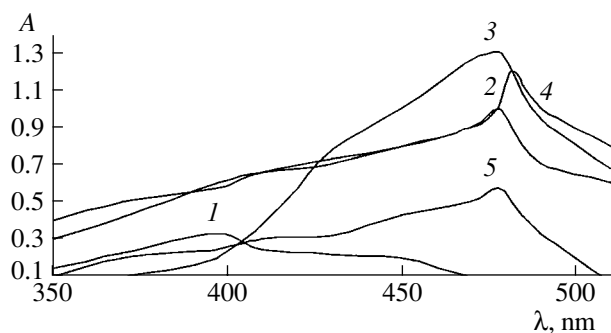


Fig. 1. Absorption spectra of solutions of the reagent and its complexes with scandium(III) in the presence and absence of papaverine, dibazole, or urotropine under optimal pH conditions: (1) R; (2) ScR; (3) ScR-Pap; (4) ScR-Dib; (5) ScR-Ur; $c_{Sc} = 1 \times 10^{-3}$ M; $c_R = 1 \times 10^{-3}$ M; $c_{Pap} = 0.2\%$; $c_{Dib} = 0.1\%$; $c_{Ur} = 1 \times 10^{-2}$ M.

formed in the presence of papaverine, dibazole, or urotropine exhibited the following absorption maxima at pH_{opt} 2: $\lambda_{max} = 482$ nm for ScR-Pap, 479 nm for ScR-Dib, and 478 nm for ScR-Ur (Figs. 1, 2). The main spectrophotometric parameters of scandium(III) complexes are given in Table 1.

It can be seen in Table 1 that the absorption maxima of binary and mixed-ligand complexes of scandium(III) differ from that of the reagent. They form more rapidly and are stable for more than 24 h and under heating to 70°C.

The ratio between the reagents in the complexes was determined by the Starik-Barnabel relative yield, equilibrium-shift, and isomolar-series methods [5]. Using the Astakhov method [6], the number of protons released in the complexation reaction was determined and the component ratios in the complexes were confirmed. The molar absorption coefficients of the complexes were calculated from the absorption curves [5]. The concentration ranges where Beer's law was obeyed were determined.

The stability constants were calculated for the binary and mixed-ligand complexes of scandium(III). The stability constant of complex ScR was calculated by the curve-crossing method [7]. From calculations, $\log K_1 = 4.21 \pm 0.09$ ($n = 4$; $P = 0.95$).

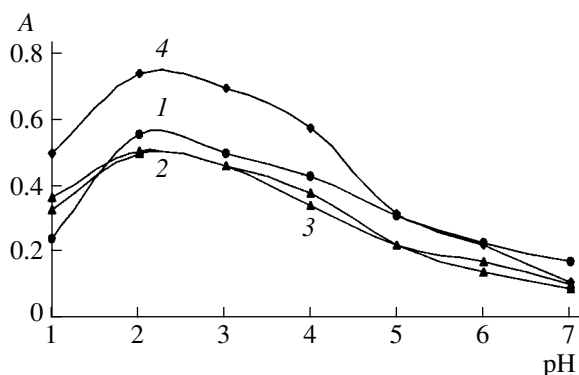


Fig. 2. Absorbance of scandium(III) complex solutions vs. pH in the presence and absence of papaverine, dibazole, or urotropine at λ_{opt} against the control: (1) ScR; (2) ScR-Pap; (3) ScR-Dib; (4) ScR-Ur.

From the saturation curve of a 8×10^{-5} M solution of complex ScR with solutions of papaverine, dibazole, and urotropine, the stability constants of mixed-ligand complexes were determined by the curve-section method: $\log K_1 = 5.26 \pm 0.05$ (ScR-Pap); $\log K_1 = 5.01 \pm 0.07$ (ScR-Ur); $\log K_1 = 4.93 \pm 0.08$ (ScR-Dib).

The complexes were also studied by conductometric titration [8]. A comparison of the specific conductivities of binary and mixed-ligand scandium(III) complexes at pH 2 shows that ScR-Pap, ScR-Dib, and ScR-Ur are more stable (Table 2).

The effect of foreign ions and masking agents on the formation of binary and mixed-ligand complexes of scandium(III) was studied. It was shown that the reaction selectivity was significantly enhanced in the presence of papaverine, dibazole, and urotropine. The developed procedures for determining scandium(III) with the reagent in the presence of papaverine, dibazole, and urotropine are highly selective. The determination of scandium as mixed-ligand complexes does not interfere with multiple amounts of alkaline and alkali-earth metals (Table 3).

Determination of scandium in hard rocks (altered pyrite-bearing diorite). A portion of hard rock (1 g) was dissolved in a mixture of 15 mL HF + 5 mL HNO₃ + 5 mL HCl and heated in a graphite cru-

Table 1. The main photometric properties of scandium(III) reactions with organic reagents

Reagent	λ_{max} (nm)	pH	Sc : reagent ratio	$\epsilon_{max} \times 10^{-3}$	Range the Beer law is obeyed ($\mu\text{g/mL}$)
Eriochrome cyanine [9]	540	6	1 : 2	17.2	0.18–1.8
H ₅ R	477	2	1 : 2	18.5	0.03–2.5
H ₅ R + Pap	482	2	1 : 2 : 1	25.5	0.1–2.5
H ₅ R + Dib	479	2	1 : 2 : 1	28.0	0.05–2.9
H ₅ R + Ur	478	2	1 : 2 : 1	25.0	0.05–2.2

Table 2. Electric conductivity ($m \times 10^{-3}, \Omega^{-1} \text{ cm}^{-1}$) of binary and mixed-ligand scandium complexes at pH 2

Complex	V_R (mL)									
	1	2	3	4	5	6	7	8	9	10
ScR	9.02	9.02	9.01	8.92	8.86	8.72	8.64	8.57	8.43	8.3
ScR + Pap	8.28	8.28	8.27	8.26	8.25	8.25	8.24	8.23	8.19	8.1
ScR + Ur	8.27	8.26	8.25	8.24	8.23	8.22	8.21	8.17	8.13	8.1
ScR + Dib	8.32	8.31	8.3	8.29	8.28	8.27	8.25	8.21	8.18	8.0

Table 3. Permissible multiple amounts of foreign species in determining scandium(III) as binary (ScR) and mixed-ligand (ScR–Pap, ScR–Dib, and ScR–Ur) complexes (error 5%)

Ion or compound	ScR	ScR–Ur	ScR–Pap	ScR–Dib	Eriochrome cyanine [9]	Alizarin Red C [4]
Na(I)	50	2556	3066	3067		
K(I)	90	4333	5200	5200		interferes
Mg(II)	27	267	427	267		
Ca(II)	444	622	889	444		interferes
Ba(II)	1522	2436	2436	1827	does not interfere	the same
Zn(II)	72	722	1011	722	the same	
Cd(II)	124	249	1493	1493		
Mn(II)	61	122	1100	611		
Ni(II)	66	656	1311	656	does not interfere	
Co(II)	131	656	1180	656	the same	
Cu(II)	711	853	1137	711	interferes	interferes
Pb(II)	46	232	46	46	the same	the same
Al(III)	60	300	360	300	does not interfere	"
In(III)	13	15	18	18		"
Ga(III)	8	8	9	10		"
Bi(III)	23	232	279	230	interferes	"
Cr(III)	12	578	1156	578	does not interfere	"
Zr(IV)	101	1011	1011	1011		
V(V)	6	11	57	34	interferes	
Mo(VI)	21	1067	1280	107		
W(VI)	204	2044	2862	2044	interferes	interferes
$\text{C}_2\text{O}_4^{2-}$	2	4	4	5		
Urea	667	800	933	667	interferes	
Thiourea	846	1015	870	1182	the same	
EDTA	8	17	17	25		
Citric acid	43	128	85	85		interferes

cible at 50–60°C. For the complete removal of excess HF, 7 mL of conc. HNO_3 and 1 mL of conc. HCl were added three times. The resulting solution was dissolved in water, transferred to a 50-mL flask, and diluted with water to the mark. Aliquot portions were placed in three 25-mL flasks. Two milliliters of 1×10^{-3} M reagent solution + 1 mL of 0.2% papaverine solution were

added to the first flask; 2 mL of 1×10^{-3} M reagent solution + 1 mL of 0.1% dibazole solution were added to the second flask; 2 mL of 1×10^{-3} M reagent solution + 1 mL of 0.01% urotropine solution were added to the third flask; and the solutions were then diluted to the mark with a solution with pH 2. The absorbances of solutions were measured at 490 nm on a KFK-2 against

Table 4. Determination of scandium in hard rocks

Analytical species	Certified value (%)	Found (%)
ScR	0.0678	0.0675
ScR-Ur	0.042	0.045
ScR-Dib	0.089	0.09
ScR-Pap	0.060	0.063

the control solution. The concentration of scandium in the test sample was determined from the calibration graph. The results obtained are given in Table 4.

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