Rapid Spectrophotometric Determination of Scandium(III) with (Pyridylazo)- and (Thiazolylazo)naphthols

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Synopsis. Scandium(III) reacts with 1-(2-pyridylazo)-2-naphthol [PAN] and 1-(2-thiazolylazo)-2-naphthol [TAN] in weakly acidic media to yield red colored 1:1 and 1:2 chelates, respectively. These complexes are sparingly soluble in water but readily soluble in $\geq$24% (v/v) acetone and $\geq$32% (v/v) methanol, giving maximum absorbances at 545 and 570 nm for the PAN and TAN complexes, respectively. Beer's law is obeyed over the concentration ranges of 0.16 to 1.40 μg and 0.08 to 1.40 μg of Sc(III) per ml with PAN and TAN. The scandium(III) complexes formed with PAN and TAN have the molar absorptivities of 1.90×10^4 and 2.93×10^4 dm^3 mol^{-1} cm^{-1} at their absorption maxima, respectively. The effect of diverse ions on the determination of scandium with these reagents is also investigated.

Pyridylazo and thiazolylazo dyes are sensitive chromogenic reagents for metal ions and a wide range of applications in analytical chemistry have been reported with these dyes. 5-Ethylamino-2-(2-pyridylazo)-*p*-cresol and 5-ethylamino-2-(2-thiazolylazo)-*p*-cresol[1] yield intensely colored complexes with scandium, but these reagents are relatively less selective for scandium(III). The reaction of scandium with 4-(2-pyridylazo)resorcinol [PAR] requires 10 min for complete color development[2] at room temperature and a large number of ions have been reported[2,3] to interfere. The complex formation between scandium(III) and 4-(2-thiazolylazo)resorcinol [TAR] is quite sensitive but a preliminary separation of scandium(III) by ion-exchange chromatography[4] is needed to prevent metal interferences. Among various other types of dyes, chrome azurol S has been widely studied[5–8] for the spectrophotometric determination of scandium. It has been found that the addition of various surfactants is very effective for obtaining intensely colored complexes. In the absence of surfactants, the method requires 90 min for full color development at room temperature. Even in the presence of surfactants, the reaction is not always instantaneous.[7,8] Similarly, the color development for the complexes with xylenol orange,[9] arsenazo I[10] and chromotrope 2B[11] requires 10 to 30 min at room temperature. The present method involves the instantaneous reactions of scandium(III) with 1-(2-pyridylazo)-2-naphthol [PAN] and 1-(2-thiazolylazo)-2-naphthol [TAN] at room temperature in the absence of any surfactant.

Experimental

Apparatus and Reagents. All absorbance measurements were made on a EC Spectrophotometer GS 866C with 10-mm cells. The absorption spectra were recorded on a Varian Superscan 3 UV-Visible Spectrophotometer. An EC-pH meter (Model 822) was used for pH measurements.

A 0.768 g amount of scandium oxide (AnalaR) was heated with 30 ml of concentrated nitric acid. The clear solution obtained was diluted to 250 ml with doubly distilled water and the scandium content [2.227×10^{-2} M(1 M=1 mol dm^{-3})] was verified complexometrically. A 0.5 g amount of 1-(2-pyridylazo)-2-naphthol, PAN [Fluka A.G. purum] was dissolved in 250 ml of acetone to give a 0.2% solution. A 0.1% (w/v) methanolic solution of TAN was prepared from 1-(2-thiazolylazo)-2-naphthol [Fluka A.G. purum]. A buffer solution of pH 5.0 was prepared from 0.05 mol dm^{-3} hydrochloric acid and 0.05 mol dm^{-3} hexamine (AnalaR) solutions.

General Procedure. An aliquot of solution containing $\leq$35 μg of scandium was taken, for both systems, in a 25 ml volumetric flask containing 5 ml of hexamine buffer adjusted to pH 5.0. After the addition of 3.5 ml of 0.2% PAN, the scandium(III) complex formed was dissolved in 10 ml of acetone. On the other hand, the scandium(III)–TAN complex obtained with 3.0 ml of 0.1% TAN was dissolved in 10 ml of methanol. The content was made upto 25 ml with doubly distilled water and the absorbance of the complex was measured against a reagent blank at 545 nm for the PAN complex or 570 nm for the TAN complex.

Results and Discussion

Scandium(III) reacts instantaneously with PAN and TAN in weakly acidic media to form sparingly soluble red-colored chelates, which are soluble in acetone and methanol, respectively.

Effect of pH. The pH of the reaction mixture was varied in both the systems from 1.0 to 10.0. A constant maximum absorbance was observed in the pH range 4.5—5.5 and 4.2—5.6 for the scandium(III)–PAN and scandium(III)–TAN systems, respectively. Hence all the studies were carried out in a hexamine–hydrochloric acid buffer solution adjusted to pH 5.0.

Effect of Reagents Concentration. Volume of 0.2% PAN was varied from 0.2 to 5.0 ml for 25 μg of scandium(III), a constant maximum absorbance being obtained on addition of $\geq$3.0 ml reagent. Similarly for the same amount of scandium(III), a constant maximum absorbance was obtained on addition of $\geq$2.2 ml of 0.1% TAN. Thus, 3.5 ml of 0.2% PAN or 3.0 ml of 0.1% TAN was employed in further studies.

Choice of Solvent. It was found that, of the solvents examined, acetone and methanol were the best solvents for dissolving the PAN and TAN complexes, respectively. Since these complexes exhibited maximum absorbance in the solutions containing $\geq$24% (v/v) acetone and $\geq$32% (v/v) methanol, 10 ml each of acetone and methanol was employed to dissolve the complexes with PAN and TAN, respectively.

Table 1. Effect of Diverse Ions
(Amount of scandium(III) 25 μg/25 ml)

Sc(III)-PAN		Sc(III)-TAN	
Foreign ion added	Tolerance limit/μg	Foreign ion added	Tolerance limit/μg
Cl^-, Ca(II), Sr(II), Ba(II), As(III)	>25,000	Cl^-, Br^-, Mg(II), Ca(II), Sr(II), Ba(II)	>25,000
Br^-, urea, Mg(II)	20,000	Urea	20,000
$S_2O_3^{2-}$	8,000	I^-	15,000
NH_2OHHCl	7,000	Acetate	10,000
Thiourea	5,000	Thiourea	5,500
I^-	4,000	NH_2OHHCl, SCN^-	5,000
SCN^-, Ag(I)[a]	3,000	$S_2O_3^{2-}$, succinate	2,500
Pt(IV)[b]	1,400	Pt(IV)[d]	1,500
Acetate	1,000	CN^-, Al(III)	1,000
Au(III)	750	Rh(III)	750
Hg(II)	500	Au(III)	600
Sb(III)	400	Ag(I)[e]	450
Ce(III)	250	Citrate	400
Al(III), Rh(III), La(III)	200	Cr(III)	300
Cd(II), Cr(III), Ru(III), Th(IV)	150	Hg(II)[d]	200
Fe(III)	125	Cd(II)[d], La(III)	150
CN^-, citrate, succinate	100	Ascorbate, Ru(III)	100
$N_2H_4H_2SO_4$, phthalate, Sn(II), Mo(VI), U(VI)	50	Pb(II)[f], Sn(IV)	80
Ascorbate, Pb(II)[c], Zr(IV)	40	Ce(III)	60
In(III), Tl(III), Bi(III), Ti(IV), Hf(IV)	25	Fe(III)[g], Bi(III)[h]	40
$C_2O_4^{2-}$, Mn(II), Ga(III)	20	Mn(II)[g], Tl(III)[g], Th(IV)	30
F^-, $EDTA^{4-}$, Co(II), Ni(II), Cu(II), V(IV, V)	nil	Y(III), Se(IV), Zr(IV)[g], Hf(IV)[g], Mo(VI)	25
		Cu(II)[i], Sb(III)	20
		Fe(II)[g], Ni(II)[g]	10
		F^-, $C_2O_4^{2-}$, $EDTA^{4-}$, Co(II), Ti(IV), V(IV, V)	nil

Masked with a) $Na_2S_2O_3$ (2.02×10^{-3} M). b) NaSCN (1.48×10^{-3} M). c) $NaCH_3COO$ (4.87×10^{-4} M). d) NaSCN (2.47×10^{-3} M). e) $Na_2S_2O_3$ (6.32×10^{-4} M). f) $NaCH_3COO$ (4.87×10^{-3} M). g) KCN (6.14×10^{-4} M). h) KI (3.6×10^{-3} M). i) NH_2CSNH_2 (2.89×10^{-3} M).

Stability. The scandium(III) complexes thus formed are stable for 24 h (PAN complex) and 10 h (TAN complex).

Spectral Characteristics. The absorption spectra of the scandium(III) complexes with PAN and TAN and those of the respective reagent blanks are given in Fig. 1. The PAN and TAN complexes exhibited their absorption maxima at 545 and 570 nm, respectively.

Composition of Complex. The composition of the Sc(III)-PAN and Sc(III)-TAN complexes, established by the mole ratio method and the Job's method, was found to be 1 : 1 and 1 : 2, metal-to-ligand, ratios respectively.

Beer's Law and Sensitivity. The Sc(III)-PAN and Sc(III)-TAN complexes obeyed Beer's law over the concentration ranges 0.16 to 1.40 μg and 0.08 to 1.40 μg respectively of scandium(III) per ml, the molar absorptivities being 1.90×10^4 (at 545 nm) and 2.93×10^4 (at 570 nm) $dm^3\,mol^{-1}\,cm^{-1}$; the Sandell sensitivities, 2.30 and 1.50 ng cm^{-2}, respectively.

Effect of Diverse Ions. The effect of various anions and cations was studied in both the systems by setting the tolerance limit at an amount to cause an

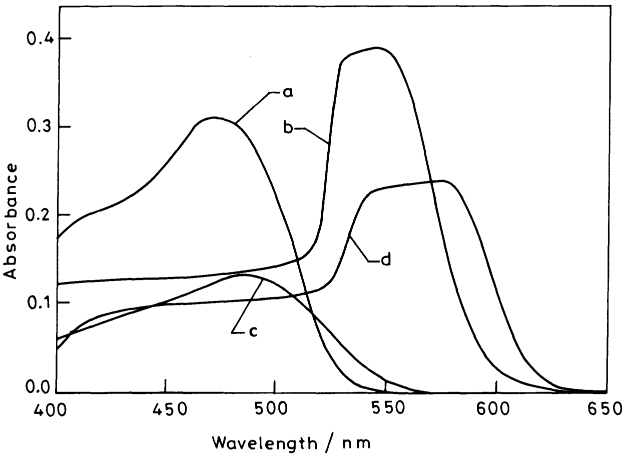

Fig. 1 Absorption Spectra.
Curves a): Reagent blank vs. solvent, [PAN] = 4.02×10^{-4} mol dm^{-3}. b): Sc(III)-[PAN] complex vs. reagent blank, [Sc(III)] = 1.78×10^{-5} mol dm^{-3}, [PAN] = 1.12×10^{-3} mol dm^{-3}. c): Reagent blank vs. solvent, [TAN] = 7.84×10^{-6} mol dm^{-3}. d) Sc(III)-TAN complex vs. reagent blank, [Sc(III)] = 7.77×10^{-6} mol dm^{-3}, [TAN] = 4.71×10^{-4} mol dm^{-3}.

error of ±2.0% in the determination of scandium. The effect of diverse ions is presented in Table 1.

Precision and Accuracy. The coefficient of variation and the relative mean error, calculated from ten replicate determinations with 25 μg of scandium(III), were found to be ±0.86 and ±0.98% for the scandium–PAN system and ±0.90 and ±1.41% for the scandium–TAN system.

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