Rapid Spectrophotometric Determination of Chromium(III) with 1-(2-Thiazolylazo)-2-naphthol in Presence of Surfactant

Gogineni V. Rathaiah and Muppalla C. Eshwar*
Department of Chemistry, Indian Institute of Technology, Bombay-400 076, India

(Received May 7, 1984)

Synopsis. Chromium(III) reacts with 1-(2-thiazolylazo)-2-naphthol at 80—95 °C in acid media (pH 5.7), in presence of benzoate and sodium dodecyl sulfate. Presence of surfactant increases sensitivity of the complex and reduces heating time to 5 min, thus giving rise to perhaps the most rapid method for absorptiometric determination of chromium(III). The 1:1 complex obeys Beer's law for 0.2 to 2.4 μg of Cr(III) per ml, has molar absorptivity and Sandell sensitivity of $1.46\times10^4\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ and 3.5 ng $\mathrm{cm^{-2}}$ respectively, at 575 nm.

Among various pyridylazo and thiazolylazo derivatives, 1-(2-pyridylazo)-2-naphthol (PAN),[1] 4-(2-pyridylazo)resorcinol (PAR),[2] 4-(2-thiazolylazo)resorcinol (TAR)[3] have been reported for spectrophotometric determination of chromium(III). These methods require 45, 35, and 45 min of heating time respectively, at elevated temperatures. The methods reported by Yotsuyanagi *et al.*[4] Yamamoto[5] with PAR require 130 and 20 min of heating respectively, and the latter method employs hydrogen peroxide to oxidise Cr(III) to Cr(VI). Sodium benzoate has been reported to exert catalytic influence in reducing the heating time for chromium(III)–EDTA reaction.[6] Surfactants find increased application in studies of metal–ligand complexes due to enhanced sensitivity obtained. Hence, the reaction between chromium(III) and 1-(2-thiazolylazo)-2-naphthol (TAN) has been studied in presence of surfactants and benzoate.

Experimental

Apparatus and Reagents. A Spectromom 204 spectrophotometer with matched 10 mm cells was used for all absorbance measurements. The absorption spectra were recorded on a Varian Superscan 3 UV-Visible spectrophotometer. For pH measurements an EC-pH meter (Model 822) was used.

1.923 g of chromium nitrate was dissolved in 250 ml of 2% nitric acid, the solution standardised titrimetrically[7] and diluted as required. A 0.2% (w/v) methanolic solution of TAN was prepared from 1-(2-thiazolylazo)-2-naphthol (Fluka A.G. purum). A buffer solution of pH 5.7 was prepared from 0.5 mol $\mathrm{dm^{-3}}$ solutions of sodium benzoate (dissolved in warm water and cooled) and benzoic acid. A 5% (w/v) solution of sodium dodecyl sulfate was prepared with hot water and cooled to room temperature.

General Procedure. An aliquot of solution containing <60 μg of chromium(III) was taken in a 25 ml volumetric flask, added 5 ml of buffer solution, 4 ml of SDS solution and 3 ml of TAN solution. The reaction mixture was heated on a water bath for 5 min around 90 °C, flask cooled to room temperature and contents diluted to 25 ml. The absorbance of the complex was measured at 575 nm against a reagent blank, prepared under identical conditions.

Results and Discussion

Due to inert nature of $[\mathrm{Cr(H_2O)_6}]^{3+}$, the reaction between chromium(III) and TAN at room temperature required 24 and 4 h in presence of acetate and benzoate respectively, maximum absorbance being attained in 50% solutions of methanol or *t*-butyl alcohol. Eventhough ionic surfactants dissolved the sparingly soluble complex, it was still necessary to wait for very long intervals of time. For example, in presence of SDS, maximum absorbance was reached only after 38 and 8 h in presence of acetate and benzoate respectively. Hence, the reaction was studied at elevated temperatures in presence of SDS, acetate and benzoate.

Effect of Heating. When the reaction mixture was heated to different temperatures, from 40 to 100 °C, maximum absorbance was observed on heating at ≥80 °C. Hence, reaction mixture was heated at 90 °C.

Complications arose when the time of heating was varied. When the reaction was carried out with 1 ml of 0.1% TAN, time required for complexation was reduced to 30 and 10 min in presence of acetate and benzoate respectively, the resulting complex requiring 50% methanol or *t*-butyl alcohol for dissolution. On further addition of TAN, the complex did not dissolve in any of the water-miscible solvents, but was soluble in some immiscible solvents (max. absorbance in 1-butanol). In latter case, complexation required heating for 60 and 40 min in presence of acetate and benzoate respectively and even then results were not satisfactorily reproducible. However, addition of SDS resulted, besides dissolution of the complex, in a further decrease in reaction time to 4 min at 90 °C both in presence and absence of acetate or benzoate. Hence, reactants were heated for 5 min at 90 °C.

Effect of Sodium Dodecyl Sulfate. On addition of 1 to 8 ml of 5% SDS at least 2 ml of SDS was required for dissolution of the complex, and absorbance remained uneffected with higher volumes. Hence, 4 ml of SDS solution was employed in all studies.

Effect of pH and Benzoate. pH of the solution containing 40 μg of Cr(III) and 4 ml of SDS was varied from 3.0 to 8.0, and maximum absorbance was observed in the pH range 5.4 to 6.2 (Fig. 1, curve a). Hense, pH of 5.7 was maintained in all studies. When attempts were made to maintain the pH with various buffers, only acetate and benzoate buffers were found to be satisfactory and an increase in their concentration resulted in an increase in absorbance of the complex. Maximum absorbance was observed on addition of 1 to 8 ml of 0.5 mol $\mathrm{dm^{-3}}$ solutions of benzoate, while further addition of benzoate resulted in a decrease in absorbance. Studies with acetate of different concentrations resulted in lower absorbance. Hence, 5 ml of benzoate buffer was employed in all studies. The increase in sensitivity caused by benzoate may be seen from Fig. 1, curve b, which shows the effect of pH on absorbance in presence of 5 ml of 0.5 mol

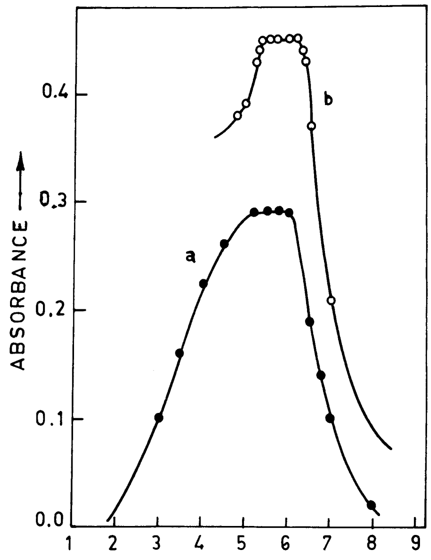

Fig. 1. Effect of pH on Absorbance.
See the text for a and b.

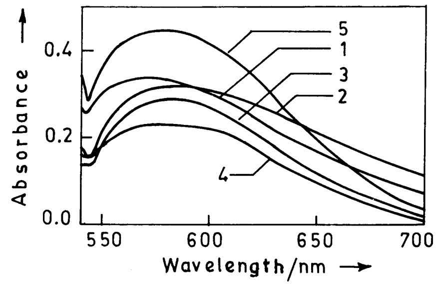

Fig. 2. Absorptin Spectra.
Curves 1, 2, 3, 4, and 5 are as in Table 1
$[Cr(III)]=3.077\times 10$ mol dm^{-3}; $[TAN]=9.4\times 10^{-4}$ mol dm^{-3}; SDS=0.8%; [Benzoate]=[Acetate]=0.1 mol dm^{-3}.

dm^{-3} benzoate.

Effect of Reagent Concentration. Amount of reagent (0.1% TAN) was varied from 0.25 to 8 ml and maximum absorbance observed with ≥5.0 ml. Hence, 3.0 ml of 0.2% TAN was employed for all studies.

Absorption Spectra. Figure 2 gives absorption spectra of different systems *vs.* appropriate reagent blank. Since the complex formed in presence of SDS and benzoate exhibited maximum sensitivity (Table 1) at 575—580 nm, all measurements were made at 575 nm. Reagent blank for all systems exhibited maxium absorbance at 490 nm. All systems were heated for 5 min.

Composition. Composition of the complex established by Job's continuous variation method and mole ratio method, was found to be 1 : 1, metal to ligand.

Beer's Law, Sensitivity, and Stability. The Cr(III)–TAN-benzoate–SDS complex obeyed Beer's law in the concentration range 5 to 60 μg of chromium(III) per 25 ml. The apparent molar absorptivity of the complex, calculated from Beer's law plot, was 1.46×10^4 dm^3 mol^{-1} cm^{-1} and Sandell sensitivity 3.5 ng cm^{-2}. Table 1 presents sensitivity of complexes obtained by various systems. The complex was found to be stable for 24 h.

TABLE 1. SENSITIVITY OF THE COMPLEXES

Sr. No.	Complex	λ_{max}/nm	Sensitivity ng cm^{-2}	ε 10^4 dm^3 mol^{-1} cm^{-1}
1	Cr(III)+TAN+ acetate[a)]	565	4.7	1.09
2	Cr(III)+TAN+ benzoate[a)]	580—590	5.0	1.04
3	Cr(III)+TAN+ SDS	580	5.5	0.95
4	Cr(III)+TAN+ SDS+acetate	580	6.9	0.75
5	Cr(III)+TAN+ SDS+benzoate	575—580	3.5	1.46

a) In 50% *t*-butyl alcohol.

Effect of Diverse Ions. Effect of various ions, usually associated with chromium(III), was studied in the determination of 40 μg of Cr(III) per 25 ml. $EDTA^{4-}$ caused negative interference, while positive interference was shown by Fe(II), Ni(II), Zn(II), and Bi(III) in all proportions. Tolerance limits (in μg) of various ions are: Cl^- Br^-, I^-, 10000; Mg(II) 2500; Ca(II), thiourea, $NH_2OH\cdot HCl$, $N_2H_4H_2SO_4$ 2000; Pt(IV) 1500; Sr(II), Ba(II), Th(IV), CN^- 1000; SCN^- 750; Be(II), Mo(VI), $S_2O_3^{2-}$ 500; Au(III), W(VI), PO_4^{3-} 250; Mn(II), V(V) 200; tartrate, oxalate, Ag(I), Hg(II), Sc(III), Zr(IV), Cr(VI) 100; Pd(II), Ru(III), V(IV) 50; citrate, Co(II), Pb(II), Fe(III), Y(III), Ce(III), Ga(III), Hf(IV), Sb(III), U(VI) 25; In(III) Rh(III) 10. Fluoride was employed to mask Be(II), Sc(III), Zr(IV), and Th(IV), whereas CN^- was employed to mask Mn(II), Co(II), Cu(II), Hg(II), and Fe(III).

Precision and Accuracy. Relative standard deivation and relative mean error, calculated from ten repeat determinations, were found to be ±0.41% and ±0.72% respectively.

Application to Analysis of High Speed Steel. 0.2 g of high speed steel was treated with 15 ml of concd HCl and 5 ml of concd HNO_3, the precipitated tungstic acid filtered off, and filtrate diluted to 100 ml. An aliquot of this was acidified with HCl to 3.5 mol dm^{-3} and iron removed by extraction with mesityl oxide.[8)] Aqueous layer was evaporated to dryness, dissolved in water, pH adjusted to 5.7 and chromium content determined as described in general procedure. From duplicate analysis, amount of chromium was found to be 3.9 and 3.94% against theoretical value of 4.0%. Other constituents of alloy are W=18%, V=1.0% and rest iron.

References

1) S. G. Nagarkar and M. C. Eshwar, *Indian J. Tech.*, **13**, 377 (1975).

2) B. Subrahmanyam and M. C. Eshwar, *Bull. Chem. Soc. Jpn.*, **49**, 347 (1976).

3) B. Subrahmanyam and M. C. Eshwar, *Mikrochim. Acta*, **1976II**, 579.

4) T. Yotsuyanagi, Y. Takeda, R. Yamashita, and K. Aomura, *Anal. Chim. Acta*, **67**, 297 (1973).

5) K. Yamamoto, *Bunseki Kagaku*, **27**, 460 (1978).

6) V. Linder, *Mikrochim. Acta*, **1980I**, 107.

7) A. I. Vogel, "A Text-book of Quantitative Inorganic Analysis," Longman, London (1968) p. 311.

8) V. M. Shinde and S. M. Khopkar, *Separ. Sci.*, **4**, 161 (1969).