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3-Hydroxy-3-*m*-Sulphonato (Sodium Salt) Phenyl-1-*o*-Nitrophenyltriazene: An Indicator for the Simultaneous Complexometric Determination of Cr(III) with Fe(III), Cu(II) and Ni(II)

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3-Hydroxy-3-*m*-sulphonato(sodium salt)phenyl-1-*o*-nitrophenyltriazene as an indicator for the simultaneous complexometric determination of Cr(III), Fe(II) and Ni(II) in binary and ternary metal ion mixtures has been studied. The presence of 20-fold excess of eleven diverse cations and anions did not interfere with the determination of 5.2 mg of Cr(III). The amount of metal ions found was in good agreement with the amount of metal ions actually present; so the determinations are quite accurate. This establishes hydroxytriazene as a metallochromic indicator for the complexometric determination of Cr(III).

INTRODUCTION

Use of hydroxytriazene as metallochromic indicator for the complexometric determination of Cr(III) has hardly been attempted although this class of reagents has been extensively used as metallochromic indicators for the complexometric determination of transition metal ions.[1–7] Hydroxytriazenes have advantages over other reagents owing to their easy preparatory methods and higher yields. Thus in the present study 3-hydroxy-3-*m*-sulphanato(sodium salt)phenyl-1-*o*-nitrophenyltriazene has been used as metallochromic indicator for the complexometric determination of Cr(III) and from binary and ternary metal ion mixtures. In the binary mixtures determination of Cr(III) has been done taking advantage of kinetic masking. In ternary mixtures both pH adjustments and kinetic masking were used for the determination of other two ions present with chromium(III).

EXPERIMENTAL

A. Preparation of solutions

(i) *Metal ions*: A stock solution of Cr(III) 1.0×10^{-2} M was prepared by dissolving the weighed amount of chromium(III) chloride hexahydrate in double distilled water. A few drops of conc. HCl were added to prevent hydrolysis. The

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solution was standardised by EDTA solution between pH 3.0 to 4.0 with 1 M H_2SO_4[8–10] using xylenol orange indicator. Weaker solutions were pepared by appropriate dilution of the stock solution with double distilled water. Stock solutions of 1.0×10^{-2} M Cu(II) and Ni(II) were prepared by dissolving requisite amount of A.R. grade sulphates of these metal ions in double distilled water which are standardised by usual methods.[11] Weaker solutions were prepared by appropriate dilution with double distilled water.

A 1.0×10^{-2} M stock solution of iron(III) was prepared by dissolving the weighed quantity of ferric nitrate in double distilled water. Few drops of conc. HNO_3 were added to prevent hydrolysis of the solution. It was then standardised by titrating it against 1.0×10^{-2} M EDTA solution using sulphosalicylic acid indicator.[12] Weaker solutions were prepared by appropriate dilution.

(ii) *Indicator*: A 0.2% indicator solution was prepared by dissolving the requisite quantity of 3-hydroxy-3-*m*-sulphonato (sodium salt) phenyl-1-*o*-nitrophenyltriazene in ethanol. Fresh solutions were prepared as and when needed.

(iii) *Buffer*: A fresh 1% hexamine buffer solution was prepared by dissolving it in minimum quantity of double distilled water and then diluting it with ethanol.

B. Method of Titration of Chromium(III) Soution Using 3-Hydroxy-3-*m*-Sulphonato (Sodium salt) Phenyl-1-*o*-Nitrophenyltriazene as Indicator

In a 500 cm^3 beaker fitted with magnetic stirrer 10.0 cm^3 of 1.0×10^{-2} M standard Cr(III) ion solution and 15.0 cm^3 of 1.0×10^{-2} M EDTA solution were taken. This solution mixture was diluted with deionized water and the pH of the solution was adjusted between 3.0 to 4.0 with 1 M H_2SO_4. The mixture was boiled for about 30 min when a red violet chromium(III)-EDTA complex was formed and the colour of the complex did not change any further from its red violet colour. This was cooled to room temperature and the pH was adjusted between 5.2 to 6.0 with hexamine buffer. Now 2.0 to 3.0 cm^3 of 0.2% hydroxytriazene indicator in ethanol was added. Further 100–150 cm^3 of ethanol was also added to remove any turbidity. The solution was titrated against 1.0×10^{-2} M $Fe(NO_3)_3$ solution to find out the volume of excess EDTA. At the end point the colour of the solution sharply changes from violet to yellow.

RESULTS AND DISCUSSION

(a) Optimum conditions of pH for titration were established by carrying out a series of titrations in different buffer solutions. The best results were obtained between pH 5.2 to 6.0 with hexamine. At the pH value less than 5.2 the colour sharpness of Fe(III) with the indicator was minimum. A brown tinge was developed at $pH > 6$. Therefore titrations were carried out between pH 5.2 to 6.0. The effect of temperature on the accuracy of complexometric determination of Cr(III) with hydroxytriazene as indicator was studied in different temperature ranges between 20–60°C and gave best results in the temperature range of 20–50°C.

(b) *Chromium(III) concentration range*: To find out the minimum concentration of chromium(III) in the solution which could be satisfactorily determined using hydroxytriazene as indicator, chromium(III) solutions of the following concentrations, *viz.*, 1.0×10^{-2} M, 5.0×10^{-3} M, 2.0×10^{-3} M, 1.0×10^{-3} M, 5.0×10^{-4} M and 2.0×10^{-4} M were prepared and each of these solutions was complexed with EDTA solutions of corresponding concentrations. Titrations were performed under optimum conditions of pH and temperature with Fe(III) solutions of required concentrations to find out excess EDTA. For sake of comparison parallel titrations were also carried out using xylenol orange indicator. The results obtained have been presented in Table-1.

TABLE-1
RESULTS OF Cr(III) DETERMINATION WITH 3-HYDROXY-3-*m*-SULPHONATO (SODIUM SALT) PHENYL-1-*o*-NITROPHENYLTRIAZENE AS INDICATOR

S. No.	Conc. of Cr(III) solution	Vol. of EDTA consumed by Cr(III) with		Colour change at the end point using hydroxytriazene indicator
		hydroxytriazene indicator (cm^3)	Xylenol orange indicator (cm^3)	
1.	1.0×10^{-2} M	10.0	10.0	Violet to yellow
2.	5.0×10^{-3} M	10.0	10.0	Violet to yellow
3.	2.0×10^{-3} M	10.0	10.0	Violet to yellow
4.	1.0×10^{-3} M	10.0	10.0	Violet to yellow
5.	5.0×10^{-4} M	10.0	10.0	Violet to yellow
6.	2.0×10^{-4} M	end point is not perceptible	end point is not perceptible	end point is not perceptible

Interference Studies

Interference studies in presence of 10, 50 and 100 ppm of the following 26 cations and anions were performed: Na(I), K(I), Ag(I), Ca(II), Mg(II), Co(II), Ni(II), Cu(II), Ba(II), Zn(II), Pb(II), Hg(II), Al(III), Zr(IV), U(VI), F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, CO_3^{2-} and PO_4^{3-}. It was found that in the determination of 5.2 mg of chromium(III), 10 ppm of Ag(I), Co(II), Zn(II), Pb(II), Hg(II), Al(III), Zr(IV), U(VI), F^-, $S_2O_3^{2-}$ and PO_4^{3-} ions interfered while Mg(II), Ni(II), Cu(II) and SO_3^{2-} were tolerated up to 50 ppm. The remaining 11 ions, *viz.* Na(I), K(I), Ca(II), Ba(II), Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_4^{2-} and CO_3^{2-} which did not interfere up to 50 ppm level also did not interfere at 100 ppm level in the Cr(III) determination.

Complexometric Determination of Chromium(III) in Binary Mixtures of Cr(III)—Fe(III), Cr(III)—Cu(II) and Cr(III)—Ni(II)—Kinetic Masking

A new procedure was developed to determine both the components of binary mixtures of Cr(III)-Fe(III), Cr(III)-Cu(II) and Cr(III)-Ni(II) using 3-hydroxy-3-*m*-sulphonato (sodium salt) phenyl-1-*o*-nitrophenyltriazene as indicator with the use of kinetic masking. In a 500 cm^3 beaker containing 10 cm^3 of a standard 1.0×10^2 M chromium(III) solution, 10 cm^3 of any one of the other metal ions *viz.*, Fe(III), Cu(II) or Ni(II) were added. The pH of the solution was adjusted between 5.2 to 6.0 in case of Cr(III)-Fe(III) couple, 4.0 to 5.0 in case of Cr(III)-Cu(II) and 3.0 to 4.0 for Cr(III)-Ni(II) mixture. Few drops of hydroxytriazene indicator solution in ethanol were added to this solution. A further 50 cm^3 of ethanol were added to remove any turbidity. The advantage of kinetic masking was taken in the determination of two metal ions from the mixture. When the solution was cold Cr(III) did not react with the standard EDTA solution whereas the other ions, *viz.*, Fe(III), Cu(II) or Ni(II) could be determined by directly titrating it with standard EDTA solution in cold.

Thus using standard 1.0×10^{-2} M EDTA solution, first the solution was kept cold and the ion, *i.e.*, Fe(III), Cu(II) or Ni(II) was determined using hydroxytriazene indicator. The solution was then used for Cr(III) determination. For this, the solution was acidified to attain a pH between 3.0 to 4.0 and an excess of EDTA solution was added to it. The mixture was boiled for 30 minutes till a red violet Cr(III)-EDTA complex was formed. It was cooled to room temperature and diluted with 100 to 150 cm^3 of ethanol to remove any turbidity. The pH of this solutioin was adjusted between 5.2 to 6.0 using hexamine. The excess EDTA from this solution was determined by titration with standard 1.0×10^{-3} $Fe(NO_3)_3$ solution using 2.0 to 3.0 cm^3 of 0.2% hydroxytriazene indicator solution. The colour change at the end point was violet to yellow. The volume of excess EDTA found was used to determine the volume of EDTA consumed to form Cr(III)-EDTA complex. Thus the difference in total volume of EDTA taken to form Cr(III)-EDTA complex and the volume of excess EDTA found gave the volume of Cr(III). The results obtained have been shown in Table-2.

TABLE-2

COMPLEXOMETRIC DETERMINATION OF CHROMIUM(III) IN BINARY MIXTURE USING 3-HYDROXY-3-*m*-SULPHONATO(SODIUM SALT) PHENYL-1-*o*-NITROPHENYLTRIAZENE AS INDICATOR

S. No.	Binary metal ion mixtures	Titre value of EDTA in direct titration correspond to other metal ion cm^3	Vol. of excess EDTA added (a) cm^3	Vol. of EDTA consumed by $Fe(NO_3)_3$ in back titration (b) cm^3	Vol. of EDTA consumed by Cr(III) (c) c = (a – b) cm^3
1.	Cr(III)-Fe(III)	10.0	20.0	10.0	10.0
2.	Cr(III)-Cu(II)	10.0	20.0	10.0	10.0
3.	Cr(III)-Ni(II)	10.0	20.0	10.0	10.0

Thus 3-hydroxy-3-*m*-sulphonato (sodium salt) phenyl-1-*o*-nitrophenyltriazene can be used as metallochromic indicator for the selective complexometric determination of chromium from binary mixtures. Further, the amounts of metal ions experimentally determined from their mixtures have ben found to be in good agreement with the actual amounts of the metal ions taken in mixtures.

Complexometric Determination of Chromium(III) in Ternary Mixtures

General procedure of titration

Complexometric determination of chromium(III) in ternary mixtures of Cr(III)-Fe(III)-Cu(II), Cr(III)-Fe(III)-Ni(II) and Cr(III)-Cu(II)-Ni(II) was done by taking advantage of kinetic masking as well as pH adjustments. Since the Cr(III) did not react with EDTA in cold, first the two metal ions were determined using hydroxytriazene as indicator by titrating them against standard EDTA solution. Secondly the Cr(III) was determined by forming Cr(III)-EDTA complex, adding excess of EDTA and then back titrating the excess to know the concentration of Cr(III) in the mixture. For this, in a 500 cm^3 conical flask 15 cm^3 of the solution containing the three metal ions, *viz.*, Cr(III)-Fe(III)-Cu(II), Cr(III)-Fe(III)-Ni(II) or Cr(III)-Cu(II)-Ni(II) of 1.0×10^{-2} M were taken. The pH of the solution was adjusted between 5.0 to 6.0 for Fe(III), 4.0 to 5.0 for Cu(II) and 3.0 to 4.0 for Ni(II) determination in cold. Few drops of 0.2% hydroxytriazene indicator solution were added and 50 cm^3 of ethanol was also added to remove any turbidity. This solution was titrated against 1.0×10^{-2} M standard EDTA in cold to determine each of the other metal ions present at the respective pH. The colour at the end point changes from blue to yellow in case of Fe(III), yellow to green for Cu(II) and green to greenish yellow for Ni(II). The colour change was very sharp and perceptible. After recording this end point the solution was used for Cr(III)-EDTA complex formation and the same procedure described in case of binary mixture was used. The Cr(III) was finally determined by way of back titration in the same way as has been done earlier. Thus out of the ternary mixture all the three metal ions could be successfully determined complexometrically using hydroxytriazene as metallochromic indicator. The results obtained for Cr(III) determination in ternary mixtures of metal ions have been presented in Table-3.

TABLE-3
COMPLEXOMETRIC DETERMINATION OF Cr(III) IN TERNARY MIXTURES USING 3-HYDROXY-3-*m*-SULPHONATO (SODIUM SALT) PHENYL-1-*o*-NITROPHENYLTRIAZENE AS INDICATOR

S. No.	Ternary metal ion mixtures	Titre value of EDTA in direct titration corresponding to other metal ion cm^3				Vol. of excess EDTA added (a) cm^3	Vol. of EDTA consumed by $Fe(NO_3)_3$ in back titration (b) cm^3	Vol. of EDTA consumed by Cr(III) (c) c = (a–b) cm^3
1.	Cr(III)-Fe(III)-Cu(II)	Fe(III)	5.0	Cu(II)	5.0	10.0	5.0	5.0
2.	Cr(III)-Fe(III)-Ni(II)	Fe(III)	5.0	Ni(II)	5.0	10.0	5.0	5.0
3.	Cr(III)-Cu(II)-Ni(II)	Cu(II)	5.0	Ni(II)	5.0	10.0	5.0	5.0

The result shows that the amounts of metal ions actually present and found are in good agreement.

Conclusion

Thus the recommended method can be used for the selective complexometric determination of Cr(III) in very dilute solutions in presence of 20-fold excess of eleven diverse cations and anions. Also the use of this reagent in binary and ternary metal ion mixtures fosters the possibility of applying this reagent in trace amount for Cr(III) determination.

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