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Complexometric Determination of Chromium(III) from Binary and Ternary Mixtures Using 3-Hydroxy-3-Phenyl-1-*m*-Nitrophenyltriazens as Metallochromic Indicator

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A method for the use of 3-hydroxy-3-phenyl-1-*m*-nitrophenyl-triazene as metallochromic indicator for the complexometric determination of chromium(III) and for the complexometric determination of Cr(III) by kinetic masking in presence of other metal ions viz. Fe(III), Cu(II) and Ni(II) in binary mixtures containing ion pairs Cr(III), Fe(III), Cr(III), Cu(II) and Cr(III)-Ni(II) has been described. The study has been further extended to determine Cr(III) in ternary mixtures containing any of the three ions, *viz.*, Cr(III)-Fe(III)-Cu(II), Cr(III)-Fe(III)-Ni(II) and Cr(III)-Cu(III)-Ni(II). The amount of metal ions found was in good agreement with the amount of metal ions actually present; so the determinations are quite accurate. For the sake of comparison parallel titrations were carried out using xylenol orange as indicator. This establishes use of hydroxytriazene as metallochromic indicator for Cr(III) determination.

INTRODUCTION

Hydroxytriazenes are well established analytical reagents[1-5]. They have been used as metallochromic indicators for the complexometric determination of a number of transition and non-transition metals[6-12]. The survey of literature reveals that hydroxytriazenes have been recently used for both spectrophotometric and complexometric determination of Cr(III) in recent years in our laboratory.[13-19] In the present work 3-hydroxy-3-phenyl-1-*m*-nitrophenyl-triazene has been used as metallochromic indicator in the complexometric determination of Cr(III) from binary and ternary metal ion mixtures. In binary mixtures determination of Cr(III) has been done taking advantage of kinetic masking. In the ternary mixture both pH adjustment and kinetic masking were used for the determination of other two ions present with chromium.

EXPERIMENTAL

Preparation of Solutions

Metal ions: A stock solution of chromium(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 concentrated hydrochloric acid were added to prevent hydrolysis. The solution was standardized against EDTA at a pH between 3 to 4 adjusted using 1 M H_2SO_4[20-22] and xylenol orange was used as an indicator. Weaker solutions were prepared by appropriate dilution of the stock solution with double distilled water. Stock solutions of 1.0×10^{-2} M of Cu(II) and Ni(II) were

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prepared by dissolving requisite amounts of A.R. grade sulphates of these metal ions in double distilled water which were standardized by usual methods[23]. 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. A few drops of conc. HNO_3 were added to prevent hydrolysis of the solution. It was then standardized by titrating it against 1.0×10^{-2} M EDTA solution using sulphosalicylic acid as indicator[24]. Weaker solutions were prepared by appropriate dilutions.

***Indicator*:** A 0.2% indicator solution was prepared by dissolving the requisite quantity of 3-hydroxy-3-phenyl-1-*m*-nitrophenyl-triazene in acetone. Fresh solutions were prepared as and when needed.

***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.

Procedure of Titration of Chromium(III) Solution using 3-Hydroxy-3-phenyl-1-*m*-nitrophenyltriazene as Indicator

In a 5000 cm^3 beaker fitted with magnetic stirrer 10.0 cm^3 of 1.0×10^{-2} M standard Cr(III) solution and 15.0 cm^3 of 1.0×10^{-2} M EDTA solution were taken. This solution mixture was diluted with 25 cm^3 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 acetone were added. Further 100–150 cm^3 of acetone were also added to remove any turbidity. Turbidity was caused by slight precipitation of hydroxytriazene owing to its low solubility in aqueous media. 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 blue.

Results and Discussion

Optimum conditions of pH and Temperature of Titration: The effect of pH on titration was studied by carrying out a number 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 satisfactory results were obtained in the temperature range of 20°–50°C.

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 different concentrations were prepared and each of these solutions was complexed with EDTA solutions of corresponding concentrations. For back titration find out excess EDTA, Fe(III) solutions of required concentrations were also prepared. Titrations were performed under optimum conditions of pH and temperature. For the sake of comparison parallel titrations were carried out using xylenol orange as indicator. The results obtained have been shown in Table-1.

TABLE-1
COMPLEXOMETRIC DETERMINATION OF Cr(III) USING
3-HYDROXY-3-PHENYL-1-*m*-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	Sharp end point from violet to blue
2.	5.0×10^{-2} M	10.0	10.0	"
3.	2.0×10^{-2} M	10.0	10.0	"
4.	1.0×10^{-2} M	10.0	10.0	"
5.	5.0×10^{-2} M	10.0	10.0	"
6.	2.0×10^{-2} M	10.0	10.0	End point is not perceptible in both the indicators

Interference Studies: Interference studies were performed by complexing 1.0×10^{-2} M Cr(III) solution with excess 1.0×10^{-1} M EDTA solution. The excess EDTA was titrated with standard 1.0×10^{-2} M $Fe(NO_3)_3$ solution under optimum conditions in presence of varying quantities of each of the following 26 cations and anions using hydroxytriazene as indicator 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-}, $S_2O_3^{2-}$, CO_3^{2-}, and PO_4^{3-} ions. It was found that 5.2 mg of Cr(III) could be determined in presence of 10 mg of either of the following 16 cations and anions: Na(I), Ca(II), Mg(II), Ni(II), Cu(II). Ba(II), Zr(IV), Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-} and CO_3^{2-}. However 50 mg of Mg(II), Ni(II), Cu(II) and Zr(IV) ions were tolerated in the determination of 5.2 mg of chromium(III). There was not any observable colour change or formation of a precipitate due to the effect of Fe(III) on SO_3^{2-}, NO_2^- and $S_2O_3^{2-}$. Further, even in case of Zr(IV) in weakly acidic to neutral pH no such significant changes were observed. All those eleven ions which did not interfere up to 50 mg level also did not interfere at 100 mg level in the chromium 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 method 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-phenyl-1-*m*-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 in acetone were added to this solution. A further 50 cm^3 of acetone were added to remove any turbidity. The advantage of kinetic masking was taken in the determination of two metal ions from the mixture[25]. When the solution was cold Cr(III) did not react with the standard EDTA solution whereas the other ion 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 with 1 M H_2SO_4 and an excess of EDTA solution was added to i t . The mixture was boiled for 30 min 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 acetone to remove any turbidity. The pH of this solution was adjusted between 5.2 to 6.0 with hexamine. The excess EDTA from this solution was determined by titration with standard 1.0×10^{-2} M $Fe(NO_3)_3$ solution using 2.0 to 3.0 cm^3 of 0.2% hydroxytriazene indicator. The colour change at the end point was violet to blue. The volume of excess EDTA found was used to determine 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 given in Table-2.

TABLE-2
COMPLEXOMETRIC DETERMINATION OF CHROMIUM(III) IN Cr(III)-Fe(III), Cr(III)-Cu(II) AND Cr(III)-Ni(II) IN BINARY MIXTURES USING 3-HYDROXY-3-PHENYL-1-*m*-NITROPHENYLTRIAZENE AS INDICATOR

Binary metal ion mixtures	Titre value of EDTA in direct titration corres-ponds 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) (cm^3) c = (a – b)
Cr(III)-Fe(III)	10	20	10	10
Cr(III)-Cu(II)	10	20	10	10
Cr(III)-Ni(II)	10	20	10	10

This clearly reveals that hydroxytriazenes can be used as metallochromic indicator for the selective complexometric determination of Cr(III) ions from binary mixtures. Further, the amounts of metal ions experimentally determined from their mixtures have been 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 of Cr(III)-Fe(III)-Cu(II), Cr(III)-Fe(III)-Ni(II) and Cr(III)-Cu(II)-Ni(II)

General Procedure of Titration

The determination of three ions from the ternary mixture containing Cr(III) and any other two ions out of Fe(III)-Cu(II), Fe(III)-Ni(II) was done by taking advantage of kinetic masking as well as pH adjustments. Since Cr(III) did not react with EDTA in cold, first the other two metal ions were determined using hydroxytriazene as indicator by titrating them against EDTA solution. The colour change in case of Fe(III) is from blue to yellow to green for Cu(II) and green to greenish yellow in case of Ni(II) at the respective pH. 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 ternary mixture.

For this, in a 500 cm^3 conical flask 15 cm^3 of the solution containing 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 5.2 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 0.25% hydroxytriazene indicator solution were added and 50 cm^3 of acetone were 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 chromium was finally determined by way of back titration in the same way as has been done earlier. The results obtained have been summarized in Table-3.

TABLE-3
COMPLEXOMETRIC DETERMINATION OF Cr(III) IN TERNARY MIXTURE USING 3-HYDROXY-3-PHENYL-1-*m*-NITROPHENYLTRIAZENE AS INDICATOR

Ternary metal ion mixtures	Titre value of EDTA in direct titration corresponding to other metal ions (cm^3)				Vol. of excess EDTA added (a)	Vol. of EDTA consumed by $Fe(NO_3)_3$ in back titration (b) (cm^3)	Vol. of EDTA consumed by Cr(III) c = (a – b) (cm^3)
Cr(III)-Fe(III)-Cu(II)	Fe(III)	5	Cu(II)	5	10	5	5
Cr(III)-Fe(III)-Ni(II)	Fe(III)	5	Ni(II)	5	10	5	5
Cr(III)-Fe(III)-Ni(II)	Cu(II)	5	Ni(II)	5	10	5	5

A study of Table-3 reveals that determination of Cr(III) and other two metal ions from a ternary mixture can be successfully done using hydroxytriazene as indicator. The results further show that the values of metal ions actually present and found are in good agreement. So the determinations are quite accurate.

Conclusions

The recommended method can be used for the quantitative determination of chromium(III) alone in dilute solutions and also by kinetic masking in binary and ternary metal ion mixtures using 3-hydroxy-3-phenyl-1-*m*-nitrophenyl-triazene as metallochromic indicator by complexometric titrations. The method is advantageous since the titrations could be done in presence of 20-fold excess of the following eleven cations and anions, *viz.*, Na(I), K(I), Ca(II), Ba(II), Cl^-, Br^-, NO_2^-, NO_3^-, and CO_3^{2-}, 10-fold excess of Mg(II), Ni(II), Cu(II), Zr(IV) and SO_3^{2-} ions for 5.2 mg chromium(III) determination. This fosters the possibilities of applying this compound as metallochromic indicator for chromium(III) determination.

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