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Titrimetric Estimation of Hexacyanoferrate(III) With Iron(II) in Presence of Pyrophoasphate and Acetic Acid Medium

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ABSTRACT

These methods are not entirely satisfactory and suffer from one disadvantage or the other. For example, most of the reductants are not susceptable to aerial oxidation and hence required special apparatus for their storage under inert atmosphere. Potassium hexacyanoferrate(III) is well known as a oxidant particularly in alkaline medium and useful oxidemetric titrant known from a long time Berka&zyka[1] determination of numerous inorganic and organic substances. Some other reductents employed are expensive and the procedures reported are tedious and time consuming. The method developed using iron(II) in presence of fluoride affects glass-ware. Murthy and et.al; determination of HCF(III) iron(II) in phosphoric acid medium[2] for the first time not succeed in developing a visual end-point method using a redox indicator, because of the reported formation of a deep blue colour during the titration. We have now developed a direct visual end-point method for the determination of HCF(III) with iron(II) in presence of pyrophosphate and acetic acid medium employing thiazine dyes used as redox indicators keeping zinc sulphate in the rection medium to prevent the formation of blue colour during the titration. The method now developed does not suffer from any of the disadvantages associated with the earlier methods.

Keywords: Visual end-point Hexacyanoferrate(III), Thiazine dyes, Pyrophosphate

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INTRODUCTION

These methods are not entirely satisfactory and suffer from one disadvantage or the other. For example, most of the reductants are not susceptable to aerial oxidation and hence required special apparatus for their storage under inert atmosphere. Potassium hexacyanoferrate(III) is well known as a oxidant particularly in alkaline medium and useful oxidemetric titrant known from a long time Berka&zyka[1] determination of numerous inorganic and organic substances.

Some other reductents employed are expensive and the procedures reported are tedious and time consuming.

Iron(II) Solution: An approximately 0.05M solution of iron(II) in 0.1N sulphuric acid medium is prepared is prepared from (AR grade) ferrous ammonium sulphate and standardized[3] against a standard dichromate solution using diphenylamine as an indicator.

Hexacyanoferrate(III) solution:An approximately 0.05M solution of HCF(III) is prepared by dissolving the required amount of AR grade potassium hehacyanoferrate(III) salt (which is dried at 1000C) in distilled water. The strength of the solution is checked iodometrically[4] The solution is transferred into an amber coloured bottle and stored in dark place.

Pyrophosphate: A 0.2Msolution has been prepared in distilled water from AR grade tetra sodium pyrophosphate decahydrate.

Acetic acid: Glacial acetic acid [Sp.Gr. 1.05g] of AR grade has been utilized.

Zinc sulphate solution: A 3.0 M solution of zinc sulphate is prepared from AR grade zinc sulphate [ZnSO4.7H2O]

***Indicato*r:** Thiazine dyes like Azure-B, Azure-C, Toludine blue, Methyline blue, Thionine aqueous solutions of all the dyes[0.05%, (50mg in 100ml)] are prepared and standardized by titrating against a standard solution of titanium(III) chloride as described by Knecht and Hibbert[5].

METHODS

Experimental Data Table

Indicator	Amount Reference Method	$[Fe(CN)\ 6]^{-3}$ Authors Method x,mg	Pooled Standard Deviation, (sg)mg	$\frac{1.96Xsg.mg}{n}$	95% Confidenc limits $\frac{1.96Xsg.mg}{n}$
Azure-B	63.60	63.41	0.06	0.05	63.36 to 63.46
Azure-C	62.32	62.20	0.05	0.04	62.16 to 62.24
Toludine Blue	62.37	62.48	0.04	0.03	62.45 to 62.51
Methyline Blue	63.46	63.31	0.06	0.05	63.26 to 63.36
Thionine	64.13	63.98	0.05	0.04	63.94 to 64.02

To an ALIQUOT (3-12ml)of 0.05 M HCF(III) solution taken in a titration cell, required volume of zinc sulphate, pyrophosphate and aceticacid are added to give desired concentrations of about 0.05M, 5M and 1M respectively toowards the end-point and the total volume diluted to about 50ml.purified carbon dioxide gas is passed through the reaction mixture for about 3-4 minutes [to expel any dissolved oxygen], 4-5 drops of an indicator solution (above mentioned Thiazine dyes like Azure-B, Azure-C, Toludine blue, Methyline blue, Thionine) are added and it is

titrated against a standard(0.05M) iron(II) solution to a sharp colour transition of the indicator. The titrant iron(II) must be added drop-wise(3-4 seconds interval) near the end-point. The colour transitions of all the indicators are sharp and reversible. These are, disappearance of dark-blue colour. No indicator correction need be applied.

RESULTS AND DISCUSSION

In the present redox reaction, HCN(III) is reduced to HCN(II) by iron(II) in one electron reaction step while iron(II) is oxidized to iron(III) as per the eqution-I

$$Fe(II) + [\ Fe(CN)_6\ ]^{3-} \text{ --------} \rightarrow \quad Fe(II) + [\ Fe(CN)_6\ ]^{4-} \text{ …….1}$$

Thus, iron(II) functions as a powerful reductant in phosphoric acid medium. The decrease in potential is caused by the complex formation between iron(III) and phosphoric acid phosphoric acid as [Fe(HPO4)]+ . Based on these facts Murthy and co-workers could not develop a visual end-point method because of the reported formation of blue coloured complex between iron(III) and [Fe(CN) 6]4 - or HCF(II) as per eqution-2

$$4Fe(III) + 3[Fe(CN)_6]^{4-} \text{ --------} \rightarrow \quad Fe_4[Fe(CN)_6]^{3-} \text{……2}$$

The use of zinc sulphate in the reaction medium no doubt enabled the authors to develop a direct visual end-point method for the determination of HCF(III) with iron(II). This is because, zinc sulphate prevent the formation of blue coloured complex between iron(III) and [Fe(CN) 6] 6- or HCF(III) by removing the latter in the formation of a sparingly soluble complex as given in equation-3

$$2[Fe(CN)_6]^{4-} + 2K^{+} + 3Zn^{2+} \text{ --------} \rightarrow \quad K_2Zn_3[Fe(CN)_6]^{2-} \text{ ……3}$$

Further , since the titration is a crried out in a medium containing a high concentration of pyrophosphate(6M) most of the iron(III) formed during the titration gets complexed with pyrophosphate . Thus , it is evident from the above discussion that both zinc sulphate and pyrophosphate present in the reaction medium decrease the tendency of the complx formation (equation-2) between iron(III) and HCF(II) and thus help to the intensity of the blue coloured complex, facilitating the use of the redox indicators.

In fact the authors found that if the concentration HCF(III) exceeds1.50mg/ml in the overall reaction medium, the blue colour of the complex formed is too intense to detect the end-point during the titration using a redox indicator. Hence, the titration have been carried out using a 0.03 M HCN(III) solution such that the concentration does not exceed the limit.

Interferences: Chloride, sulphate, acetate, zinc(II), aluminium(III) and mercury(II) ions do not interfere. However, nitrate ion interferes at all concentration.

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