Reductimetric Determination of Copper (II) with Iron (II) in Phosphoric Acid Medium and in Presence of Bromide ion

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Abstract

A simple, accurate and convenient reductimetric titration method has been developed for the determination of copper(II) with iron(II). The method consists in titrating copper(II) against iron(II) in a medium containing 7.8M phosphoric acid and about 1.8M potassium bromide, either potentiometrically or visually using a thiazine dye, an oxazine dye or cacotheline as a redox indicator. Copper (II) in the range of 10-30 mg has been determined by the two methods. The accuracy of the potentiometric method is found to be ± 0.5% while that of the visual indicator method is ± 0.6%. The precision of the methods has been assessed by computing the pooled standard deviations and 95% confidence limits. The conditional redox potentials of the oxidant and reductant systems have been measured. Based on these potentials data the feasibility of the redox reaction has been explained. The interferences due to diverse ions have been studied.

Key Words: Copper (II), iron (ii), phosphoric acid medium, bromide ion, oxazine and thiazine dyes, cacotheline.

Introduction

Numerous reductimetric titration methods[1,2] have been reported in literature for the determination of copper(II). These methods generally utilize the reducts such as tin(II), titanium(III), vanadium(II), chromium (II), iodine, thiocyanate, ascorbic acid, hydroquinone, mercury(I)nitrate. All these methods have been discussed by Kothoff[1] and Berkas&Jyka[2]. Some complexometric titration methods have also been developed utilizing the titrants such as EDTA[3]. DTPA[4],dimethylglyoxime[5], cacotheline[6] etc. Further a few titrimetric methods involving the use of iron (II) as a reductant in a medium containing phosphoric acid[7] oxalate[8] or triethanolamine[9] (TEA) have also been reported. However, all these methods suffer from one disadvantage or the other. For example, the methods involving the conventional reductants [eg. Sn(II), Ti(III), V(II) Cr(II) etc.] Require special storage apparatus to preserve them under inert atmosphere, as they are highly sensitive to atmospheric oxidation. Some of the other methods[5,6] are expensive while in some other methods, the titration need be carried out in a narrow pH range[8] or at elevated temperatures.

In the method developed using iron(II) as a reductant in phosphoric acid medium containing thiocyanate[7], all the indicators must be added near the end-point, while that in alkaline TEA medium[9], iron(II) undergoes rapid aerial oxidation.

We have now developed both potentiometric and visual end-point methods for the determination of copper (II) using iron (II) as a reductant in phosphoric acid medium and in presence of bromide ion. The methods now developed do not suffer from any of the

disadvantages associated with the earlier methods.

Material and Methods

Preparation of solutions: Copper (II) Solution: A 0.05M solution of copper (II) is prepared from AR grade copper (II) sulphate pentahydrate and its strength checked iodometrically[10].

Iron (II) Solution: An approximately 0.05M solutioin of iron (II) [in 0.5M sulphuric acid medium] is prepared and standardized against a standard solution of dicthromate[11].

Orthophosphoric Acid: Orthophosphoric Acid of AR grade has been made use of in this investigation.

Potassium Bromide solution: About 6.0M aqueous solution of potassium bromide is prepared from its AR grade salt.

Hydrochloric Acid Solution: An AR grade hydrochloric acid has been made use of in this investigation.

Indicator Solutions: 0.1% (w/v) aqueous solutions of the following thiazine dye solutions: Azure A, AzureB, AzureC, Toluidine Blue, Methylene Blue have been prepared.

0.1% (w/v) aqueous solutions of the following oxazine dyes: Severon Blue 5g; Solochrome Prune AS have also been prepared.

A 0.2% (w/v) solution of cacotheline dissolved in 0.02M hydrochloric acid solution has been used.

Apparatus: A digital potentiometer is used for measuring the potentials. A bright platinum rod (02mm diameter) and a saturated calomel electrode serve as indicator and reference electrodes respectively. A porous glass plate end salt bridge filled with saturated potassium chloride is used.

Recommended procedure: To an aliquot (3-10 ml) of copper(II) solution taken in a 150ml beaker, enough orthophosphoric acid and potassium bromide solutions are added to give the strengths of 7.0M and 1.8M respectively towards the equialence point. Purified carbon dioxide gas is passed for about 3-4 minutes to expel any dissolved oxygen. The contents are then titrated against iron (II) solution either potentiometrically or visually using any one of the indicators mentioned above to detect the end-point. The break in potential at the end-point is found to be about 60mv in the potentiometric method. The colour transition of the indicator is sharp and reversible in all visual titrations. These are from blue to colourless in the case of thiazine dyes; red to colourless with an oxazine dye and yellow to pink in the case of cacotheline. No indicator correction need be applied in all visual determinations.

Results and Discussion

Some of the typical results obtained by the above recommended procedure have been given in the table no.1.

The accuracy of the potentiometric method is $\pm$ 0.5%, while it is $\pm$ 0.6% in all visual determinations. The precision of the methods is expressed in the form of pooled standard deviation and 95% confidence limits computed as described by Skoog and West[12].

In all these determinations, copper (II) is rapidly and quantitatively reduced to copper (I) by iron (II). At the end point all the indicators, except resorufin and cacotheline are reduced to their corresponding colourless leuco-bases in a two electron reduction step[13,14.] Cacotheline is reduced to pink coloured reduction product in a two electron reduction[15], while Resorufin is reduced to its blue-green semiquinone in a one electron reduction step[16,17]. The structures of all these dyes and their corresponding reduction compounds are available in literature[13-17].

When copper (II) solution in phosphoric acid medium is treated with potassium bromide solution, a redish brown colour is noticed, most probably, it is due to the complex formation between copper (II) and bromide ion. During the titration of copper (II) with iron(II), however, the red coloured copper(II) bromide

complex, may be reduced to colourless copper(I)-bromide complex. However, the colour transition, without the use of a redox indicator is not sharp enough to detect the end-point. Therefore, different redox indicators have been made use of in this determination successfully.

It is a well known fact that copper (I) is highly sensitive to atmospheric oxidation and must be stabilized by complexation with a ligand. The authors presume that bromide ion [log K_2 = 5.9] complexes[18] copper (I) better than chloride ion [log K_1 = 2.7, log K_2 = 5.5; log K_3 = 5.7]. Our presumption is strengthened by our observation that no potentiometric and visual end point-point methods have been found feasible even in the presence of a high concentration of chloride ion.

To explain the conditions needed in the reductimetric determination, the formal redox potentials of the oxidant system [eg. Cu(II) / Cu(I)] and that of the reductant system [Fe(III) / Fe(II)] under the optimum titration conditions [this is called the conditional potential] are necessary. Hence, these potentials have been measured adopting the procedure of Conant and Fieser[19] and found them to be 760mv $\pm$ 10mv and 440mv $\pm$ 10mv for oxidant and reductant systems respectively. From these potentials data it may be seen that there is a potential difference of about 320mv between the two systems facilitating the rapid reduction of copper (II) by iron (II). Thus these potentials data neatly explain the conditions needed in the titration.
However, it is known fact that iron (II) functions as a powerful reductant [7,17,20] in phosphoric acid medium, hence the titrotions are carried out in this acid medium.

Study of interferences: Chloride, sulphate, acetate, oxalate, zinc (II), manganese (II) and aluminium (III) do not interfere with the determination of copper (II). The colours of chromium (III), nickel (II) and cobalt (II) interfere, if the concentration of these ions exceeds 0.8mg/ml.,4mg/ml and 2mg/ml respectively. Nitrite and nitrate ions interferes at all concentrations.

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Table-1: Reductimetric Determination of Copper (II) with Iron (II)

Copper (II) Found*		Pooled standard deviation Sg, mg	$\frac{1.96 \times Sg}{\sqrt{n}}$ mg	95% confidence limits $\frac{x \pm 1.96 \times Sg}{\sqrt{n}}$
Ref. Method[10] mg	Author's method x, mg			
A. Potentiometric Method				
9.53	5.97			9.52 to 9.62
15.88	15.95			15.90 to 16.00
22.24	22.13	0.06	0.05	22.08 to 22.18
28.59	28.49			28.44 to 28.54
31.97	31.86			31.81 to 31.91
B. Visual Method [A Thiazine Dye as an Indicator]				
10.36	10.30			10.24 to 10.36
12.25	15.32			15.26 to 15.38
20.33	20.41	0.08	0.06	20.35 to 20.47
31.45	31.33			31.27 to 31.39
C. Visual Method [An oxazine Dye as an Indicator]				
10.48	10.45			10.38 to 10.52
15.57	15.65			15.57 to 15.73
21.92	21.82	0.08	0.07	21.72 to 21.90
29.55	29.66			29.58 to 29.74
D. Visual Method [Cacotheline as an Indicator]				
11.12	11.06			11.00 to 11.12
14.29	14.35			14.29 to 14.41
20.65	20.73	0.07	0.06	20.67 to 20.79
30.18	30.06			13.00 to 30.12