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Reductimetric Determination of Copper(II) With Iron(II) in Phosphoric Acid Medium And in Presence of Bromide Ion

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A simple, convenient and accurate reductimetric titration method has been developed for the determination of copper(II)(in the range 10-30 mg) with iron(II) in phosphoric acid medium (*ca.* 7 M) and in presence of bromide ion (*ca.* 2.0 M). The end point can be detected either potentiometriclly (accuracy ± 0.4 %) or using cacotheline as a redox indicator (accuracy ± 0.6 %). The precision of the method is determined by computing the pooled standard deviation and 95 % confidence limits. The method has been extended to the determination of copper content in a sample of brass and copper-nickel alloy. The formal redox potentials of the oxidant [Cu(II)/Cu(I)] and reductant [Fe(III)/Fe(II)] systems in the optimum titration conditions and the transition potential of the indicator have been measured and explained the conditions needed in the titration as well as the effect of bromide ion. The interference due to diverse ions has been studied and the advantages of the present method over the existing ones have been discussed.

Key Words: Copper(II), Iron(II), Phosphoric acid medium, Bromide, Cacotheline.

INTRODUCTION

Reductimetric methods for the determination of copper(II) are mainly based on the reduction of copper(II) to copper(I) using suitable reductants like tin(II)[1,2], titanium(III)[2-4], vanadium(II)[5,6], chromium(II)[7], iodide[8], thiosulphate[9], ascorbic acid[10], mercury(I) nitrate[11], *etc*. Procedures employing iron(II)[12-16] [in phosphoric acid medium and in presence of thiocyanate[12,13], in buffer medium containing oxalate and thiocyanate[14,15] or in alkaline triethanolamine medium[16]] *etc*., have been developed. Methods involving the trivial reductants like hydroquinone, hydrazine sulphate, bismuth amalgam, sulphur dioxide *etc*., are available in litrrature[17,18]. Complexometric titration methods involving the use of EDTA[19], DTPA[20] have also been developed. All these methods suffer from one disadvantage or other. For example, the first mentioned four reductants (called the conventional reductants) are highly sensitive to atmospheric oxidation and require special apparatus for their storage. The iodometric method is expensive and must be carried out in a pH range 0.5-3.0. The methods developed with other reductants except iron(II) are feasible for the use of only to a few redox indicators. In the procedures developed using iron(II) as a reductant in phosphoric acid medium and in presence of thiocyanate, the indicators must be added near about the end-point. In buffer-oxalate medium, the titration must be carried out in a narrow pH range of 4-5; while in alkaline triethanolamine medium iron(II) undergoes rapid aerial oxidation and so, a vigorous inert atmosphere is needed.

We have now developed a convenient reductimetric titration method for the determination of copper(II) with iron(II) in phosphoric acid medium of about 7-8 M and in presence of about 2 M bromide ion. This new method now reported obviates most of the disadvantages of the earlier methods. The end-point in the method can be detected either potentiometrically or using cacotheline as a redox indicator. The present method has also been extended to the determination of copper content in a sample of brass and copper-nickel alloy.

EXPERIMENTAL

All the solutions were prepared in distilled water using analytical grade reagents unless otherwise stated.

A 0.05 M solution of iron(II)[21] [from ammonium iron(II) sulphate hexahydrate] in 0.5 N sulphuric acid medium and a 0.05 M solution of copper(II)[8] [from copper(II) sulphate pentahydrate] were prepared and standardized[8,21]. Solutions of potassium bromide (6.0 M), cacotheline[22] 0.2 % (w/v) have been prepared. Orthophosphoric of AR grade has been utilized.

A digital potentiometer with a bright platinum rod (as indicator electrode) and a saturated calomel electrode (as reference electrode) has been used for potential measurement. All the titrations have been carried with the help of a magnetic stirrer.

Recommended procedure: To an aliquot (3-10 mL) of 0.05 M copper(II) solution taken in a 150 mL beaker, enough phosphoric acid and potassium bromide (6.0 M) solutions are added to get the strengths of about 7.0 and 2.0 M, respectively towards the end-point. After passing purified nitrogen gas for about 2 min to expel any dissolved oxygen, the contents are titrated against iron(II) solution either potintiometrically or using cacotheline as a redox indicator. The break in potential at the end-point is found to be about 70-90 mV [for the addition of 0.05 mL of 0.05 M iron(II)] in the case of potentiometric method. The colour transition of the indicator, cacotheline, at the end-point is from yellow to pink and it is found to be sharp and reversible. Some of the typical results obtained by both methods have been furnished in Table-1.

Procedure for the analysis of copper-nickel alloy and brass for copper content

Copper nickel alloy: 1-2 g of an accurately weighed alloy, in the form of drillings, is dissolved in about 50 mL of 10 M nitric acid and gently warmed to get a clear solution[23]. To decompose, nitrate which interferes in the method, the reaction mixture is treated with about 5 g of urea and boiled briskly for 4-5 min. Then, it is cooled to room temperature, transferred into a 100 mL standard flask along with its washings and diluted to the mark. A 10 mL aliquot of the solution is analyzed for copper content either potentiometrically or using cacotheline as a redox indicator as described in the recommended procedure, in phosphoric acid medium and in presence of bromide ion. The results are compared with the standard iodometric method[8] and presented in Table-2.

Analysis of brass: 1-2 g of the accurately weighed sample in the form of drillings is dissolved in about 100 mL of 10 M nitric acid and heated on a water bath to about half of its original volume[23]. The solution is cooled to room temperature and filtered through a Whatmam No. 42 filter paper. The nitrate (interferes in the method) present in the solution is removed by boiling with concentrated sulphuric acid to fumes and cooled to room temperature. The solution along with its washings is transferred into a 100 mL standard flask and diluted to the mark. A 10 mL aliquot is now analyzed for copper content as described above (in the case of copper nickel alloy) and the results are compared with a standard method[8]. Some of the typical results obtained are presented in Table-2.

RESULTS AND DISCUSSION

The accuracy of potentiometric method has been found to be ± 0.4 % while that for the visual end-point method it is ± 0.6 %. The precision of the methods expressed in the form of pooled standard deviation or relative standard deviation has been included in Tables 1 and 2. In order to explain the conditions necessary for the rapid reduction of copper(II) by iron(II) [based on the redox potentials data], the author has measured the formal redox potentials of the copper system or oxidant system [Cu(II)/Cu(I) couple] and those of iron system or reductant system[iron(III)/iron(II) couple] at different concentrations of orthophosphoric acid (in the range 7-10 M, at a fixed bromide ion concentration of 2 M) and at different concentrations of bromide ion (in the range 2-3 M, at a fixed concentration of phosphoric acid concentration of 7.0 M). The

TABLE-1
REDUCTIMETRIC DETERMINATION OF COPPER(II) WITH IRON(II)

Copper(II) found		Pooled standard deviation (S_g) (mg)	$\frac{1.96 \times S_g}{\sqrt{n}}$	95 % Confidence limits (mg) $\overline{X} \pm \frac{1.96 \times S_g}{\sqrt{n}}$
Reference method[8]	Present method*			
Potentiometric method				
9.53	9.55	0.06	0.05	9.50-9.60
15.89	15.85			15.80-15.90
22.24	22.30			22.25-22.35
31.77	31.66			31.61-31.71
Visual end-point method (cacotheline as indicator)				
9.85	9.90	0.09	0.07	9.83-9.97
16.20	16.27			16.20-16.34
22.56	22.46			22.39-22.53
31.14	31.01			30.94-31.08

*Average of six determinations.

TABLE-2
ANALYSIS OF COPPER-NICKEL ALLOY AND BRASS FOR COPPER CONTENT

Sample taken (g)	Copper(II) found* (%)			Relative standard deviation (%)	
	Standard Method[8]	Author's Method			
		Potentiometric method	Indicator method	Potentiometric method	Indicator method
Copper-nickel alloy					
1.0	74.78	75.07	74.39	0.335	0.341
1.5	74.80	74.56	74.50	0.326	0.331
2.0	74.70	74.48	74.93	0.298	0.302
Brass-sample					
1.0	59.30	59.55	59.59	0.270	0.277
1.5	59.38	59.15	59.65	0.269	0.275
2.0	59.14	59.25	58.93	0.259	0.263

*Avarage of six determinations.

potentials of the copper systems have been measured adopting the procedure of Canant and Fieser[24], while those of iron by the method of Rao and Dikshitulu[25], respectively and shown in Tables 3 and 4. The redox potentials of copper system obtained by the previous authors in phosphoric acid medium only[26] (in the absence of bromide ion) have been shown in Table-3 for comparison. Since bromide ion found to have no effect on the redox potential of iron system, in phosphoric acid medium, the potentials of the system measured in the acid medium (in the range 7-10 M) at a fixed bromide concentration of 2.0 M have been shown in Table-3 for comparison.

TABLE-3
CONDITIONAL REDOX POTENTIALS OF COPPER(II)/COPPER(I) AND IRON(III)/IRON(II) COUPLES AT A FIXED BROMIDE ION (2.0 M) AND AT VARIED CONCENTRATIONS (7-10 M) OF PHOSPHORIC ACID

Concentration of phosphoric acid (M)	Cu(II)/Cu(I) potential, (NHE), ± 5 mV		Fe(III)/Fe(II) potential, (NHE), mV ± 5 mV
	In the absence of bromide ion[26]	In the presence of bromide ion	
7.0	430	750	448
8.0	483	763	438
9.0	510	775	429
10.0	515	780	421

TABLE-4
FORMAL REDOX POTENTIAL OF Cu(II)/Cu(I) SYSTEM AT DIFFERENT BROMIDE ION CONCENTRATIONS AND AT A FIXED PHOSPHORIC CONCENTRATION OF 7.0 M

Concentration of bromide ion (M)	Cu(II)/Cu(I) potential, (NHE), mV ± 5mV
2.0	749
2.4	752
2.8	760
3.0	764

NHE = Normal hydrogen electrode.

From the potentials data presented in Table-3, it may be seen that the redox potentials of copper system in phosphoric acid medium are found to be higher in presence of bromide ion than in the acid medium alone. It may further be seen that under the optimum titration conditions (7-10 phosphoric acid and 2.0 M bromide ion), the difference in potentials of the oxidant and reductant systems is found to be more than 300 mV which is theoretically more than sufficient to bring rapid reduction of copper(II) by iron(II).

In the absence of bromide ion, the potential difference between the two couples is found to be too small (45-95 mV) to achieve reduction of copper(II) by iron(II). Rao and Sagi[27] earlier reported that the formal redox potential of iron system decreases from about 680-380 mV with increase in phosphoric acid concentration from zero to 12 M. Thus iron(II) functions as a better reducing agent in phosphoric acid medium. However, the observed increase in potential of copper system in presence of bromide ion (Table-4) may be due to the complex formation between copper(I) and bromide ion which also prevents the aerial oxidation of copper(I). The log K_2 value of this complex, 5.9 reported in literature[28] strengthens our above contention. Recently, a report on the redox and spectral behaviour of copper(II) chloro and bromo complexs has been published[29]. Thus, these potentials data neatly explain the conditions needed in the titration.

The author has measured the transition potential of the indicator as described by Belcher *et al*.[30] and observed it to be 590 ± 5 mV. It is found to be intermediate between the formal potentials of the copper (750 mV) and iron (448 mV) systems observed under optimum titration conditions (7.0 M phosphoric acid and 2.0 M bromide ion). Thus, these potentials data explain the feasibility of cacotheline as a redox indicator in the titration.

Study of interferences: The interference of foreign ions has been studied and found that chloride, sulphate, oxalate, Zn(II), Mn(II),and Al(III) do not interfere. The colours of Cr(III), Ni(II) and Co(III) interfere if the concentrations of these ions exceed 0.8, 4.0 and 2.0 mg/mL, respectively. Nitrate and nitrite ions interfere at all concentrations.

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