Resorufin as a New Redox Indicator in the Determination of Copper(II) with Iron(II)

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A simple accurate and convenient reductimetric titration method has been developed for the determination of copper(II) using iron(II) as a reductimetric reagent and employing resorufin as an advantageous redox indicator. The method consists in titrating copper(II) with iron(II) in 7-8 M phosphoric acid medium and in presence of 1.8 M bromide or 2.0 M chloride ions using resorufin as a redox indicator. The colour transition of the indicator at the end-point (red to green) is sharp and reversible and no indicator correction need to be applied. Copper(II) in the range 10-30 mg has been determined with an accuracy of ± 0.6 %. The precession of the method has been determined by computing the pooled standard deviation and 95 % confidence limits. The method developed has been extended for the determination of copper content in a sample of brass. The formal redox potentials of [copper(II)]/[copper(I)] couple or oxidant system and those of [iron(III)]/[iron(II)] couple or reductant system have been measured under the above mentioned optimum titration conditions and explained the conditions needed in the titration. The role of chloride and bromide ions has been briefly discussed. The transition potential of the indicator resorufin has been measured and explained its suitability as a redox indicator in the method. The interferences due to diverse ions have also been studied.

Key Words: Copper(II), Iron(II), Resorufin, Phosphoric acid, Bromide, Chloride, Brass.

INTRODUCTION

Resorufin (RSF) belongs to an oxazine group of dye. Earlier workers investigated its use as a redox indicator[1-4] in the determination of only a few metal ions. Recently, we have investigated its use as the most advantageous redox indicator in numerous reductimetric determinations[5-7] carried out in phosphoric acid medium using iron(II) as a reducing agent. Previous authors[8-11] employed some oxazine and thiazine group of dyes, cacotheline *etc.*, as redox indicators in these reductimetric determinations. However, the use of these indicators made the maintenance of inert atmosphere imperative because, the reduced products (or leuco bases) of these dyes obtained at the end-point by reduction with iron(II) are sensitive to atmospheric oxygen. More over the colour transition of most of these indicators (from blue, pink or yellow, to colourless) is difficult to detect. In all these determinations resorufin is found to be an advantageous redox indicator, because its colour transition at the end-point from red to dark green is conspicuous, thus it can be easily detected. The dark green reduced product obtained by the reduction of iron(II) at the end-point is stable to atmospheric oxidation for 5-6 min[6]. Hence, no inert atmosphere needs to be maintained when resorufin is employed as a redox indicator in these determinations. In view of these advantages associates with resorufin as an indicator, we have

now investigated its use as a redox indicator in the determination of copper(II) with iron(II) in phosphoric acid medium and in presence of either chloride or bromide ions.

The existing methods so far available for the reductimetric determination of copper(II) are mainly based on the reduction of copper(II) to copper(I) using suitable reductants like tin(II)[12], titanium(III)[13], vanadium(II)[14], chromium(II)[15], iodide[16], thiosulphate[17], ascorbic acid[18] mercury(I) nitrate[19], *etc*. Procedures employing iron(II)[4,6,20-22] as a reductant (in phosphoric acid medium and in presents of thiocyanate[6,20], in buffer medium containing oxalate and thiocyanate[4,22] or in alakaline triethanol-amine medium[22]), *etc*. have been reported. Methods involving less common reductants like hydroquinone, hydrazine sulphate, bismuth amalgam, sulphur dioxide, *etc.*, are available in literature[23,24]. Complexometric titration methods involving the use of EDTA[25], DTPA[26] have also been developed. These methods are not entirely satisfactory because some of the reductants[12-15] are sensitive to atmospheric oxidation and hence need a special storage apparatus to prevent this. The iodometric method[16] is expensive further, it was recommended to be carried out in a narrow pH range of 3-4. The disadvantageous associated with the methods developed using iron(II) as a reductant in different media may be summarized as follows: In phosphoric acid medium and in presence of

thiocyanate all the indicators are suggested to be added near about the end-point and the titration was recommended to be carried out in an inert atmosphere; in buffer medium and in presence of oxalate, the determination must be carried out in a narrow pH range of 4-5 and in alkaline triethanolamine medium iron(II) undergoes very rapid aerial oxidation.

Recently, we reported reductimetric titration methods for the determination of copper(II) in phosphoric acid medium in presence of bromide ion and employing cacotheline[27] and some oxazine and thiozine[28] dyes as redox indicators. In these methods, however, the colour transition of most of the indicators being from blue/red/yellow to colourless is difficult to detect. Further, inert atmosphere must be maintained throughout the titration to prevent the aerial oxidation of the leuco-dyes obtained at the end-point by the reduction of iron(II). The method now developed using resorufin as a redox indicator in the reductimetric determination of copper(II) with iron(II) in phosphoric acid medium does not suffer from any of the disadvantages associated with the earlier methods.

EXPERIMENTAL

All the solutions were prepared in distilled water and all the reagents used are of analytical reagents grade unless otherwise stated. An approximately 0.05 M solution of iron(II) has been prepared from ammonium iron(II) sulphate hexahydrate in 0.5 M sulphuric acid medium and standardized[29]. An 0.05 M aqueous solution of copper(II) has been prepared from copper(II) sulphate pentahydrate and standardized[16]. A 6.0 M aqueous solution of potassium bromide has been prepared. An 0.05 % (50 mg in 100 mL) solution of resorufin (Aldrich, USA) has been prepared in 0.05 M sodium hydroxide medium. A digital potentiometer with bright platinum rod (as an indicator electrode) and a saturated calomel electrode (as a reference electrode) has been used for potential measurements. All the titrations have been carried with the help of a magnetic stirrer.

Recommended procedure: To an aliquot of (3-10 mL) of 0.05 M copper(II) solution taken in a 150 mL beaker, required volumes of syrupy phosphoric acid, 10 M hydrochloric acid or 6 M potassium bromide solutions are added to get their strengths as 7-8, 1.8 and 2.0 M, respectively towards the equivalence point. The solution is now diluted to 50 mL and 0.2-0.3 mL of the indicator solution is added. Purified carbon dioxide gas is passed through the reaction mixture for 3-4 min and the contents are then titrated against iron(II) solution (0.05 M) on a magnetic stirrer to a sharp colour transition from red to green. No inert atmosphere need be maintained during the titration. No indicator correction need be applied. Some of the typical results obtained by the recommended procedure have been presented in Table-1.

Analysis of copper in brass sample: The method now developed has been extended for the determination copper content present in a sample of brass as per the following procedure: A brass sample taken was converted into fine drillings. Three different accurately weighed (1.0, 1.5 and 2.0 g) samples of the drillings were taken into three different beakers and each one of them was dissolved in 100 mL of 10 M nitric acid and heated on a water bath to about half of its original

| TABLE-1 |||||
| RESORUFIN AS A NEW REDOX INDICATOR IN THE DETERMINATION OF COPPER(II) WITH IRON(II) |||||
Ref. method[16] (mg)	Author's method $\bar{x}$ (mg)	Pooled standard deviation (Sg) (mg)	$\dfrac{1.96 \times Sg}{\sqrt{n}}$ (mg)	95 % confidence limits $\bar{x} \pm \dfrac{1.96 \times Sg}{\sqrt{n}}$
9.54	9.58			9.54-9.62
13.04	12.98			12.94-13.02
15.90	15.82			15.78-15.86
19.71	19.78	0.05	0.04	19.74-19.82
23.21	23.14			23.10-23.18
26.08	26.13			26.09-26.17
30.21	29.82			29.78-29.86

volume[30]. Each of the solution was cooled to room temperature and filtered through a Whatman No. 42 filter paper. The nitrate content present in the sample was removed by boiling with 5 mL of concentrated sulphuric acid to fumes and cooled to room temperature. Each of the solution along with its washings is transferred into a 100 mL standard flask and diluted to volume. From each of the flask, a 10 mL aliquot was analyzed for copper content (six times) as described above by carrying out the titration against a standard iron(II) solution in 7-8 M phosphoric acid, 1.8 M potassium bromide or 2.0 M hydrochloric acid medium employing resorufin as a redox indicator. From the titre value the percentage of copper content has been computed for each solution and compared with the value obtained by the standard iodometric method. The percentage copper content obtained by present method has been found to be 59.30 ± 0.07 and this is in good agreement with the value of 59.32± 0.06 % obtained by the standard iodometric method[16].

RESULTS AND DISCUSSION

The accuracy of the method has been found to be ± 0.6 %, the precision of the method expressed in the form of pooled standard deviation and 95 % confidence limits has also been included in Table-1. The accuracy and precision of the method are found to be the same whether the medium contains chloride or bromide ion.

In order to explain the conditions needed in the titration for rapid reduction of cpper(II) with iron(II), we have also measured formal redox potentials of the oxidant system ([Cu(II)]/[Cu(I)] couple) and those of the reductant system ([iron(III)]/[iron(II)] couple) under the optimum titration conditions (7 M phosphoric acid and 1.8 M bromide or 2 M chloride ion medium) adopting the procedure of Murthy and Murthy[31] (in the case of oxidant system) and that of Rao and Dikshitulu[32] (in the case of reductant system). These potentials so obtained have been shown in Table-2.

From these potentials data (Table-2), it may be seen that the difference in potential between the two systems is 300 mV or above in 7 M phosphoric acid medium and in presence of either chloride or bromide ions. In the absence of chloride or bromine ions, the potential of oxidant system (copper system) has been observed to be too low to achieve the reduction of copper(II) by iron(II); further stable potentials of the oxidant system have not been obtained in the absence of the halide ions. Thus, these potentials data satisfactorily accounted for the conditions needed in the observed redox reaction.

TABLE-2 FORMAL REDOX POTENTIALS OF OXIDANT (COPPER) AND REDUCTANT (IRON) SYSTEMS		
Medium	Formal redox potentials, mV ± 5 mV (NHE)*	
	[Cu(II)]/[Cu(I)] couple	[Fe(III)]/[Fe(II)] couple
7 M H_3PO_4 and 2 M chloride ion	740	440
7 M H_3PO_4 and 1.8 M bromide ion	770	450
*With respect to normal hydrogen electrode.		

It is a known fact that copper(I) forms stronger complex with either chloride or bromide ions than with copper(II), because the stability constants of chloro or bromo complexes of copper(I) were reported[33,34] to be considerably higher than those of the corresponding complexes of copper(II) in aqueous medium. It is presumed that copper(I) is more strongly bound by either of the halide ions in the form of a complex than copper(II), causing considerable increase in the potential of [Cu(II)]/[Cu(I)] couple in the presence of chloride or bromide ions. The stability constants of the complexes formed between copper(I) and chloride ($\beta_2 = 1.14 \times 10^6$; $\beta_3 = 0.87 \times 10^6$) and copper(I) bromide ($\beta_2 = 1.89 \times 10^6$; $\beta_3 = 2.80 \times 10^7$) reported in literature[34] confirm this view. Further, from the above values of stability constants, it may be seen that bromo-complexes were reported to be slightly higher values than those of the chloro-complexes, indicating that copper(I) forms stronger complex with bromide ions rather than with chloride ions. However, the titration using resorufin as an indicator is found feasible either in the presence of chloride or bromide ions.

The transition potentials of the indicator in the above determination as described by Belcher *et al.*[35] were also measured. In order to explain the suitability of the redox indicator in the determination. These values are found to be 595 ± 10 and 610 ± 10 mV, respectively in the presence of chloride and bromide ions. These potentials are found to be intermediate between the formal potentials of the oxidant and reductant systems observed under optimum titrations conditions. Thus these potential data explain the feasibility of resorufin as a redox indicator in the titration.

Study of interferences: The interference of foreign ions has been studied and found that chloride, sulphate, oxalate, zinc(II), manganese(II) and aluminium(III) do not interference. The colours of chromium(III), nickel(II) and cobalt(III) interference 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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