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# Spectrophotometric Determination of Micro Amounts of Copper(II) using Resacetophenone

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Copper(II) forms a light green colour soluble complex with resacetophenone (2,4-dihydroxy acetophenone) in acetic acid-sodium acetate buffer medium of pH 4.7–5.4 and in aqueous dimethyl formamide solution containing very low concentrations of boric acid. The complex has maximum absorbance at 370 nm. The complex is stable for more than 24 h. Beer's law is obeyed upto 19 ppm of Cu(II) at 385 nm and 400 nm. The effect of various diverse ions is also studied. The method is applied for the estimation of micro amounts of copper in brass sample and the results are found to be in good agreement upto 8 ppm of Cu(II).

## INTRODUCTION

Various chromophoric reagents have been reported in literature for the spectrophotometric analysis of copper(II) in recent years. They include resacetophenone (2,4-dihydroxy acetophenone) derivatives such as resacetophenone oxime[1] and thiocarbazone and semicarbazone of resacetophenone[2] as potential reagents. On the other hand, the parent ketone, resacetophenone itself has been successfully employed as a sensitive analytical reagent for the indirect spectrophotometric determination of micro quantities of vanadium(V)[3], anions[4] like fluoride, oxalate, tartrate and citrate and direct spectrophotometric analysis of uranium(IV)[5]. The authors noticed that copper(II) forms a light green colour soluble complex in pH range 5–7, under specific conditions and this prompted them to study the versatility and use of resacetophenone as an analytical reagent for the spectrophotometric analysis of copper(II).

## EXPERIMENTAL

Absorbance measurements are made on Milton Roy Spectronic 1001 plus and pHs are read on Elico-Digital pH meter model LI-120.

Resacetophenone is prepared by the standard procedure[6]. Stock solutions of 0.1 MRP in pure dimethyl formamide and 0.01 M Cu(II) in double distilled water are used for the studies. All dilutions are made using double distilled water. All other chemicals used are of AR/GR grade.

## RESULTS AND DISCUSSION

The colour reaction is tested in both acid and alkaline media using buffer systems, sodium acetate-acetic acid, ammonium chloride-ammonia and boric acid media.

In sodium acetate-acetic acid buffer solution the complex is found to be in soluble form in the pH range 4.7–5.4. In ammonium chloride-ammonia buffer solution although a clear green colour solution is obtained at lower pH values (6.0–7.0) immediately after mixing, it turned into brown colour solution followed by precipitation with time. The complex is found to be insoluble form in aqueous dimethyl formamide solution but in very low boric acid concentrations only, the pH range being 5–7. 40 Per cent dimethyl formamide containing $8 \times 10^{-4}$ M boric acid reading 6.45 pH is chosen as optimum medium for further studies based on the studies of colour and stability. 1 ml of 0.01 M Cu(II) solution, 2 ml of 0.01 M borate solution, 5 ml of dimethyl formamide and 5 ml of 0.1 M resacetophenone in dimethyl formamide in a total volume of 25 ml are taken in all measurements except in studies where the concentration of the respective species is to be varied. The reagent blank is used in each case containing all species except Cu(II) solution in the same concentration as that of the solution.

### Absorption Spectra

The spectrum of the complex is recorded over the wavelength range 350–435 nm against reagent blank. The complex has maximum absorption at 370 nm in the optimum experimental conditions, but the reagent has considerable absorption at this wavelength. Hence, the study is made at two other wavelengths, 400 nm and 385 nm, based on the following factors. At 400 nm the reagent has negligible absorption compared to the absorption of the complex. However, the absorption due to complex is also less. At 385 nm the absorption of the reagent is less and the difference in the absorption values of the complex and the reagent is considerably more than at 400 nm and thereby affords a more sensitive study.

### Effect of Reagent

The study is made by measuring absorbances at 385 nm and 400 nm of various solutions containing different amounts of the reagent. The study reveals that a minimum of 20-fold excess of the reagent is essential for complete complexation. Notwithstanding, a 50-fold excess of the reagent is maintained in the studies.

### Effect of Borate Concentration

The absorbances of various solutions containing different volumes of 0.01 M borate solution are measured both at 385 nm and 400 nm against reagent blank and found that the absorbance is maximum with 2 ml of borate solution. The studies on the effect of time reveal that the complex is stable for more than 24 h under these conditions. Hence, 2 ml of 0.01 M borate solution in a total volume of 25 ml ($8 \times 10^{-4}$ M borate) corresponding to the pH of 6.45 is chosen as optimum volume for further studies.

## Beer's Law Obedience

The absorbances of various solutions containing different amounts of Cu(II) are measured both at 385 nm and 400 nm against reagent blank under the above established optimum conditions of study. From the graph it is observed that at both the wavelengths Beer's Law is obeyed upto $3 \times 10^{-4}$ M copper(II) corresponding to 19 ppm of Cu(II). At 400 nm the molar absorptivity and Sandell's sensitivity are found to be $1.167 \times 10^3$ lit mole$^{-1}$ cm$^{-1}$ and 0.0545 μg cm$^{-2}$ respectively. At 385 nm the molar absorptivity and Sandell's sensitivity are found to be $3.2 \times 10^3$ lit mol$^{-1}$ cm$^{-1}$ and 0.019862 μg cm$^{-2}$ respectively.Tthe standard deviation is found to be 0.04 ppm and 0.12 ppm at 385 nm and 400 nm respectively.

## Composition of the Complex and Stability Constant

The composition of the complex is established to be 1 : 2 : : Cu(II) : RP by Job's method by studying the absorbances of various solutions containing varying volumes of equimolar (0.01 M) solutions of Cu(II) and RP at 385 nm against reagent blank. The stability constant evaluated from Job's curve is $4.19 \times 10^9$. The composition of the complex is verified by slope-ratio and mole-ratio methods at 385 nm and is found to be in agreement with Job's method.

## Effect of Diverse Ions

The study of various cations and anions has been carried out under optimum experimental conditions keeping the concentration of the copper(II) at $3 \times 10^{-4}$ M. The tolerance limit is set at 2 per cent of absorbance values *i.e.* 0.009 and 0.025 scale units in absorbance value at 400 nm and 385 nm respectively. The tolerance limit in ppm for various ions is evaluated at both the wavelengths of study and found to be almost the same for an ion at both the wavelengths. The value is indicated against each ion in parentheses in ppm.

Carbonate (10), sulphate (40), phosphate (2), fluoride (2), tartrate (4), oxalate (0.4), borate (4), citrate (1), nickel (2), cadmium (0.4), aluminium (2), zinc (30), manganese (>500), chromium (1), tin (0.5), lead (2), cobalt (3), vanadium (0.6), molybdenum (1), cerium (1.5) and iron (1.5).

The method is applied for the estimation of micro amounts of copper in brass sample and the results obtained are in good agreement upto 8 ppm.

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