# Solvent Extraction and Spectrophotometric Determination of Cu(II) with 3,4-Diaminobenzophenone

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A method is proposed for the solvent extraction and spectrophotometric determination of Cu(II) at microgram levels using 3,4-diaminobenzophenone as a complexing agent. Cu(II) forms a wine red coloured complex with 3,4-diaminobenzophenone, which can be extracted into chloroform under optimum conditions. The chloroform extract shows maximum absorbance at 400 nm wavelength. Beer's law was obeyed over the range of 50 to 100 μg of Cu(II). The stoichiometry of the extracted species was found to be 1:2. The interference due to diverse cations and anions has been studied.

## INTRODUCTION

Copper is one of the coinage metals and constitutes 70 ppm in the earth's crust. Copper is one of the most important metals after iron. It plays an important role in many fields in the form of metal or as its compounds such as catalyst in organic reactions, in alloys, in laboratories and industries, colour technology, medicines, food and beverages, *etc*. It has a variety of engineering applications, especially in electrical industries. Cu(II) has been determined spectrophotometrically using Schiff base, N,N-*bis*(2-hydroxy-4-*n*-butoxyacetophenylidine) ethylene diamine as an analytical reagent[1]. Cu(II) has also been determined in micro amounts in biological samples and Al alloys with satisfactory results using chromogenic reagent *i.e.*, 1,5-(2-hydroxy-5-bromophenyl)-3-cyanoformazan[2]. Many other workers have also reported different methods of determination of copper using spectrophotometry[3-8].

## EXPERIMENTAL

The absorbance measurements were made on a spectro Genesys-8 spectrophotometer of Spectronic make, over a range of 200 nm to 1100 nm wavelength. The chemicals used were of AR grade and all solutions were prepared in deionized double distilled water. AR grade concentrated sulfuric acid was added to the stock solutions wherever necessary to avoid hydrolysis.

The stock solution of Cu(II) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ and 1 mL of AR grade concentrated $H_2SO_4$ and was standardized according to the procedure described by Vogel[9]. Necessary dilutions were done from this solution using distilled water. 1 mg/mL solution of 3,4-diaminobenzophenone (3,4-DABP) was prepared by dissolving 0.1 g of the reagent in distilled ethyl alcohol and diluted to 100 mL.

1 mL of diluted Cu(II) solution containing 50 μg of Cu(II) was pipetted in a 125 mL separating funnel containing 8 mL of water. The pH of the solution was adjusted to 10 using ammonia solution. 5 mL of 1 mg/mL reagent solution was added to this mixture. The mixture was allowed to stand undisturbed for 15 min to ensure complete complex formation. The complex so formed was extracted into 12 mL distilled chloroform by equilibrating for 1 min. The phases were allowed to separate. An aliquot of this organic phase was used to measure the absorbance of the complex at 400 nm.

The interference of foreign ions was studied. For this, aliquots of different cations containing a quantity of 100, 250 and 1000 μg and anions containing a quantity of 5, 500, 1000 μg and 10 mg were taken. 1 mL of the cation solution was added to the mixture containing 50 μg Cu(II), 8 mL water and 5 mL of 1 mg/mL reagent solution. All the optimum conditions were adjusted and the absorbance was measured at 400 nm. Similar procedure was carried out to study the interference by anions also.

The stoichiometry of the complex was determined by the method of sub-stoichiometric extraction. For this, increasing amounts of Cu(II) solution from 50 to 1400 μg was taken in a separating funnel containing little water. The total volume was adjusted to 9 mL. The pH of the solution was adjusted to 10 using ammonia solution. 5 mL of 1 mg/mL reagent solution was added to this mixture. The mixture was allowed to stand undisturbed for 15 min to ensure complete complex formation. The complex so formed was extracted into 12 mL distilled chloroform by equilibrating for 1 min. The phases were allowed to separate. An aliquot of this organic phase was used to measure the absorbance of the complex at 400 nm as specified earlier. A plot of metal concentration against absorbance was drawn. The stoichiometry of the complex was determined from this plot. To support the results of this method, slope ratio method was also studied. For this, aliquots of sample solution containing increasing amounts of Cu(II) were used. The quantity of reagent used was 10 mg/mL (5 mL). The further procedure was allowed as usual.

Volume concentration and back extraction were studied for the quantitative extraction of copper. In volume concentration, Cu(II) was extracted from 1 L aqueous phase. The time of complex formation was 0.5 h and the time of equilibration was 0.75 h. The organic layer was separated and the further

prcedure followed was the same as given earlier. In back extraction, the sample and the blank were prepared as usual and the absorbance was measured. After that, the organic phases of both, sample and blank were equilibrated with 10 mL of acidic aqueous phase adjusted at pH 3. The absorbance of the organic phases of both sample and blank were again measured after back extraction.

## RESULTS AND DISCUSSION

The optimum pH for extraction of Cu-DABP was found to be 10 as the absorbance was maximum at this pH. Various solvents such as benzene, toluene, chloroform, carbon tetrachloride, cyclohexanone, xylene, solvent ether, nitrobenzene, N,N-dimethyl aniline and acetophenone were tested for the extraction of the complex, amongst which chloroform was found to be the most effective. The distribution ratio under the experimental conditions was found to be 199 by single extraction whereas with other solvents it is found to be lesser than this. For the complete extraction, 1 min equilibration time was adequate. The stoichiometry of the complex was found to be 1:2 by sub-stoichiometric extraction and was supported by the slope ratio method.

In this study, 1 mg each of $K^+$, $Sr^{2+}$, $Bi^{3+}$, $Zn^{2+}$, $V^{2+}$, $Ti^{2+}$, $Sn^{2+}$, $Sn^{4+}$, $Ni^{2+}$, $Co^{2+}$, $Mg^{2+}$, $Ba^{2+}$; 25 µg of $Na^{2+}$, $Al^{3+}$, $Fe^{3+}$, $Cd^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Te^{4+}$, $Tl^+$, $Mn^{2+}$, $Ce^{4+}$, $Pb^{2+}$; 50 µg each of $Mn^{4+}$, $Cr^{6+}$, $V^{3+}$ did not interfere in the spectrophotometric determination of Cu(II) (Table-1). 10 mg each of chromate, citrate, sulfate, sulphide and nitrite; 1 mg each of $Cl^-$ and $I^-$; 500 µg of $Br^-$ and 50 µg each of $SO_3^{2-}$ and $PO_4^{3-}$ did not interfere in the spectrophotometric determination of Cu(II). $CH_3COO^-$, $C_2O_4^{2-}$, $CO_3^{2-}$, $NO_3^-$ and thiourea interfere even at 50 µg levels. These have to be decomposed prior to complexation

TABLE-1
STUDY OF INTERFERING IONS

| Interfering ions (µg) | Cations |
|---|---|
| 1000 | $K^+$, $Sr^{2+}$, $Bi^{3+}$, $Zn^{2+}$, $V^{5+}$, $Ti^{4+}$, $Sn^{2+}$, $Sn^{4+}$, $Ni^{2+}$, $Co^{2+}$, $Mg^{2+}$, $Ba^{2+}$ |
| 250 | $Na^{2+}$, $Al^{3+}$, $Fe^{3+}$, $Cd^{2+}$, $Ca^{2+}$, $Fe^{2+}$, $Te^{4+}$, $Tl^+$, $Mn^{2+}$, $Ce^{4+}$, $Pb^{2+}$ |
| 100 | $Mn^{4+}$, $Cr^{6+}$, $V^{3+}$ |

| Interfering ions | Anions |
|---|---|
| 10 mg | $CrO_4^{2-}$, $SO_4^{2-}$, $S^{2-}$, $NO_2^-$ and Citrate |
| 1 mg | $Cl^-$, $I^-$ |
| 500 µg | $Br^-$ |
| 50 µg | $SO_3^{2-}*$, $PO_4^{3-}*$, $CH_3COO^-*$, $C_2O_4^{2-}*$, $CO_3^{2-}*$, $NO_3^-*$ and thiourea*, |

*Ions removed by decomposing.

of Cu(II). $CO_3^{2-}$ and $NO_3^-$ can be removed by decomposing with conc. HCl, while $CH_3COO^-$, $C_2O_4^{2-}$ and thiourea can be removed by heating with auqa regia to dryness, expelling nitrate by heating with conc. HCl to dryness and finally extracting with 5 mL water.

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