CHAPTER - II

DETERMINATION OF COPPER

2.1 INTRODUCTION

Copper was probably the first metal known to man and it is associated with the development of human civilization. Although it is less abundant in the earth's crust than any other metals, for ages it has served mankind as metal, alloys and salts. Its sources made it possible for the ancient man to use it for weapons, ornaments, utensils and statues. Analytical chemistry of copper covers macrolevel studies to traces in biological samples and is one of the widely studied subject.

Except for silver and gold, copper is the most malleable and ductile of all the metals, and this in conjunction with its very high electrical conductivity and moderate cost, has resulted in its very wide employment in electrical machinery.

The industrially important alloys of copper are brass, bronze and gun metal. The chief copper alloys are the brasses which are essentially copper-zinc alloys and the bronzes which are essentially copper-tin alloys, but small amounts of other metals are frequently added to confer special properties. Monel metal is a copper-nickel alloy which shows good resistance to corrosion. During recent years, copper-beryllium alloys which can be obtained as hard

as steel have attracted considerable attention.

Copper is also associated with iron, sulphur etc. in principal minerals. Copper plays an important role in living organisms. Copper is one of the trace metals of greatest interest in petroleum analysis. Copper is one of the important micronutrients for crops. Also, large number of copper compounds are used as insecticides. The trace determination of copper in foods, beverages, feeds, soils and biological materials is of great interest and also in research, industries and in quality control.

Copper is an element with which innumerable organic compounds give sensitive colour reactions. Many colorimetric reagents have been proposed for the determination of copper, but only few are sensitive and selective. A well established reagent for copper is diethyldithiocarbamate[1-3] but suffers from several interferences. Dithizone[4] is one of the most sensitive copper reagents but it is not specific. The strong colour of dithizone and low stability of its solutions are disadvantages. Other classic reagents for copper are derivatives of bipyridine and phenanthroline. Diehl and Smith[5] have reviewed analytical reagents for copper which are the derivatives of above compounds. Cuproin[6-8] and neocuproin[9,10] suffer from interferences and are not

selective. Hydroxy substituted 1,10-phenanthroline[11] and termethylthiurams[12] are not selective and in the latter case the rate of formation of complex is slcw and so, heating is necessary. Phenyl-2-(6-methyl-pyridyl ketone) oxime[13] complex is extracted into iso-amyl alcohol but in this method cobalt interferes strongly.

Methods involving phenyl thiosemicarbazide[14], catechol sulphonaphthalein[15], neocuproin[16], T-sulphonamidine[17], pentyl-2-pyridyl ketoxime[18], stilbazo[19], 3,5-dimethyl pyrazole[20] and biacetyl monoxime thiosemicarbazone[21] form complexes cf copper very slowly and require a time period of 15 minutes to 2 hours. In dithioxamide[22] method the order of addition of reactants is also very critical. Complex of 6-amino-4-hydroxy-2-mercapto-5-nitrosopyrimidine[23] is unstable. Sensitivity of 2,2'-biquinoline[24] and 2,9-dimethyl-1,10-phenanthroline[24] is much less (0.01 and 0.008 $\mu g/cm^2$ respectively). Sensitive reagents nitroso-R-salt[25], orotic acid[26], calcichrome[27], zephiramine[28] and ammonium pyrophosphate[29] are not selective.

Different thiosemicarbazones[21,30-35] of aldehydes and ketones can effectively be used in determination of copper. Recently, copper is determined in tracer quantities with bromopyrogallol red and benzyldimethyl phenylammonium

chloride[36], diphenylcarbazone[37] and syn-phenyl-α-pyridyl ketoxime[38] by extractive spectrophotometric method. Other analytical reagents such as 2-thioquinaldinanilide,[39] 2-hydroxy-4-ethoxyacetophenone[40], 2-(α-pyridyl) thioquinalidinamide[41] and 1-phenyl-3-thiobenzoyl thiocarbamide[42] were also used for the determination of coppr recently.

Complex salts of Cu(II) with Schiff base derived from aminoguanidine and salicylidine and O-hydroxy acetophenone[43] have been prepared and characterized on the basis of analytical UV and IR data.

Cinnamaldehyde guanylhydrazone is used for photometric determination of traces of copper at pH 9.5 as a yellow complex in distilled water. The complex is measured at 385 nm. The proposed method is simple, rapid and highly sensitive.

2.2   EXPERIMENTAL

All the chemicals used were of analytical grade.

2.2.1   Standard Solutions

Standard Copper(II) Solution :

A stock solution of Copper(II) (1 mg/ml=0.01574 M) was prepared by dissolving 0.3929 g of copper sulphate pentahydrate in distilled water containing a drop of

sulpuric acid and was diluted to 100 ml. It was standardized volumetrically[44]. Lower concentration solutions were prepared by diluting stock solution with distilled water.

Reagent Solution :

A stock solution of 0.01 M reagent (CAG) was prepared by dissolving 0.188 g of CAG in 100 ml ethyl alcohol (1.88 mg/ml).

Buffer Solution :

Buffer solution of pH 10 was prepared by dissolving appropriate amount of boric acid and sodium hydroxide.

2.2.2 Recommended Procedure :

An aliquot of the solution containing about 10 µg of copper(II) was taken in 10 ml volumetric flask. To it was added 2.5 ml of 0.001 M reagent (CAG) solution. The pH of the solution was adjusted to 9.5 by adding 0.5 ml of pH 10 buffer and was adjusted upto the mark with ethyl alcohol. The absorbance of the complex was measured at 385 nm against reagent blank. The concentration of copper in an unknown solution was determined from standard calibration curve obtained under identical conditions.

2.3 RESULTS AND DISCUSSION

2.3.1 Spectral Characteristics :

The absorption spectrum of Copper(II)-CAG complex of the solution containing 10 µg of Cu(II) [1 ml of 0.01 mg/ml i.e. 0.0001574 M] and 2.5 ml of 0.001 M of the reagent (CAG) was recorded at pH 9.5 against reagent blank. The complex shows absorption maximum at 385 nm. The molar extinction coefficient at 385 nm is 0.2211×10^4 l mole^{-1} cm^{-1}. The reagent does not absorb in this region. Absorption spectra of the complex and the reagent are shown in figure 2.1. Observations are given in table 2.1.

Table2.1 : Molar extinction coefficient of the Cu(II)-CAG
complex and the reagent (CAG).

Wavelength λ, nm	Molar extinction coefficents, ϵ	
	Cu(II)-CAG complex $\epsilon \times 10^4$ l mole^{-1} cm^{-1}	Reagent, CAG $\epsilon \times 10^4$ l mole^{-1} cm^{-1}
365	0.1327	0.0215
370	0.1390	0.0150
375	0.1958	0.0125
380	0.2148	0.0100
385	0.2211	0.0075
390	0.2148	0.0060
400	0.1958	0.0030
410	0.1516	0.0020
420	0.1137	0.0010
430	0.0708	0.0005
440	0.0442	-
450	0.0316	-
460	0.0190	-
470	0.0126	-
480	0.0063	-
490	0.0063	-
500	0.0063	-

2.3.2 Effect of pH :

To study the effect of pH of the solution on the absorbance of the complex, a series of solutions containing 1 ml of 0.01 mg/ml of Cu(II) [0.0001574 M] and 2.5 ml of 0.001 M reagent (CAG) was prepared as per the recommended procedure over a range of pH 2.0 to 13.0. The absorbances were measured against corresponding reagent blank. It was found that the complex has maximum and constant absorbance over the pH range 9 to 10. Therefore, pH 9.5 was selected as the optimum pH for further studies. The observations are given in table 2.2 (Fig 2.2).

Table 2.2 Effect of pH

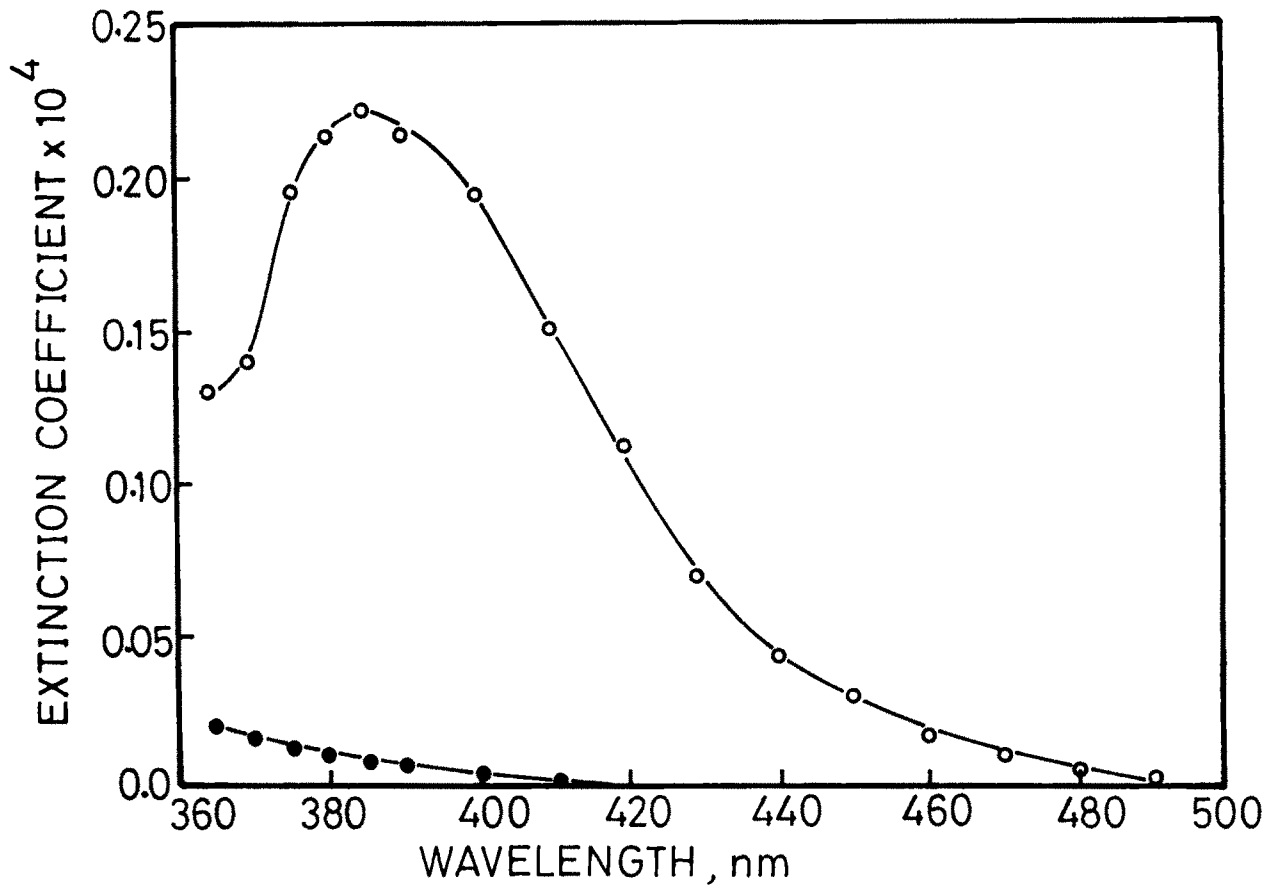| pH	Absorbances at 385 nm
2	-
4	0.01
6	0.02
8	0.24
9	0.35
10	0.35
11	0.15
12	0.15
13	0.12

FIG.2·1 − (○——○) ABSORPTION SPECTRUM OF COPPER-CAG
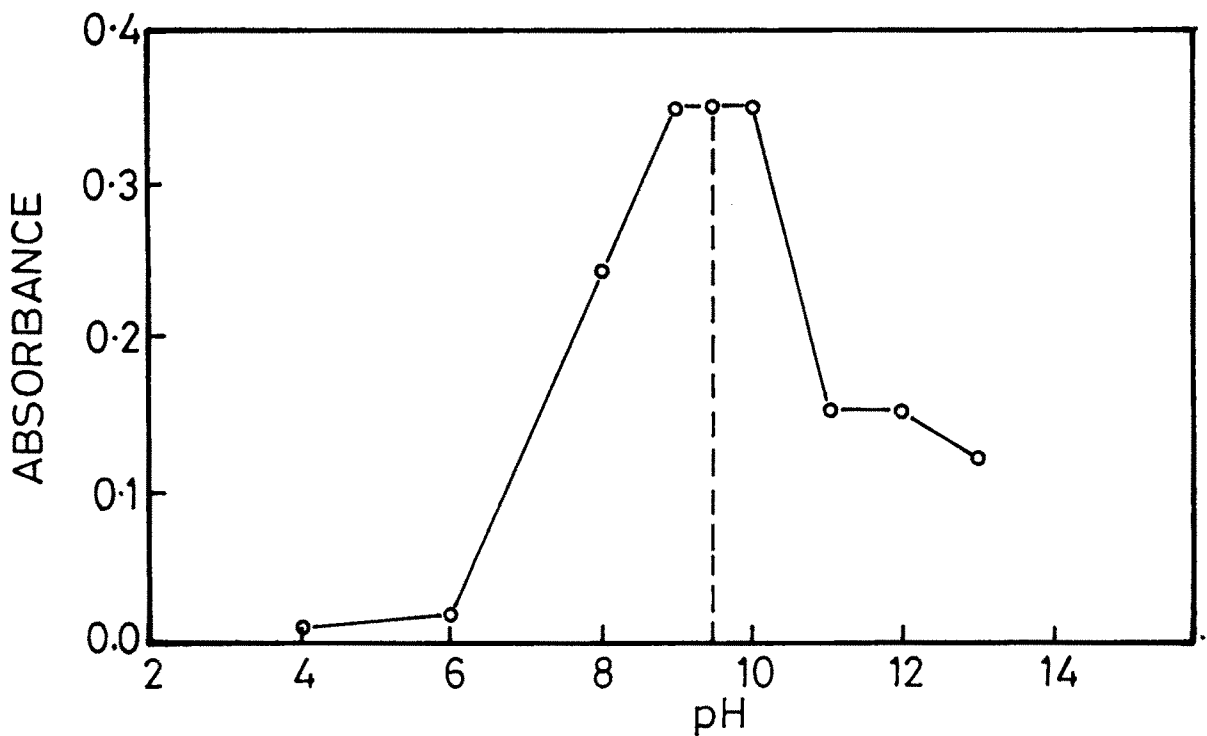COMPLEX,
(●——●)ABSORPTION SPECTRUM OF REAGENT(CAG)

FIG. 2·2 − EFFECT OF pH .

2.3.3 Effect of reagent concentration :

A series of solutions containing same amount of copper (1.574×10^{-4} M) and different amounts of reagent (5.0×10^{-4} M to 4.0×10^{-3} M) were prepared at pH 9.5. The complex was developed as per the recommended procedure. Results in the table 2.3 show that two fold molar excess of the reagent is sufficient for full colour development.

Table 2.3 : Effect of reagent concentration

[Cu(II)] = 10 ppm; [CAG] = 1.0×10^{-3} M.

ml of reagent	Absorbance at 385 nm
0.5	0.18
1.0	0.28
1.5	0.30
2.0	0.32
✓ 2.5	0.35
3.0	0.35
3.5	0.35
4.0	0.35

2.3.4 Stability and Reaction Rate :

Copper(II)-CAG complex is stable for several hours and complex formation is instantaneous.

2.3.5 Validity of Beer's Law

For the study of validity of Beer's law, the solutions containing different amounts of copper and the same amount of reagent (CAG) 2.5 ml of 0.001 M were taken. The absorbance measurements were recorded at 385 nm against corresponding reagent blank. It was found that Beer's law is valid upto 12 ppm (Table 2.4; Fig 2.3). The Ringbom plot[45] indicates that optimum concentration range is from 6 ppm to 12 ppm of Cu(II) at 385 nm (Fig. 2.4).

Table 2.4 : Validity of Beer's Law

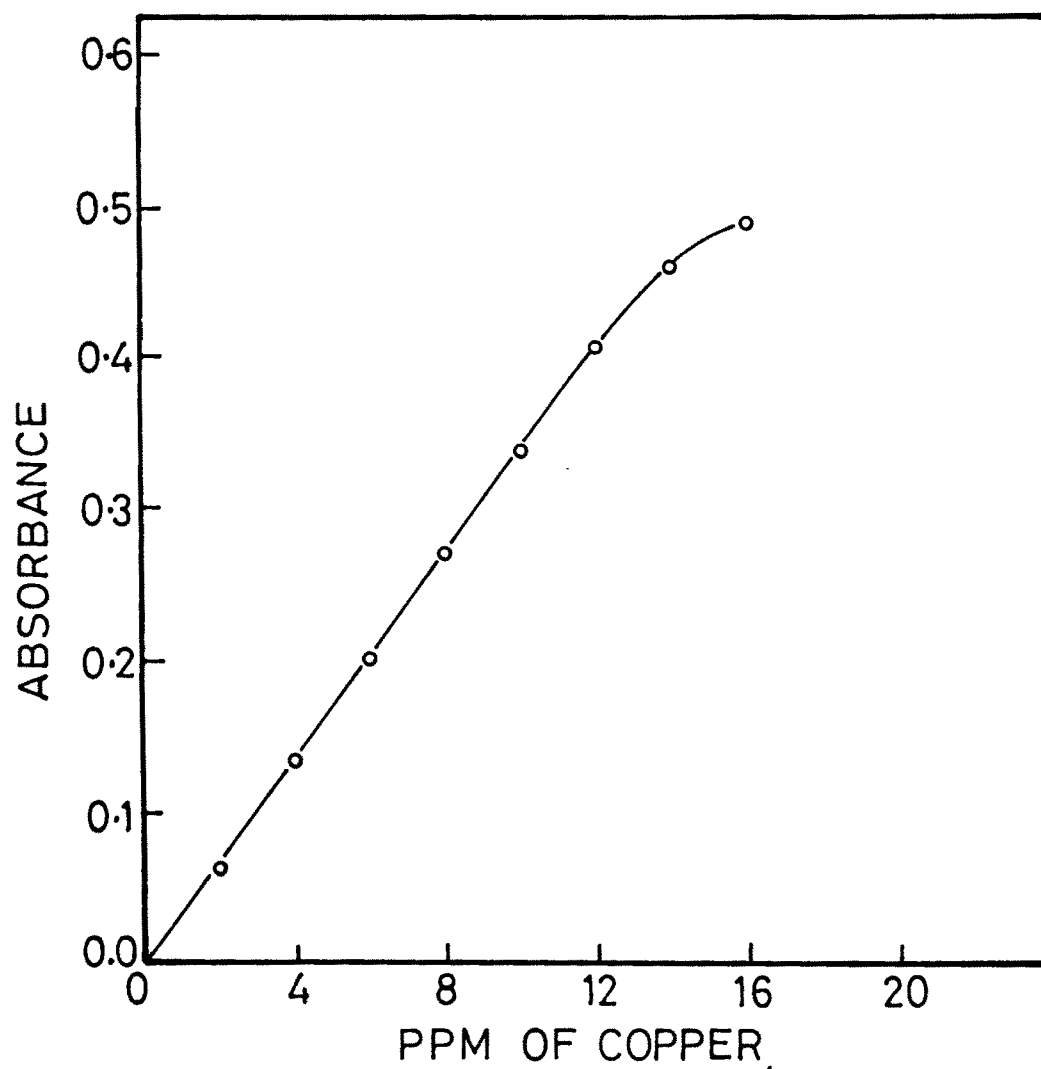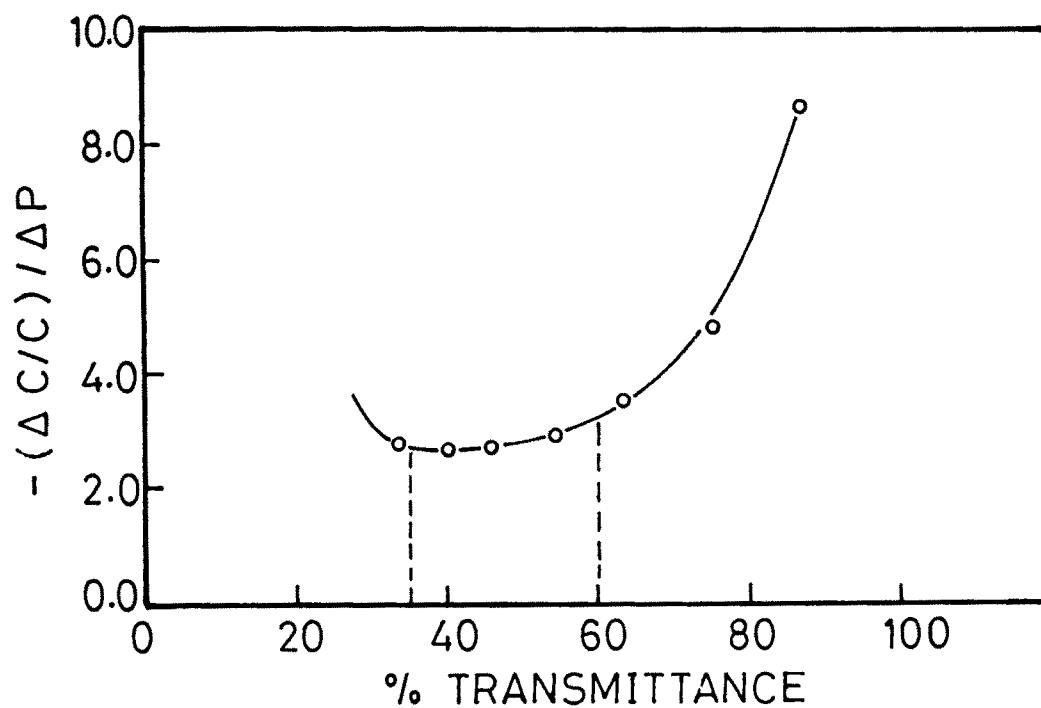| Amount of Copper(II) ppm	Absorbance at 385 nm
2	0.06
4	0.12
6	0.20
8	0.27
10	0.34
12	0.41
14	0.46
16	0.48

FIG. 2·3 – VALIDITY OF BEER'S LAW.

FIG. 2·4 – RINGBOM PLOT.

2.3.6 Composition of the complex :

The composition of the complex Cu(II)-CAG was determined by Job's continuous variation method[46], mole ratio method[47] and slope ratio method[48]. The complexes were developed as per the recommended procudure and absorbances were measured (Table 2.5). The plot of absorbances against the mole fraction of the reagent indicated the existence of 1:2 complex with respect to metal and ligand (Figure 2.5). For mole ratio method, solutions containing same concentration of reagent $(1.574 \times 10^{-3} M)$ and varying amounts of copper ranging from $3.148 \times 10^{-4} M$ to $3.148 \times 10^{-3} M$ were prepared and absorbances of solutions were measured (Table 2.6). The plot of absorbance against metal to reagent ratio (Figure 2.6) shows the formation of 1:2 complex which confirms the results of Job's method.

In slope ratio method, a series of solutions were prepared by keeping the metal concentration variable and a very large excess of ligand concentration and vice versa. Slope ratio method also confirms the 1:2 complex.

Table 2.5 : Job's continuous variation method

$$[Cu(II)] = [CAG] = 1.574 \times 10^{-3} \text{ M}$$

Copper(II) ml	Reagent (CAG) ml	Molar Ratio M:L	Absorbances at λ		
			385 nm	395 nm	410 nm
0.0	1.8	-	-	-	-
0.2	1.6	1:8	0.040	0.025	0.015
0.4	1.4	2:7	0.055	0.040	0.025
0.6	1.2	1:2	0.060	0.045	0.030
0.8	1.0	4:5	0.050	0.035	0.024
1.0	0.8	5:4	0.040	0.025	0.015
1.2	0.6	2:1	0.025	0.015	0.005
1.4	0.4	7:2	0.015	0.005	0.004
1.6	0.2	8:1	0.005	0.003	0.002
1.8	0.0	-	-	-	-

Table 2.6 :   Molar ratio method

$$[Cu(II)] = [CAG] = 1.574 \times 10^{-3} \text{ M}$$

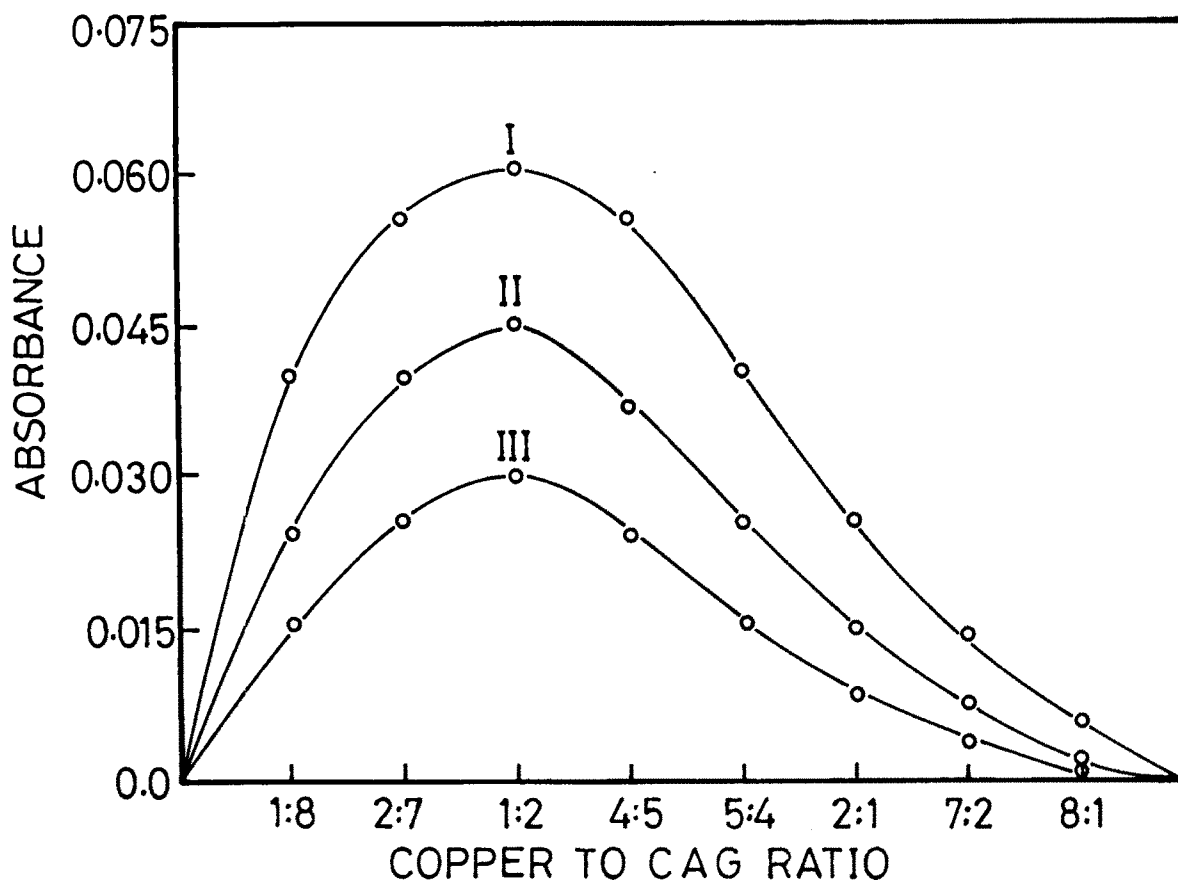| Copper(II) ml	Reagent (CAG) ml	Molar Ratio M:L	Absorbances at λ	
			385 nm	400 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.020	0.015
0.4	2.0	1:5	0.040	0.030
0.6	2.0	3:10	0.060	0.045
0.66	2.0	1:3	0.080	0.060
0.8	2.0	2:5	0.100	0.070
1.0	2.0	1:2	0.110	0.080
1.2	2.0	3:5	0.125	0.090
1.33	2.0	2:3	0.135	0.095
1.4	2.0	7:10	0.140	0.100
1.6	2.0	4:5	0.140	0.105
1.8	2.0	9:10	0.145	0.105
2.0	2.0	1:1	0.150	0.110

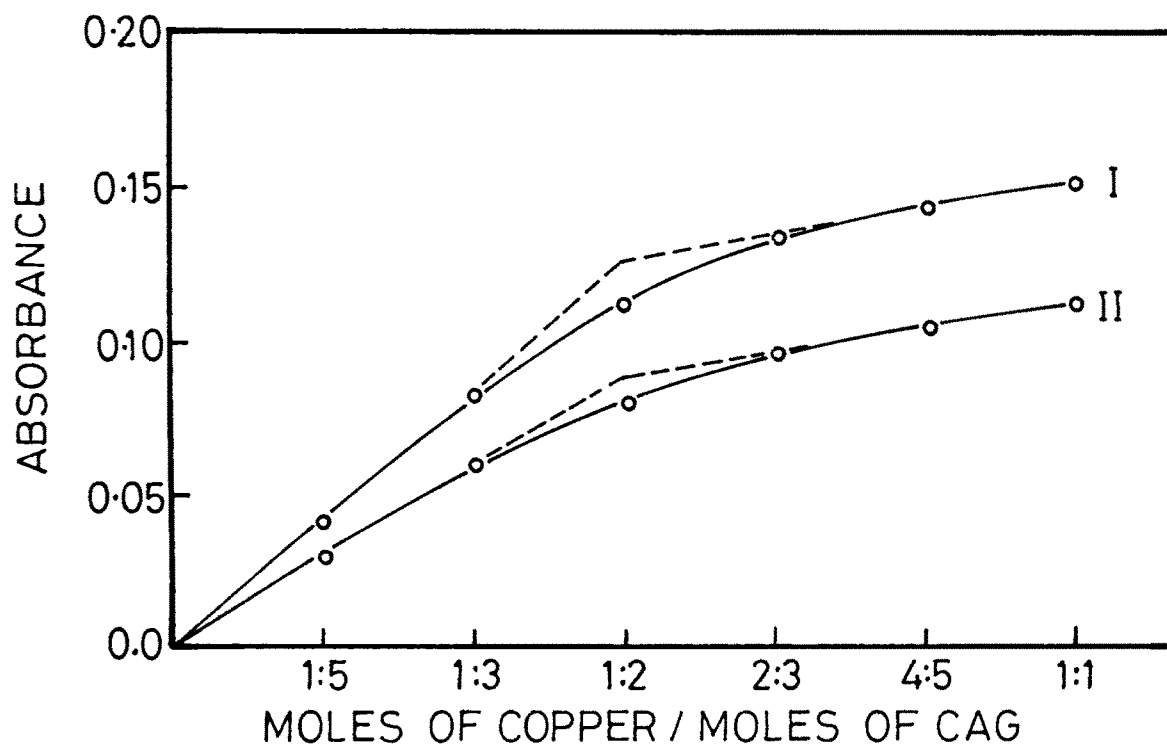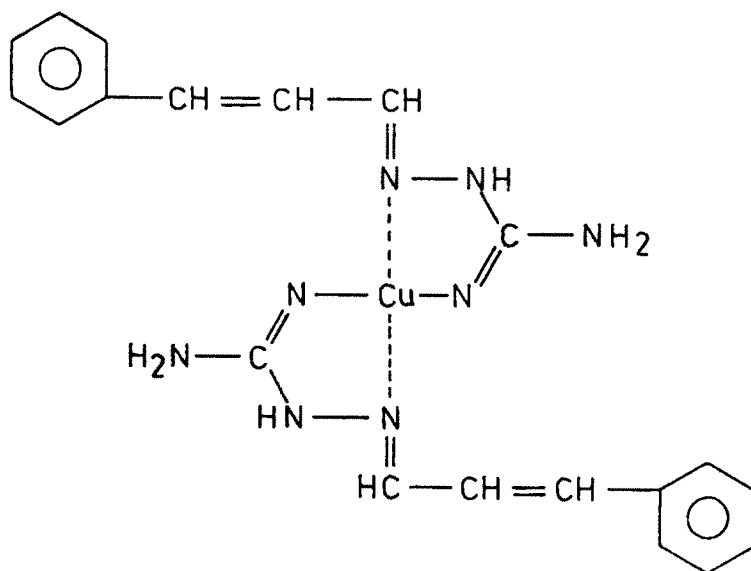FIG. 2·5 — JOB'S CONTINUOUS VARIATION METHOD.
I — 385 nm , II — 395 nm , III — 410 nm .

FIG. 2·6 — MOLE RATIO METHOD.
I — 385 nm , II — 400 nm

The probable structure for Cu(II)-CAG complex may be presented as

CH = CH — CH
N — NH
C — NH2
N — Cu — N
H2N — C
HN — N
HC — CH = CH

2.3.7 Sensitivity of the method :

The photometric sensitivity of the system was calculated by Sandell's method[49] and was found to be $0.1988 \ \mu g/cm^2$ at 385 nm.

2.3.8 Degree of Dissociation and Instability Constant

The instability constant is calculated from the mole ratio plot (Fig 2.6).

The equation is

$$K = \frac{(m \alpha c)^m (n \alpha c)^n}{c (1-\alpha)}$$

where,

K = Instability constant

α = Degree of dissociation

c = Concentration of the complex in moles per litre

m & n = 1 and 2 respectively.

The degree of dissoication α, is calculated from the relationship,

$$\alpha = \frac{d_E - d_o}{d_E}$$

where,

d_E = Optical density when complex is completely formed (extrapolated value of O.D.)

d_O = Optical density observed actually at stoichiometric molar ratio

The degree of dissociation of the complex at 385 nm was found to be 0.12.

The apparent instability constant[50] was calculated as 1.946 x 10^{-10}.

From this value, the change in free energy[51] can be calculated by using the relation.

Δ F = R T ln K at 25°C

where,

R = Gas constant

T = Absolute temperature

and   K = Instability constant

The change in free energy of the system is -13.23 K cal/mole.

2.3.9 Reproducibility of the method :

The reproducibility of the method was studied by determining copper in sets of six observations for each concentration. The table 2.7 summarises the results and shows that the results are reproducible.

Table 2.7 : Reproducibility of the method.

Copper(II) ppm	Mean absorbance of six observations	standard deviation	coefficient of variation %
3.0	0.105	0.002	1.904
6.0	0.200	0.003	1.750
9.0	0.310	0.005	1.613

2.3.10 Effect of Diverse Ions

The effect of diverse ions was studied using fixed amount of copper(II) (2 ppm) and developing and measuring the colour intensity as per recommended procedure. An error upto 2 % in absorbance was considered to be tolerable.

It is found that Co(II), Pd(II), Fe(III), Ce(IV), Ni(II) and EDTA^{-4} interfere seriously. The tolerance limits for the ions are listed in table 2.8.

Table 2.8 : Effect of diverse ions

[Cu(II)] = 2 ppm; [CAG] = 0.001 M

Foreign ions	Added as	Tolerance limit ppm
Cations		
Cr(III)	$CrCl_3.6H_2O$	0.3
V(IV)	$VOSO_4.H_2O$	1.0
Ba(II)	$BaCl_2.2H_2O$	25.0
Co(II)	$Co(NO_3)_2.6H_2O$	None
Zn(II)	$ZnSO_4.7H_2O$	4.0
Mn(II)	$MnSO_4.H_2O$	0.2
Pd(II)	$PdCl_2$	None
Fe(III)	$Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$	None
Ni(II)	$Ni(NO_3)_2.6H_2O$	None
Cr(VI)	$K_2Cr_2O_7$	0.2
Mo(VI)	$(NH_4)_6[Mo_7O_{24}].4H_2O$	6.0
Ag(I)	$AgNO_3$	2.5
U(IV)	Uranyl nitrate $UO_2(NO_3)_2.6H_2O$	0.9
Ce(IV)	Cerium(IV) ammonium sulphate	None
Cd(II)	$3CdSO_4.8H_2O$	0.2

. . . continued

Foreign ions	Added as	Tolerance limit ppm
Anions		
Citrate	Citric acid	2.0
Oxalate	Sodium oxalate	48.0
Thiourea	Thiourea	450.0
EDTA^{-4}	Disodium salt	None
Urea	Urea	635.0
Acetate	Sodium acetate	60.0
Tartrate	Tartaric acid	30.0

2.4 APPLICATIONS

Analysis of Brass

A known weight ~ 0.05 g of the sample of brass alloy was dissolved in 10 ml concentrated hydrochloric acid and 20 ml water with mild heating. A few drops of concentrated nitric acid (2 ml) was added and was heated to dryness. The resulting mass was dissolved in distilled water and was diluted to 100 ml with distilled water. A suitable aliquot of the solution was used for determination of copper as per recommended procedure. Results are given in table 2.9.

Table 2.9 : Analysis of Brass alloy

Alloy	Certified value of Cu %	Experimental value of Cu %	Relative standard deviation for 10 obsevations
Brass	62.5	62.17	0.06

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