

CHAPTER - V

DETERMINATION OF COPPER

### 5.1 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.

The industrially important alloys of copper are brass, bronze and gun metal. 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<sup>1-3</sup> but suffers from several interferences. Dithizone<sup>4</sup> 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<sup>5</sup> have reviewed analytical reagents for copper which are the derivatives of above compounds. Cuproin<sup>6-8</sup> and neocuproin<sup>9, 10</sup> suffer from interferences and are not selective. Hydroxy substituted 1,10-phenanthroline<sup>11</sup> and termethylthiurams<sup>12</sup> are not selective and in the latter case the rate of formation of complex is slow and so, heating is necessary. Phenyl-2-(6-methyl-pyridyl ketone) oxime<sup>13</sup> complex is extracted into iso-amyl alcohol but in this method cobalt interferes strongly.

Methods involving phenyl thiosemicarbazide<sup>14</sup>, catechol sulphonephthalein<sup>15</sup>, neocuproin<sup>16</sup>, T-sulphonamide<sup>17</sup>, pentyl-2-pyridyl ketoxime<sup>18</sup>, stilbazo<sup>19</sup>, 3,5-dimethyl pyrazole<sup>20</sup> and biacetyl monoxime thiosemicarbazone<sup>21</sup> form complexes of copper very slowly and require a time period of 15 minutes to 2 hours. In dithioxamide<sup>22</sup> method the order of addition of reactants is also very critical. Complex of 6-amino-4-hydroxy-2-mercapto-5-nitrosopyridine<sup>23</sup> is unstable. Sensitivity of 2,2'-biquinoline<sup>24</sup> and 2,9-dimethyl-1,10-phenanthroline<sup>24</sup>

is much less (0.01 and 0.008  $\mu\text{g}/\text{cm}^2$  respectively). Sensitive reagents nitroso-R-salt<sup>25</sup>, orotic acid<sup>26</sup>, calcichrome<sup>27</sup>, zephiramine<sup>28</sup> and ammonium pyrophosphate<sup>29</sup>, are not selective.

Different thiosemicarbazones<sup>21,30-35</sup> of aldehydes and ketones can effectively be used in determination of copper.

However, the method proposed is simple, sensitive and selective. The complex formation is instantaneous. It permits the determination of copper at trace level.

## 5.2 EXPERIMENTAL :

### 5.2.1 Standard solutions :

#### Standard solution of copper :

A stock solution of copper (1 mg/ml) was prepared by dissolving copper sulphate pentahydrate in distilled water containing a drop of sulphuric acid. It was standardized volumetrically<sup>36</sup>. Lower concentration solutions were prepared by diluting stock solution with distilled water.

#### Reagent solution :

0.6 mg/ml in ethanol (  $2.511 \times 10^{-3}\text{M}$  )

All other reagents used were of analytical grade.

### Buffer solution :

Buffer solution of pH 12 was prepared by mixing appropriate amounts of caustic soda and glycol.

### 5.2.2 Recommended procedure :

An aliquot of the solution containing 1 to 2  $\mu\text{g}$  of copper (II) was taken in 10 ml volumetric flask. To it was added 0.8 ml of  $2.511 \times 10^{-3}\text{M}$  reagent (BPG) solution. The pH of the solution was adjusted to 12 with buffer solution, and was diluted upto the mark with distilled ethanol. The absorbance of the copper (II)- BPG complex was measured at 418 nm against reagent blank. The concentration of copper in an unknown solution was determined from standard calibration curve obtained under identical conditions.

## 5.3 RESULTS AND DISCUSSION :

### 5.3.1 Spectral characteristics:

The absorption spectrum of Cu(II)-BPG complex containing  $3.937 \times 10^{-5}\text{M}$  copper (II) and  $2.008 \times 10^{-4}\text{M}$  reagent (BPG) was recorded at pH 12 against reagent blank. The complex has absorption maximum at 418 nm and molar extinction coefficient of the complex is  $1.300 \times 10^4 \text{ l mole}^{-1}\text{cm}^{-1}$  at 418 nm. The molar extinction coefficient of the reagent at 418 nm is  $6.0120 \times 10^4 \text{ l mole}^{-1}\text{cm}^{-1}$ , (Fig.5.1). The observations for the spectra are given in table 5.1.

Table 5.1 Molar extinction coefficients of the Cu(II)-BPG complex and the reagent.

Wavelength $\lambda$ , nm	Molar extinction coefficients, $\epsilon$	
	Cu(II)-BPG complex $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	BPG $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$
360	0.375	0.2948
370	0.625	0.1115
380	0.787	0.0509
390	0.952	0.0387
395	1.041	0.0341
400	1.143	0.0298
405	1.193	0.0199
410	1.236	0.0174
415	1.295	0.0124
418	1.300	0.0120
420	1.295	0.0049
425	1.211	0.0040
430	1.130	0.0030
435	0.990	0.0027
440	0.830	0.0010
450	0.508	0.0010
460	0.325	0.0000
470	0.203	0.0000
480	0.139	=
490	0.091	-
500	0.063	-
510	0.030	-
520	0.021	-
530	0.015	-
540	0.010	-

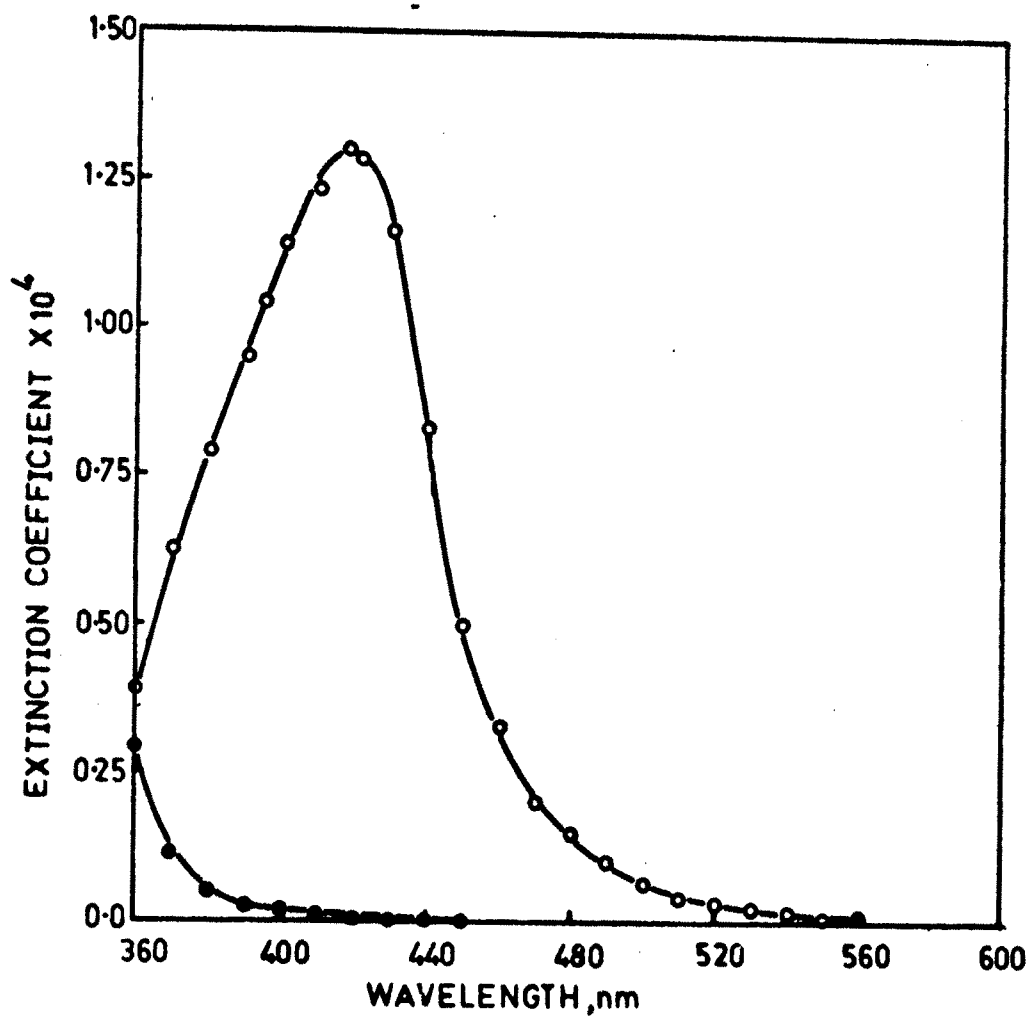


FIG.5.1 ○—○ ABSORPTION SPECTRUM OF COPPER-BPG COMPLEX  
●—● ABSORPTION SPECTRUM OF REAGENT (BPG)

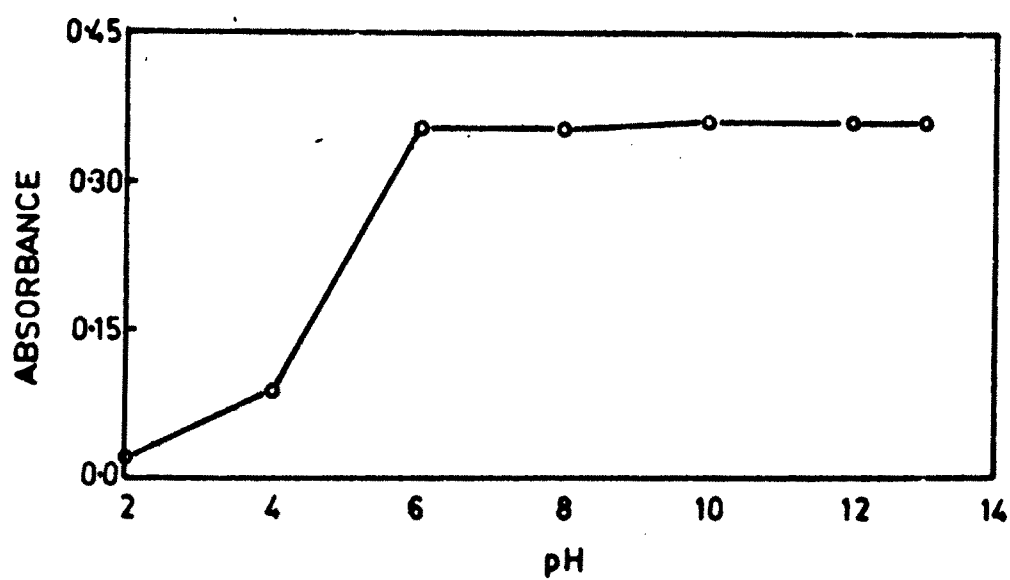


FIG.5.2 EFFECT OF pH

### 5.3.2 Effect of pH :

A series of solutions of different pH <sup>from</sup> 2.0 to 13.0 were prepared as per the recommended procedure. It was found that complex shows maximum and constant absorbance at pH 11.0 to 13.0 in alkaline medium ( Fig.5.2) and therefore the study of copper(II) -BPG complex was carried out at pH 12.0.

### 5.3.3 Effect of reagent concentration :

A series of solutions containing constant concentration of copper (2.5 ppm) and different amounts of BPG ranging in concentrations from  $5.02 \times 10^{-5} \text{ M}$  to  $3.514 \times 10^{-4} \text{ M}$  were prepared. Complex was developed as per recommended procedure and its absorbance was measured. Results in table 5.2 show that four fold molar excess of the reagent was sufficient for full colour development of 2.5 ppm of copper.

Table 5.2 : Effect of reagent concentration

$$[\text{Cu(II)}] = 2.5 \text{ ppm}$$

$$[\text{BPG}] = 2.511 \times 10^{-3} \text{ M.}$$

ml of BPG	Absorbance at 418 nm
0.2	0.33
0.4	0.40
0.6	0.41
0.8	0.41
1.0	0.42
1.2	0.42



#### 5.3.4 Stability :

The complex formation is instantaneous and colour of the complex was stable for several hours. Complex formation was independent of temperature.

#### 5.3.5 Validity of Beer's law :

The measurement of the absorbance of Cu-BPG complex at pH 12.0 containing varying amounts of copper showed that Beer's law is valid upto 28 ppm of Cu(II) (Fig. 5.3).

The optimum concentration range for the copper was studied from the Ringbom plot<sup>37</sup> and found to be 1.25 to 4.5 ppm at the conditions chosen for the experiment. ( Fig.5.4).

#### 5.3.6 Composition of the complex :

The composition of the Cu-BPG complex was ascertained by Job's method of continuous variation,<sup>38</sup> mole ratio method<sup>39</sup> and slope ratio method.<sup>40</sup> Complex was developed by using equimolar solutions of copper and the reagent. Job's plot (Fig.5.5) indicated the formation of 1:2 complex of Cu: BPG and this composition was confirmed by the mole ratio (Fig.5.6) and slope ratio method.

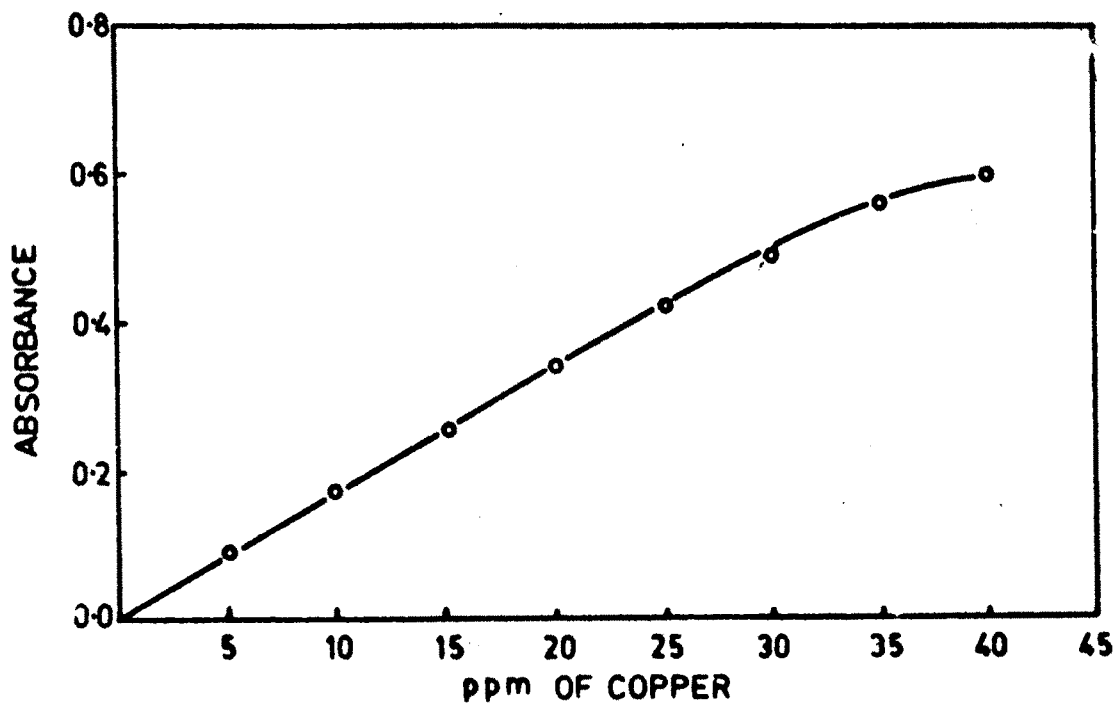


FIG.5.3 VALIDITY OF BEER'S LAW

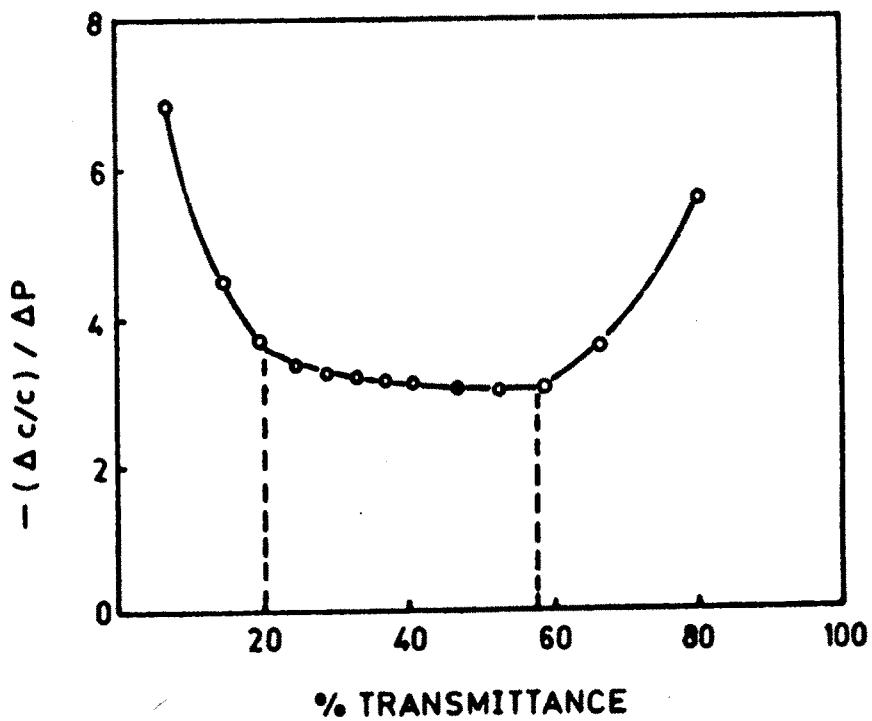


FIG. 5.4 RINGBOM PLOT

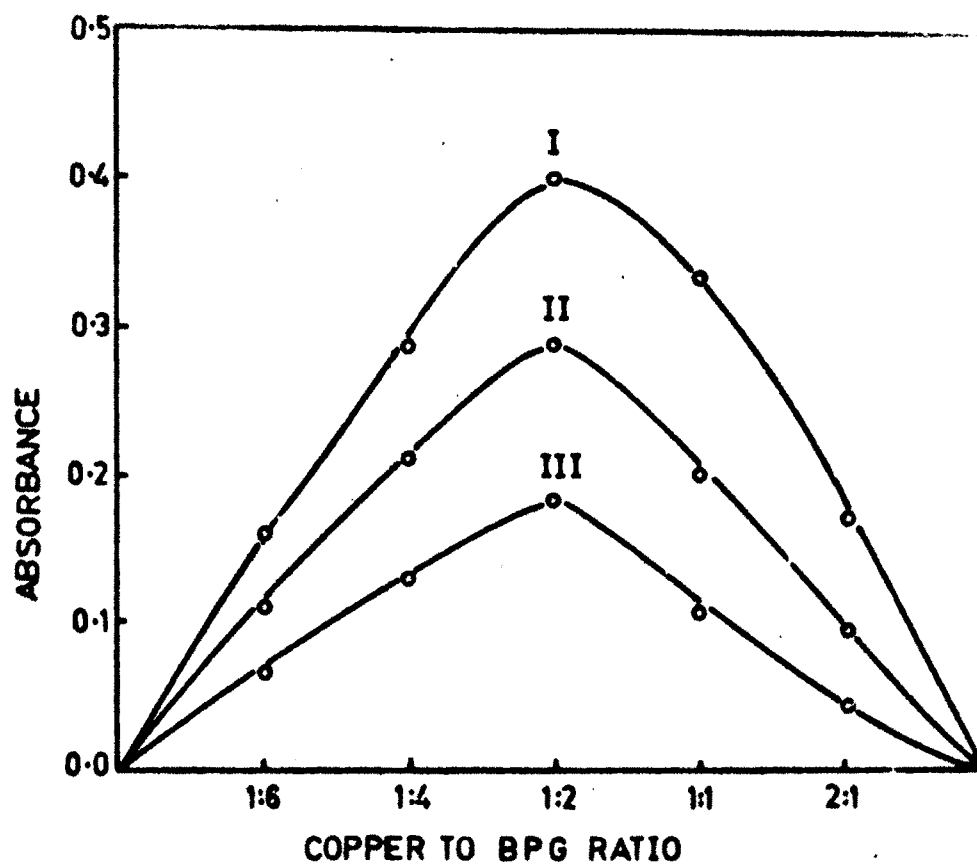


FIG. 5-5 JOB'S CONTINUOUS VARIATION METHOD.  
I- 418 nm, II- 435 nm, III- 450 nm.

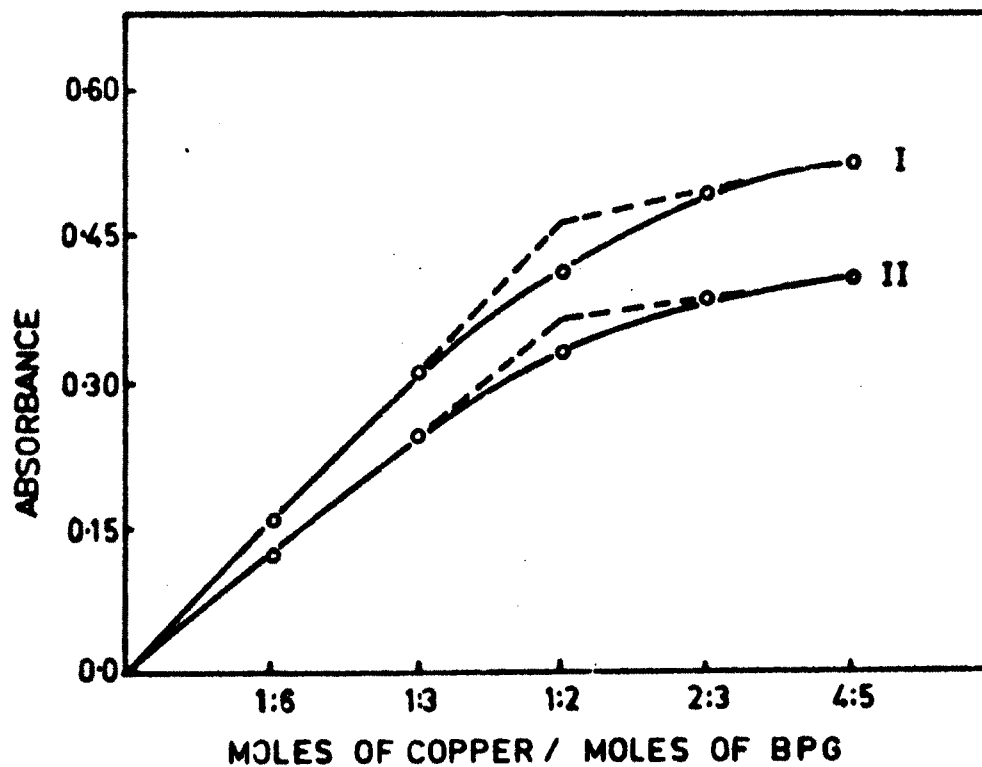


FIG. 5-6 MOLE RATIO METHOD.  
I- 418 nm, II- 440 nm.

### 5.3.7 Sensitivity :

The reagent or copper complex do not show any effect due to light.

The photometric sensitivity of the method was calculated by the method of Sandell<sup>41</sup> and found to be  $0.04151 \mu\text{g}/\text{cm}^2$  at pH 12. Molar extinction coefficient of the system at 418 nm is  $1.300 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ .

### 5.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.<sup>40</sup> The value of  $\alpha$ , degree of dissociation was found to be 0.09835.

The apparent instability constant<sup>42</sup> was found to be  $6.543 \times 10^{-12}$  for Cu-BPG complex. The change in free energy<sup>43</sup> of the system is  $-15.35 \text{ K cal/mole}$ .

### 5.3.9 Reproducibility of the method :

The reproducibility of the method was tested by determining different amounts of copper as per recommended procedure. The results are tabulated in table 5.3, which show that the method is reproducible. The standard deviations of the method calculated for 10 observations and the coefficient

of variation are also given in table 5.3.

Table 5.3 : Reproducibility of the method :

Cu(II) ppm	Mean absorbance of 10 observations	Standard deviation	Coefficient of variation, %
10	0.17	0.004	2.35
15	0.25	0.006	2.40
20	0.34	0.009	2.64

#### 5.3.10 Effect of diverse ions :

To study the effect of diverse ions of copper-BPG complex, various cations and anions were added to the solution containing 2.5 ppm of copper (II). Colour was developed at pH 12.0 and measured at 418 nm. Cations like Ce(IV), Al (III), Ni(II), Co(II), Cd(II) and Fe(II) interfere seriously, while W (VI) shows the tolerance limit up <sup>to</sup> 100 ppm. The effect of various ions tested is given in table 5.4.

Table 5.4 Effect of diverse ions.

$$[\text{Cu(II)}] = 2.5 \text{ ppm}$$

$$[\text{BPG}] = 2.008 \times 10^{-4} \text{ M}$$

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations:</u>		
V(V)	$\text{V}_2\text{O}_5$	0.5
Mn(II)	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	6
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	10
U(VI)	$\text{UO}_2(\text{NO}_3)_2$	16
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	6
Hg(II)	$\text{HgCl}_2$	1.4
Ce(IV)	$\text{Ce}(\text{SO}_4)_2$	none
Cr(VI)	$\text{K}_2\text{CrO}_4$	4
Ba(II)	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	10
Al(III)	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	none
Fe(III)	$\text{FeCl}_3$	10
Ni(II)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	none
W(VI)	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	100
Tl(I)	$\text{TlCl}$	2
Ca(II)	$\text{CaCl}_2$	6
Bi(III)	$\text{Bi}(\text{NO}_3)_3$	10
Co(II)	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	none
Ag(I)	$\text{AgNO}_3$	1
Cd(II)	$\text{Cd}(\text{NO}_3)_2$	none
Fe(II)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	none
<u>Anions:</u>		
Fluoride	Ammonium fluoride	70
Thiourea	Thiourea	10
Oxalate	Potassium oxalate	20

Contd. on next page.....

contd. from previous page.....

Foreign ions	Added as	Tolerance limit, ppm
<u>Anions:</u>		
Citrate	Sodium citrate	5
Acetate	Sodium acetate	1000
EDTA <sup>-4</sup>	Disodium salt	30
Tartrate	Antimony potassium tartrate	100
Phosphate	Potassium hydrogen orthophosphate	50
Thiocyanate	Potassium thiocyanate	800

5.4 APPLICATIONS :Analysis of Brass :

A known weight  $\approx 0.05$  g of 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 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 5.5.

Table 5.5 : Analysis of Brass alloy.

Alloy	Certified value of Cu, %	Experimental value of Cu, %	Relative standard deviation for 10 observations
Brass	62.5	62.09	0.05



5.5 REFERENCES

1. Callan, T. and Henderson, J.A.R., *Analyst*, 54, 650(1929).
2. Picotti, and Baldassi, *Mikrochemie*, 30, 77 (1942).
3. Clausen, A. and Blastings, L., *Z. Anal. Chem.*, 153, 30(1956).
4. Iwantscheft, G., *Das Dithizone und Seine Anwendung in der Mikro und Spurenanalyse*, Springer Verlag, Weinheim (1958).
5. Diehl, H. and Smith, G. F., 'The copper Reagents! The G. Frederick Smith Chemical Co., Columbus, Ohio (1970).
6. Breckenridge, J.G., Lewis, R.W.J. and Quick, L. A., *Can. J. Research*, B 17, 258 (1939).
7. Hoste, J., *Research (London)*, 1, 713 (1948).
8. Hoste, J., Gills, J. and Eeckhout, J., *Anal. Chim. Acta*, 9, 263 (1953).
9. Smith, G.F. and McCurdy, W.H. Jr., *Anal.Chem.*24, 371(1952).
10. Luke, C.L. and Cambell, M.E., *Anal. Chem.*, 25, 1588 (1953).

11. Dunbar, W.E. and Schilt, A. A., *Talanta*, 19, 1025 (1972).
12. Dhoke, M.P. and Joshi, A.P., *J. Ind. Chem. Soc.*,  
53, 413 (1966).
13. Pemberton, J.R. and Diehl, H., *Talanta*, 16, 393 (1969).
14. Komatu, S. and Utiyama, H. *J. Chem. Soc. Japan, Pura  
Chem. Sect.*, 75, 1280 (1954).
15. Svach, M., *Z. Anal. Chem.*, 149, 417 (1956).
16. Yoshihiro, I. and Yasuro, T., *Japan Analyst*, 6, 588 (1957).
17. Billman, J.H. and Chernin, R., *Anal. Chem.*, 36, 552 (1964).
18. Trusell, F. and Lieberman, K., *Anal. Chim. Acta.*,  
30, 269 (1964).
19. Bashirov, E.A., Akhmedli, M.K. and Abdullaeva, T. E.,  
*Uchen. Zap azerb., gos, Univ. Ser. Khim., Nauk*,  
1, 29 (1966).
20. Janik, B., Gawron, H. and Weyers, J., *Mikrochim.  
Ichnoanalyst. Acta.*, 5-6. 1142 (1965).
21. Valcarcel, M. and Bendito, D.P., *Inf. Quim. Analit.  
Pura. apl. Ind.*, 24, 49 (1970).

22. Williams, D.A. and Boltz., D.F., *Analyt. Lett.*, 8, 103 (1975).
23. Przeszlakowski, S. and Walesmundzki, A., *Chemia Analit.*, 9, 919 (1964).
24. Sandell, E.B., "Colorimetric Determination of Traces of Metals," Interscience Publication INC, New York, P. 443 (1965).
25. Sangal, S.P., *J.Prakt. Chem.*, 29, 76 (1965).
26. Capitan, F.G. and Arrebola, A., *Revta Univ. Ind. Santander*, 7, 241 (1965).
27. Hajime, J. and Hisahiko, E., *Bull. Chem. Soc. Japan*, 39, 1154 (1966).
28. Hiroshi, M. Sokichi, C. and Shigeki, H., *Japan Analyst.*, 15, 125 (1966).
29. Keattch, C.J. *Talanta*, 3, 351 (1966).
30. Gorski, W. and Lipiec., T., *Chemia Analit.*, 11, 759 (1966).
31. Gurman, M., Bendito, D.P. and Pino. P.F., *Inf.Quim. Analit, Pura apl. Ind.* 27, 209 (1973).
32. Burgos, F.S., Martinez, M.P. and Pino. P.F., *Inf. Quim. Analit. Pura apl. Ind.* 23, 17 (1969).

33. Cano Pavon, J.M., Vazquez, Allev, J., Bendito, D.P. and Pino., P.F., Inf. Quim. Analit. Pura apl. Ind., 25, 149 (1971).
34. Munoz., Levya, J.A., Cano Pavon, J.M. and Pino, P.F., An. Quim., 69, 251 (1973).
35. Martinez. M.P., Bendito, D.P. and Pino, P.F. Ann. Quim., 69, 747 (1973).
36. Vogal, A.I. " A Text Book of Quantitative Inorganic Analysis," 3rd Ed., Longman, London, P. 358 (1966).
37. Meitis, L., " Handbook of Analytical Chemistry", 1st Ed., McGraw Hill Book Co., New York, 6-17 (1963).
38. Job, P., Ann. Chim. Physique, 9, 113 (1928).
39. Yoe, J.H. and Jones, A.L., Ind. Engg. Chem., Anal. Ed., 16, 111 (1944).
40. Harvey, A.E. and Manning, D.L., J. Am. Chem.Soc., 72, 4488 (1950).
41. Sandell, E.B. " Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers Inc., New York, P. 688 (1965).

42. Trikha, K.C., Katyal, M. and Singh R.P., *Talanta*, 14, 977 (1967).
  
43. Grinberg, A.A., " An Introduction to the Chemistry of complex Compounds, " 2nd Ed., 1951, Translated by Leach J.R., 1st Ed., Pergamon, London (1962), P. 275.