CHAPTER - IV

EXTRACTIVE PHOTOMETRIC DETERMINATION OF COPPER (II) WITH 4'-CHLORO-2'-TOLYL -TPT

C H A P T E R - I V

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COPPER(II) WITH 4'-CHLORO-2'-TOLYL TPT

INTRODUCTION :

Copper has been known from ancient times. It is one of the few metals used to a greater extent in pure form than in alloy's forms. However, one of the features of copper is its ability to form a great number of variety of alloys. The industrially important alloys of copper are brass, bronze, gun metal and nickel-silver alloy. The electrical industry is one of the greatest users of copper. Copper alloys like cartridge brass has innumerable uses, including cartridge cases, automotive radiator cores and tanks, lighting fixtures, eyelet, rivets, screws, springs and plumbing products. Nickel-silver alloys are used for table flatware, zippers, camera parts, costume jewellery, nameplates, radio dials and some electrical switch gear. Cupronickel alloys are well suited for application in industrial and marine installations as condenser and heat exchanger tubing copper-tin alloys are widely used for springs and screens in paper making machines. Copper-silicon, tin, iron or zinc alloys are useful for hardware screws, bolts and

welding rods. Copper-sulphur-tellurium alloys increases ease of machining.

Now-a-days there is ever increasing demand for copper and its alloys as the result of rapid industrial advancement and its increasing use as structural alloys in diversified industries. This had lead to a steady exhaustion of its rich deposits. The availability of copper to present and next generation is dependent on new methods based on recovery of traces from the effluent of rich solutions and on the extraction of ores with very poor copper content. Most copper leaching operations are based on acidic systems; although extraction of copper is faster in ammonical media, it is much less selective hence acidic media are generally preferred. Hence it is worthwhile to develope a new rapid, efficient and simple method for extraction of copper from its low grade deposits.

Copper, although possessing an emetic action in large doses, is essential for growth. It is required to promote certain oxidation reactions. However, in food and beverages this effect may lead to development of off-flavours. Copper also accelerates the destruction of vitamin-C in fruits. It finds its way into the food from the machinery during the processing. It also gets into gasoline from the copper tubing used for fuel lines and brass parts of the engine. It promotes formation of peroxides that lead to knock and gum formation.

Its compound known as blue vitreoil has wide use, as an agricultural poison and algicide in water purification. The copper in the form of barium promoted copper chromite has been employed as a catalyst to convert carbon monoxide, hydrocarbon and oxides of nitrogen to less harmful products carbondioxide, water and nitrogen respectively. It is not surprising, therefore, that many methods of analysis of copper at trace level have been investigated but few are in practical use.

The analytical committee[1] have pinpointed the advantages and disadvantages of various reagents for the determination of trace amount of copper. The most sensitive reagents are neocuproine[2], diethyldithiocarbamate[3] and dibenzyldithiocarbamate[4]. However diethyldithiocarbamic acid decomposes rapidly in solutions of low pH and therefore extraction of low pH should be performed immediately, preferably with excess of reagent present. Its sodium salt react with large number of metal ions but can effect selective separation in presence of masking agents such as EDTA[5] or cyanide[6]. Although zinc dibenzyldithiocarbamate method is better than the above method, in several respects, it requires either several extractions or longer time of extraction to remove the interfering ions such as Ni(II), Co(II), Bi(II), Hg(II) and Fe(III). Other classic reagents for copper are derivatives of bipyridine and phenanthroline. Diehl and Smith[7] have reviewed analytical reagents for copper which are the derivatives of above compounds. Dithiozone[8] has the advantage of very high sensitivity and mineral acid reaction

medium. However, its strong colour and the mediocre stability of its solution are disadvatages. Biscyclohexanone oxalylhydrazide[9] Biscyclohexanone oxalyldihydrazone[10] are the reagents used for analysis of copper in chemical laboratories. Substituted thioureas react with copper in basic medium to form the complex extractable into chloroform having an absorption maximum in UV range and many metal ions interfere. The substituted thioureas which are recommended are 1-benzoyl-3-(2-pyridyl)-2-thiourea[11] 1-benzoyl-3-methyl-2-thiourea[12] diphenyl-thiourea[13], 1-phenyl-3-thiobenzoyl-2-thiourea[14] 1-p-tolyl-3-benzoylthiocarbamide[15]. In case of 1-phenyl 3-thiobenzoyl-2-thiourea 10 min. beating on boiling water bath is necessary for full colour development. Biscyclohexanone oxalyldihydrazone was one of the earliest used hydrazone for the spectrophotometric determination of copper. Several new hydrazones reported as a reagents for copper are reviewed by Singh et al[10]. Hydrazones recently investigated include thiophene-3-aldehyde-2-benzothia-zolyl hydrazone (ε=44000)[17] 2-Furaldehyde benzothiazo-2-hydra-zone (ε=44000)[18] substituted thiophen-2-aldehyde-2-benzothiazo-lylhydrazone (ε=4.5-4.9x10^4)[19] benzothiazole-2-carboxaldehyde-2-quinolyl hydrazone[20] diacetylmonoquinolylhydrazone (ε=14500)[21] 2-hydroxy-1-naphthaldehyde-4-methoxy-benzoyl hydrazone[22] biace-tyl-bis (2-quinolyl hydrazone)[23] N-N[1] oxalybis (salicylaldehyde hydrazone)[24]. Most of these react with copper in alkaline medium and are highly sensitive but suffers from several inter-ferences and prolonged time of equilibration e.g. Thiophene-2-

aldehyde-2-benzothiazolylhydrazone (15 min) and benzothiazole-2-carboxaldehyde-2-quinolyl hydrazone (15 min). Thiosemicarbazone are selective and sensitive reagents for copper. Among the thiosemicarbazones reported recently for photometric determination of copper are acetophenone thiosemicarbazone[25] cyclohexane-1-2-dione bis-thiosemicarbazone[26], di-2-pyridyl ketone thiosemicarbazone[27], Furoin thiosemicarbazone[28], biacetyl bis (4-phenyl)-3-thiosemicarbazone[29] di(2-pyridyl)glyoxal bis (4-phenyl-3-thiosemicarbazone)[30], 2,4-dihydroxy benzophenone thiosemicarbazone[31] 5-nitrosalicylaldehyde-4-phenyl-3-thiosemicarbazone[32], 2',4'-dihydroxyacetophenone thiosemicarbazone[33], 5-5'-di-methyl cyclohexane-1,2,3 trione 1,2 dioxime 3-thiosemicarbazone[34] and salicylaldehyde thiosemicarbazone[35]. Only few are used to determine the copper in highly acidic media. In determination of copper at pH 2.5 using N-thiobenzoyl-N-phenyl hydroxylamine[36] 30 min shaking with chloroform solution of the reagent is necessary. An extractive procedures have been developed for determination of copper with numerous oximes. The reactions with copper are generally carried out mostly in weakly acidic media and are less sensitive. Newly reported oximes are α-benzoin oxime[37] 2'-hydroxy-4-methoxy-5'-methylchalcone oxime[38], 5'-chloro-2'-hydroxy-4'-methyl acetophenone oxime[39] 1-10-phenanthroline phloxime[40], phenanthronequinone monoxime[41] acetyl acetone oxime[42] 2-hydroxy acetophenone oxime[43], phenylpyruvic acid oxime[44], salicylaldehydoxime[45], 3'-bromo-2'-hydroxy-5'-methyl acetophenone oxime[46], Nioxime[47] 5-bromosalicylaldoxime[48]

3'-5'-dibromo-2'-4'-dihydroxy acetophenone oxime[49] 2-hydroxy-1-
acetophenone oxime[50] 2-methoxy salicylaldoxime[51], phenanthrene
quinone monoxime[52], picolinamide oxime[53] indane 1,2,3-troane
trioxime[54] and 2-hydroxy-4-n-propoxyacetophenone oxime[55]. How-
ever, the rate of extraction of the copper complex is slow e.g.
5-bromo-salicylaldoxime (10 min) and phenanthrene quinone oxime
(2 min). α-benzoin oxime method suffers from low stability of
the complexes. In addition reagent blank is required. Some β-
diketone form the coloured complexes in the pH range 3-6, which
are extractable into nonpolar solvent these include acetyl
acetone[56], thiotropolone[57], benzoyltrifluoroacetone[58], 1,1,1-
trifluoro-3-(2-phenoyl) acetone[59], thithenoyltrifluoro ace-
tone[60], thiobenzoyl acetone[61], isonitrosoacetylacetone[62] and
Michler's thioketone[63]. Copper is determined spectrophoto-
metrically by extracting copper-benzoyltrifluoroacetone complex
from aqueous solution of pH 3 into amylalcohol with 10 min
shaking at 375 nm. Interference is caused by Fe(III), 1,1,1-
Trifluoro-3-(2-phenoyl) acetone and thiobenzoyl acetone are
sensitive reagents for copper but scrubbing of the organic
phase with alkaline solution is necessary to remove the excess
of reagent and many anions interfere. Michler's thioketone
(MTK) forms 1:4 complex which is extractable into chloroform-
butanol mixture at pH=3, the complex is measured at 495 nm.
Pt(IV) interfere. Numerous azodyes have been invesdtigated as
the sensitive reagents for copper. In 5'-amino-3-(3-carboxy-1,
2,4-triazol-5-ylazo)-4-hydroxy-naphthalene-4,5,-disulphonic

acid[64] 1-(2-pyridylazo)-2-phenanthrol[65] eriochrome azurol G[66]

chlorsulphonenol S[67], 6-(benzothiazol-2-ylazo)-2,4,-xylenol[68],

5'-dimethyl azobenzene-4-sulphonic acid (DMHAS)[69], 2-hydroxy-5

-methyl acetophenone ethylene diamine anil (HMAEA)[70]. 4-(2-qui-

nolylazo)phenol[71], 6-(6-bromo-2-benzothiazolylazo)2,4-xylenol[72]

6-(1,2,4-triazol-3-ylazo)-2,4-xylenol[73], 5-amino-2-(5,5-dime-

thyl-4,5,6,7-tetrahydrobenzothiazol-2-ylazo)phenol and 5-(die-

thylamino)2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazol-2-yla-

zo) phenol[74]. Eriochrome cyanine R[75], 4-(2-pyridylazo) resorci-

nol[76], 3-5-diamino-2-(2-thiazolylazo) benzoic and 3-5-diamino-

2-(4,5-dimethyl-2-thiazolylazo) benzoic acid[77], chromal blue[78],

3-(4-antipyrinylazo)-6-(2-arsonophenylazo) chromotropic acid[79],

ferron[80], 2-(4-hydroxy-6-methylpyrimidin-2-ylazo)-1-naphthol[81],

4-(4,5-dimethyl-2-thiazolylazo)-2-methyl resorcinol[82], 2-(3,5-

dibromo-2-pyridylazo)-5-diethylaminophenol[83], 1-(4-nitrophenyl)

3-(2-benzothiazolyl) triazene[84] 1-(2-imidazolylazo)-2-naphthol-

4-sulphonic acid[85] and 5-(4-arsonicphenylazo)-8-aminoquinoli-

ne[86] methods many ion interfere. In disodium 3-hydroxy-4-(6-

methyl-2-pyridylazo). Naphthalene[87], N-(2-aminoethyl) N-2-pyri-

dylmethylene amino ethyl dithio carbamic acid[88], and pyridine-

2-aldehyde-2'-hydroxynaphthylimine[89], methods 15,45 and 30 to

60 min waiting and also reagent blank is required. Heating of

the aqueous phase upto 20 min at 80° for salicylic acid[90], 30

min heating at 50° for N-phenylglycine[91], while 40 min heating

at 50° for bis (2,4-diaminophenyl) phosphonate[92] is required.

In photometric determination of copper with 2-salicylidene-

amino benzoic acid[93], Al(III), Cr(III), Ti(IV), V(V), tartarate, citrate while for dicyclohexyldithiophosphinic acid[94] tetravalent Bi, Pd(II), Pt(IV) and Au(III) interefere. The ethanolic solution of thiovioluric acid[95], react with copper(II) in the pH range 4.5-7.5 to form the complex which is measured at 395 nm and various ions interfere. The benzene extract of copper complex with piperidine-1-curbothionate[96] exhibits absorption maximum at 440 nm but method suffers from interference of Fe(III), Sb(III), As(III), Hg(II), Cr(III), Sn(II), V(V), Mo(VI), SCN^- and NO_3^-. 2-Methyl-3-chloro-5-hydroxy-4-naphthaquinone[97] formed red complex with copper(II), it was measured at 520 nm in 70% ethanol in the pH range 6.5 to 8.0. Zn(II) did not interfere if present upto 100 fold excess. Copper-4-(2-quinolylmethyleneamino)-1-phenyl-2,3-dimethyl-5-pyrazolone complex[98] versus reagent blank showed a bathocromic shift from 360 nm (pH=4) to 380 nm (pH=10) with increasing pH. The highest absorbance was observed at pH 8. The complex formed within 10 min and was stable for >30 min.

The proposed method describes synergetic solvent extraction of copper(II) with 4'-chloro-2'-tolyl)-4,4,6-trimethyl (1H,4H)-2-pyrimidinethiol in combination with neutral base containing an electron doner such as pyridine from an aqueous solution of pH 5. The extracted yellow complex is quite stable and hence suitable for the spectrophotometric determination of copper(II) at 390 nm. The method is rapid, extremely simple, sensitive and reproducible. The reagent is colourless and used

for determination of microgram amount of copper in alloy and drug samples.

EXPERIMENTAL

Standard Copper(II) Solution :

A standard stock solution (1 mg/ml) of Cu was prepared by dissolving 1.965 gm of copper sulphate pentahydrate (AR) in doiuble distilled water containing a few drops of sulphuric acid. The solution was diluted to 500 ml. The solution on standardisation by volumetric method[79] was found to contain 1.00 mg of Cu(II) per ml. Working solutions of lower concentration were made by diluting the stock solution with double distilled water.

Extracting Solution :

The solution of 0.5 M pyridine and 0.01 M pyrimidinethiol were prepared by dissolving 4.05 ml and 0.281 gm of pyridine and pyrimidinethiol respectively in chloroform. The solution was diluted to 100 ml. Equal volume (5 ml) of the base and pyrimidinethiol solution in chloroform were mixed and this mixture was used for the extraction experiments.

The solutions used for the study of diverse ions were prepared by dissolving AR grade chemicals in distilled water or dilute hydrochloric acid. All the organic solvents were used after double distillation. Distilled water was used throughout.

Apparatus :

Elico spectrophotometer model CL-27 with 1 cm quartz cells was used for all the absorbance measurement. For pH measurements the Toshniwal pH meter equipped with glass electrode was used.

General Procedure :

An aliquot of sample solution containing 5 to 70 μg of copper was taken and the pH of the solution was adjusted to 5.0 in a 25 ml volume with 0.1 M HCl and NaOH solutions. The solution was transferred into 125 ml separating funnel and shaken with 10 ml of extracting solution for 5 min. The layers were allowed to separate, removed in 25 ml dry beaker, dried over anhydrous sodium sulphate. Volume of organic phase was made upto 10 ml and then the absorbance was measured against chloroform as a blank at 390 nm. The amount of copper was calculated from the calibration curve.

RESULTS AND DISCUSSION

Spectral Characteristics :

The absorbance spectra of Cu(II) pyrimidinethiol complex in chloroform extract resulting from different amounts of Cu(II) solution (1,2,3,4,5,6 & 7 ppm) are shown in Fig.-1. The yellow Cu(II)-pyrimidinethiol complex exhibits an absorption maxima at 390 nm. The solution of reagent pyrimidinethiol in
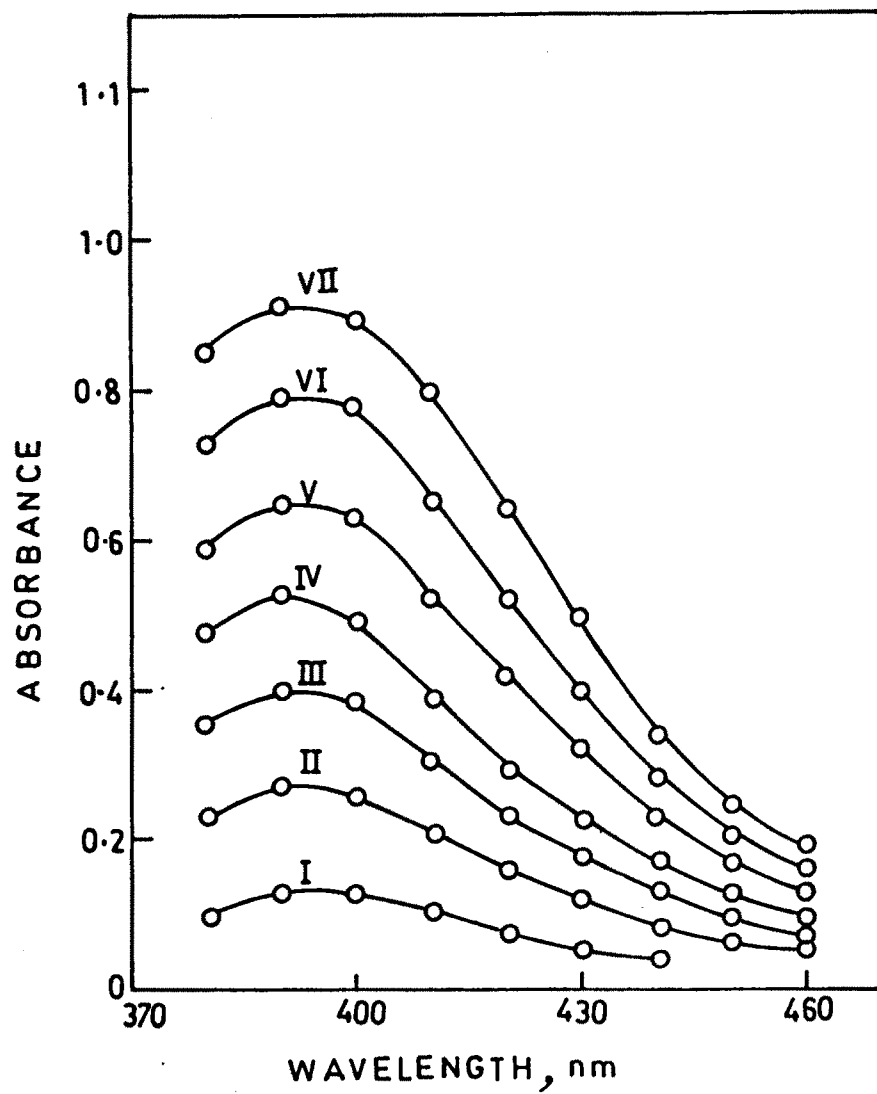
FIG. 1 — ABSORBANCE CURVES OF Cu(II) —
PYRIMIDINETHIOL COMPLEX.
Cu(II), I, 1 ppm; II, 2 ppm; III, 3 ppm;
IV, 4 ppm; V, 5 ppm; VI, 6 ppm;
VII, 7 ppm.

chloroform is colourless and hence does not absorb significantly in the visible region. The molar absorptivity of the complex is 8260 L mole^{-1}, cm^{-1}. The Sandell sensitivity of the reagent was found to be 7.6 ng/cm^2 at 390 nm. Table No.1.

Effect of pH :

The extraction of Cu(II) was studied at various pH (fig.2). In absence of pyridine extraction of Cu(II) pyrimidinethiol complex commence at pH 5 (in acidic medium) and becomes quantitative at pH 9 (in basic medium) with 5 min shaking. In presence of pyridine however extraction starts at pH 2 and becomes quantitative at pH 4. There is increase in absorbance by 27% in presence of pyridine. Pyridine thus shows a synergetic effect on the extraction of Cu(II)-pyrimidinethiol complex from acidic medium. Further studies were made at pH 5 by adjusting the pH of the solution with 0.1 M HCl and NaOH solution. After extraction the pH of the aqueous phase was found to be approximately 6.8. The results of extraction of Cu(II)-pyrimidinethiol complex in presence of pyridine as a function of pH is shown in Table-2.

Effect of Reagent Concentration :

Effect of reagent concentration on colour intensity of the Cu(II) pyrimidinethiol complex at pH=5 was studied by varying amount of reagent, while Cu(II)-concentration was kept constant at 3 ppm. The colour of Cu(II)-pyrimidinethiol complex was developed as per the recommended procedure. In absence of

TABLE-1 : Characteristics of Cu(II) Complex of

Pyrimidinethiol

Cu II = 3 ppm

Sr.No.	Characteristics	Pyrmidinethiol
1.	Solvent	Chloroform
2.	λ max, nm	390
3.	ε max, L mole^{-1}cm^{-1}	8260
4.	pH for max colour development with pyridine	5
5.	Stability in hrs	> 12
6.	Beer's range	0.5 to 7
7.	Sandell's sensitivity ng/cm^2	7.6
8.	Molar ratio of pyrimidi- nethiol needed for complete complexation	48

<u>TABLE — 2</u> : Extraction of Cu(II)-Pyrimidinethiol complex

with Pyridine as a function of pH

Cu(II) = 30 μg λ max = 390

pH	Absorbance	% Extraction	Distribution Ratio
2	0.115	28.75	1.00
2.5	0.250	62.5	4.16
3	0.320	80.0	10.0
3.5	0.360	90.0	22.5
4	0.390	97.5	97.5
5	0.400	100.0	∞
6	0.400	100.0	∞
7	0.400	100.0	∞
8	0.400	100.0	∞
9	0.400	100.0	∞
10	0.400	100.0	∞

pyridine 53 fold molar excess of reagent is required for full colour development for 3 ppm of Cu(II) only, whereas 48 fold molar excess of reagent is sufficient in presence of pyridine (Fig.3). There was increase of optical density in presence of pyridine to 27 percentage. There was no significant change in the absorbance with large excess of reagent. Table-3 shows the effect of reagent concentration on extraction of Cu(II)-pyrimidinethiol complex in presence of pyridine.

Effect of time of shaking and stability of complex :

In order to establish the optimum time for quantitative extraction of Cu(II)-pyrimidinethiol complex, the time of shaking was varied from 0.5-20 min. The curves (Fig.4) of the absorbance versus shaking time indicate that shaking for 3 min and 4 min was sufficient for quantitative recovery of 3 ppm of Cu(II) in presence of pyridine and in absence of pyridine respectively. There was also increase of optical density by 27% (Table No.4).

The yellow complex of Cu(II) was measured at 390 nm at regular interval of time, absorbance of complex remained stable for more than 12 hr. Hence the time of measurement of absorbance is not critical.

Effect of Solvent :

Of the various solvents examined as an extractants for Cu(II)-pyrimidinathiol complex, it was observed that the

TABLE – 3 : Effect of Reagent Concentration of CU(II)

Pyrimidinethiol complex in presence of pyridine

Cu(II) = 30 μg λ max = 390 nm

Pyrimidinethiol = 0.01 M

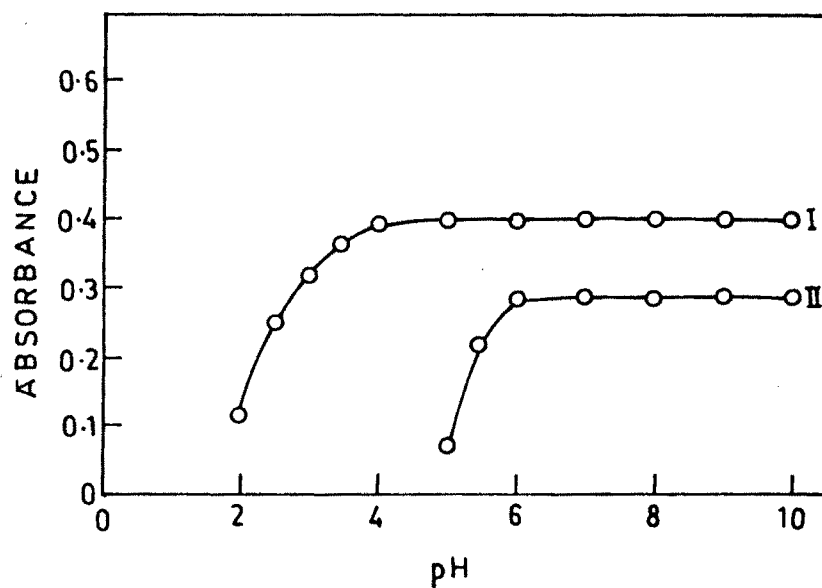| Pyrimidinethiol concentration 0.01 M	Absorbance	% Extraction	Distribution Ratio
0.5	0.080	20.0	0.625
1	0.150	37.5	1.50
1.5	0.220	55.0	3.05
2	0.275	68.75	5.50
3	0.340	85.0	14.16
4	0.380	95.0	47.5
5	0.400	100.0	∞
6	0.400	100.0	∞
7	0.400	100.0	∞

FIG. 2

EXTRACTION OF Cu (II)

PYRIMIDINETHIOL

COMPLEX WITH

PYRIDINE (I) AND

WITHOUT PYRIDINE (II)

AS A FUNCTION OF pH .

Cu (II) = 3 PPm

FIG. 3

EFFECT OF REAGENT

CONC. WITH

PYRIDINE (I) pH = 5,

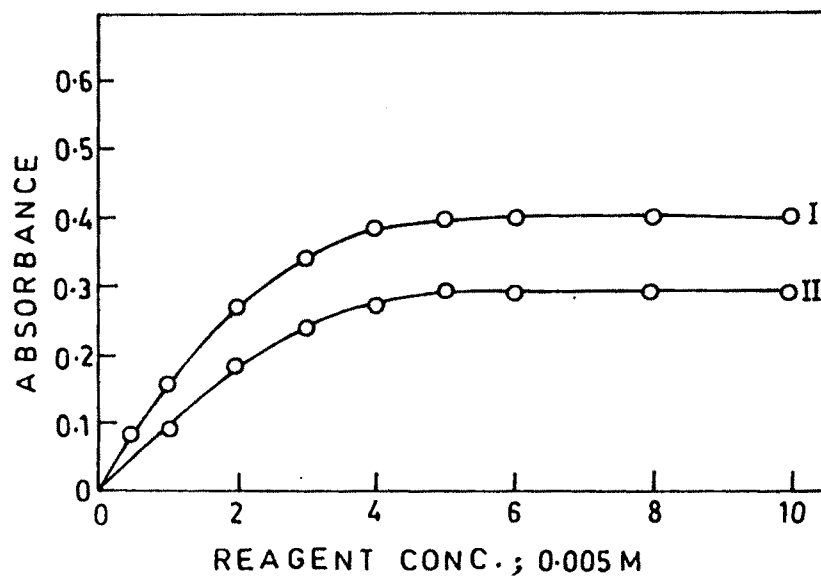AND WITHOUT

PYRIDINE (II) pH = 9 .

Cu (II) = 3 ppm .

TABLE − 4 : Effect of time of shaking with pyridine

Cu(II) = 30 μg λmax = 390

Pyrimidinethiol = 0.01 M

Time in min	Absorbance	% Extraction	Distribution Ratio
1	0.360	40.0	22.5
2	0.380	95.0	47.25
3	0.400	100.0	∞
4	0.400	100.0	∞
5	0.400	100.0	∞
7	0.400	100.0	∞
10	0.400	100.0	∞
13	0.400	100.0	∞
15	0.400	100.0	∞

complex was extractable into solvents such as chloroform, toluene, benzene, 4-methyl-2-pentanol and MIBK. However, chloroform was chosen as it offers a clear cut separation of phases and because of high distribution of the complex in it.

Effect of Pyridine Concentration :

To study the pyridine concentration a series of solutions were prepared containing fixed amount of Cu(II) 3 ppm. The complex of Cu(II) was extracted by using different amounts of the pyridine varying from 1 to 6 ml of 1 M pyridine. The colour of Cu(II) complex was developed as per the general procedure and the absorbance was measured at 390 nm against chloroform blank. The results of the studies are shown in Fig.5 which indicates that 2 ml of pyridine is sufficient for full colour development. But for all subsequent measurements 5 ml of pyridine solution was used.

Validity of Beer's Law :

The solution containing copper in the concentration range upto 9 ppm were used for study of the validity of Beer's law. The colour of the Cu(II)-pyrimidinethiol complex was developed as described in the recommended procedure using equal volumes of (5 ml) 0.5 M pyridine and 0.01 M pyrimidinethiol in chloroform. The extracted yellow complex was measured at 390 nm against solvent blank from the plot in Fig.6 it is clear that there is rectilinear relationship between the absorbance and
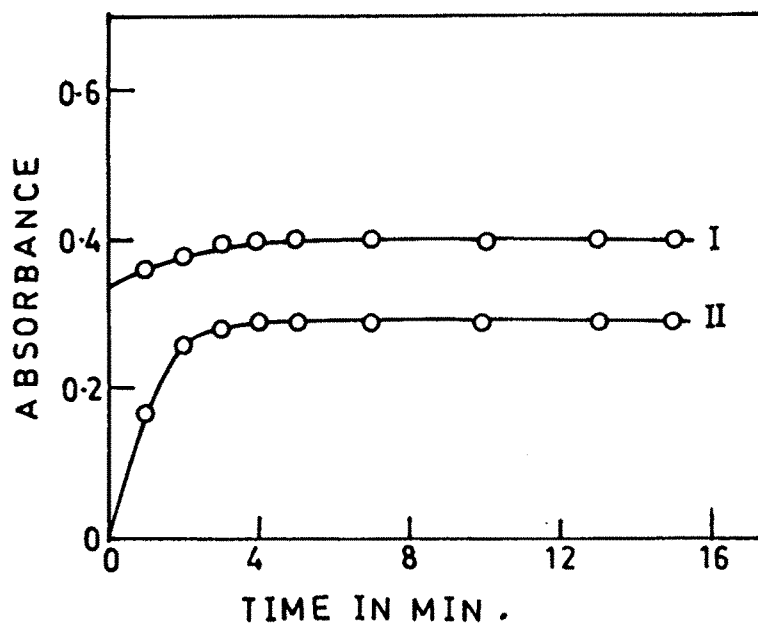
FIG.4

EFFECT OF TIME OF

SHAKING .

Cu = 3 ppm

I , WITH PYRIDINE , pH=5 .
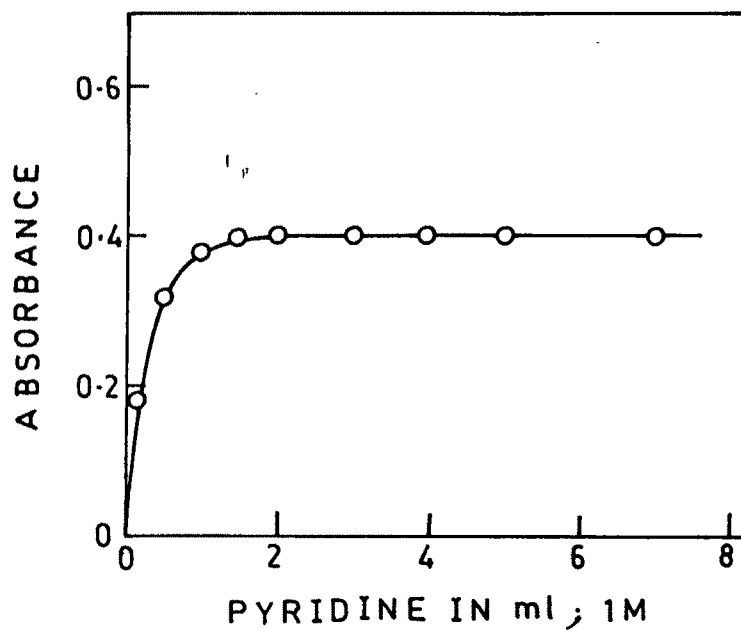
II , WITHOUT PYRIDINE , pH=9 .

FIG. 5

EFFECT OF PYRIDINE

CONC. (1 M) .

Cu(II)- PYRIMIDINE-
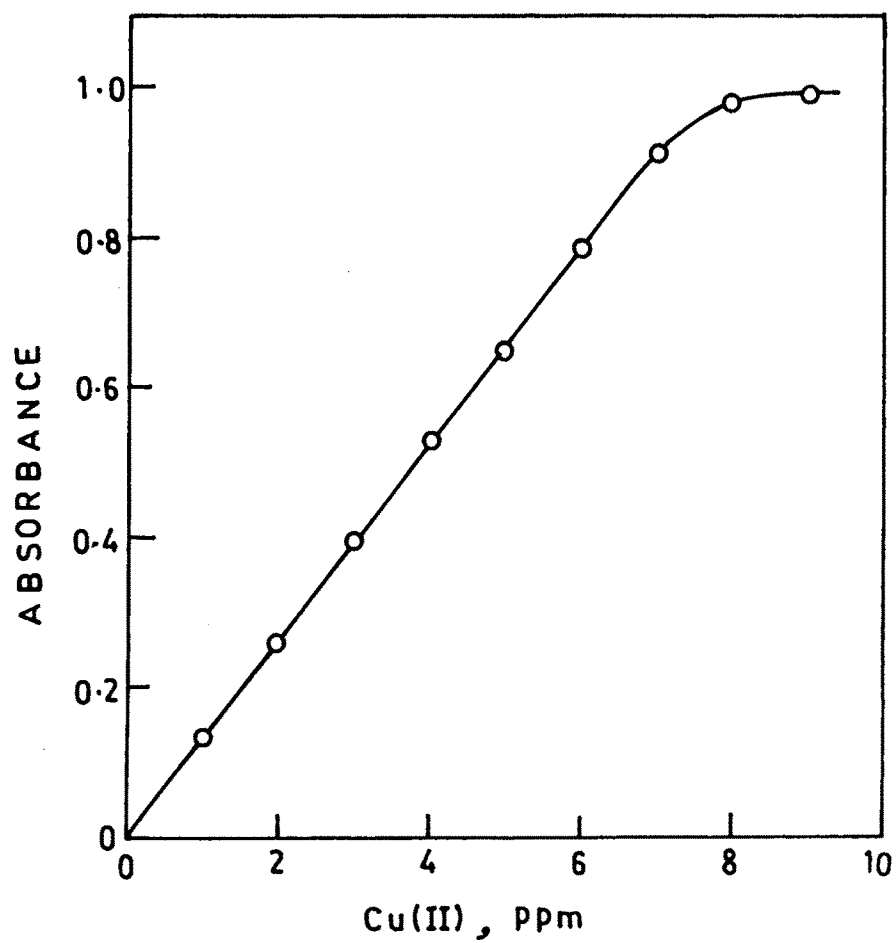
THIOL COMPLEX .

Cu = 3 ppm

FIG. 6 — VALIDITY OF BEER'S LAW FOR Cu(II)

PYRIMIDINETHIOL COMPLEX . pH = 5·0 .

concentration of Cu(II) in the range 0.5 to 7 ppm. However, the optimal concentration range was found to be 1.5 to 5.5 ppm.

Composition of the Complex :

The composition of the complex of Cu(II) with pyrimidine-thiol was determined by the method of Job's continuous variation. Equimolar solutions of metal, ligand and pyridine were used. A series of solutions were prepared by mixing different amounts of metal and pyrimidinethiol, metal and pyridine by keeping the sum constant. The colour of the complex was developed as per the recommended procedure and measured at 390 nm against solvent blank. Job's plots shown in figs. 7 & 8 indicate formation of 4:1 (L:Cu) (1:1) (Py:Cu) complex in both the cases. The Cu(II)-pyrimidinethiol complex is extractable into chloroform hence the probable composition of the uncharged complex is H_2CuL_4Py (1:4:1).

Effect of Diverse Ions :

The effect of large number of diverse ions on the determination of 0.030 mg of Cu with the reagent was investiga-ted following the recommended procedure. Initially foreign ion was added to the Cu(II) in large excess. When the interference was intensive tests were repeated with successively smaller amounts of foreign ions. The tolerance limit was set at the amount of foreign ion which gave error less than 2% in absor-
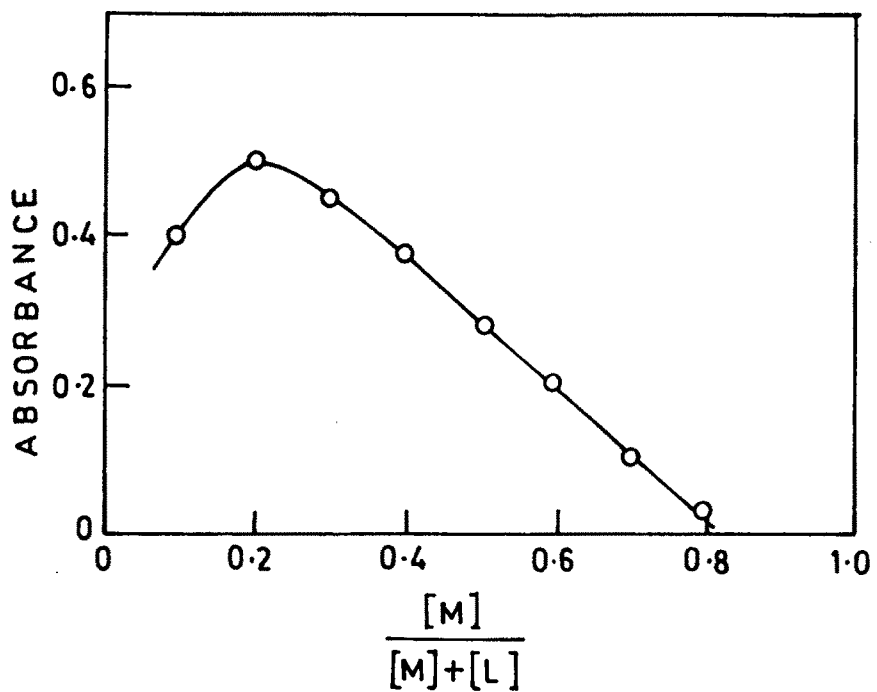
FIG·7

JOB'S PLOT

$[Cu] = [PYRIMIDINETHIOL]$

$= 2\cdot0 \times 10^{-3} M$
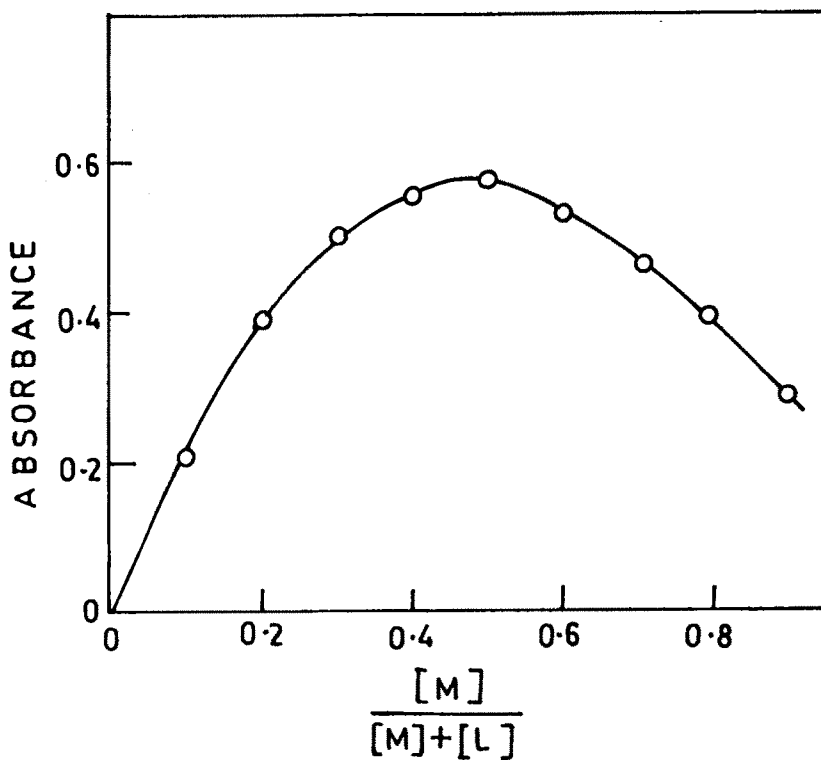
$[PYRIDINE] = 0.5 M$

FIG·8

JOB'S PLOT

$[Cu] = PYRIDINE$

$= 1\cdot5 \times 10^{-3}$

PYRIMIDINETHIOL

$= 0\cdot01 M$

bance of the complex at 390 nm. The tolerance limit of ions tested were shown in Table No.5.

Reproducibility Accuracy and Sensitivity Data :

For the study of reproducibility and accuracy of the method, absorbance measurements with ten different identical solutions containing 3.0 ppm of Cu(II) were performed as out-lined in the procedure and concentration determined using calibration curve. The result are shown in Table No.6. It is observed that there is an excellent agreement in the experimental values. The method has high precision and accuracy.

Average of the ten readings are calculated. Deviations from these average readings was found out in each case and then standard deviation was calculated. From the standard deviation, the reproducibility of the results with 95% confidence limit was calculated. The Sendell sensitivity of the reaction as calculated from Beer's plot was found out to be 7.6 ng/cm^2.

TABLE – 5 : Effect of Diverse Ions

Cu(II) = 0.030 mg λmax = 390 nm

Pyrimidinethion = 0.01 m in CHCl$_3$

Ions added	Tolerance limit, mg
V(V)	20.0
Cd(II), Cr(VI), U(VI), Mg(II)	10.0
Mn(II), Co(II), Ni(II), W(II) Zn(II), Rh(III), Ir(III), Pt(IV), Se(IV), Au(I), Ce(V), Pb(II)	5.0
Rh(III), Ti(IV)	2.0
Hg(II)	1.0
Fe(III), Zr(II), Fe(II), Sn(III) Te(IV), Ti(IV)	interfere

TABLE - 6 : Precision and Accuracy of the Method

Amount of Cu = 3.0 ppm

Sr. No.	Absorbance observed	ppm of Cu found (x)	$(x-\bar{x})$	$(x-\bar{x})^2$
1.	0.405	3.03	0.016	0.000256
2.	0.395	2.96	-0.054	0.00291
3.	0.405	3.03	0.016	0.000256
4.	0.400	3.00	-0.014	0.000196
5.	0.395	2.96	-0.054	0.00291
6.	0.405	3.03	0.016	0.000256
7.	0.410	3.07	0.056	0.003136
8.	0.405	3.03	0.016	0.000256
9.	0.400	3.00	-0.014	0.000196
10.	0.405	3.03	0.016	0.000256
	Total	30.14		0.010628

Average value $\bar{x}$ = $\dfrac{30.14}{10}$

= 3.014

Standard deviation $\delta = \sqrt{\dfrac{(x_1-\bar{x})^2+(x_2-\bar{x})^2+(x_n-\bar{x})^2}{n-1}}$

$\delta = \sqrt{\dfrac{0.010628}{10-1}}$

= 0.034

Error E =   Observed Reading – Actual Reading

  =   3.014 – 3.00

  =   0.014

Relative error $= \dfrac{0.014 \times 100}{3.0} = 0.46$

Coeff. of variation $= \dfrac{\delta \times 100}{\bar{x}} = \dfrac{0.034 \times 100}{3.014} =$

  $C \cdot V. = 1.12$

Molar exctinction coefficient

$\varepsilon = \dfrac{Absorbance}{ppm} \times 1000 \times At.wt.$

  $=$ slope $\times 1000 \times 63.546$

  $=$ 0.13 $\times 1000 \times 63.546$

  $=$ 8260 L mole^{-1}cm^{-1}

Sandell's sensitivity 'S' $10^3 \times A \times C_{min}$

  where $C_{min} = \dfrac{D_{min}}{\varepsilon \times b}$

  $= 1000 \times 63.546 \times \dfrac{0.001}{8260}$

  $7.6 \times 10^{-3} = 0.0076 \ \mu g$

  $S = 7.6 \ ng \ cm^{-2}$

Reproducibility with 95% confidence

  $= \bar{x} \pm 2.26 \times \delta/\sqrt{n} = \sqrt{n} = 3.16$

  0.01075

  $= 3.014 \pm 0.0243$

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