CHAPTER - IV

EXTRACTION SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) WITH 4'-BROMO - PTPT

CHAPTER - IV

EXTRACTION SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH PYRIMIDINETHIOL.

INTRODUCTION

Copper has known from ancient times. It is one of the elements used to a greater extent in pure form than in alloy forms. The industrially important alloys of copper are brass, bronze, gun metal and nickel-silver alloy. It is important element in electrical industry. Copper alloys like cartridge brass has innumerable uses, including cartridge cases, automotive radiator cores and tanks, lightening fixtures, eyelet, rivets, screws, springs and plumbing products. Nickel silver alloys are used for table flatwear, Zippers, Camera parts, costume jewellery, nameplates, radiodials and some electrical switch gear. Cupronickel alloys are well suited for application in industrial amd marine installation 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 hardwears. Alloys of copper with sulphur and tellurium increase ease of machining.

Now-a-days there is ever increasing demand for copper and its alloys as a result of rapid industrial advancement and its increasing use as structural alloys in diversified industries. This had led to 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.

Numerous organic reagents have been reported for the spectrophotometric determination of copper. The most extensively used reagents are derivatives of 1,10-phenanthroline[2-3] which are reported to be specific reagents for copper but many metal ions interfere during determination. Also following are the reagents reported for the determination of Copper. These include 1,5-diphenyl-3-thiocyarba-hydrazide[4] , bis(2-amino ethyl)-dithiocarbamic acid[5], 1-(2-pyridylazo)-2-phenanthrol[6], 1-benzoyl-3-(2-pyridylthiourea)[7], 6-methyl picolinaldehyde hydrazone[8], 2,4-dinitroresorcinol[9], dithio-oxamide[10] and 1-(2-pyridyl methylene amino)-2-naphthol[11]. Although these reagents are sensitive they lack selectivity and many metal ions interfere during determination. Thiosemicarbazones or azines of certain aldehydes and ketones are investigated as possible analytical reagents for spectrophotometric determination of Cu(II). These include picolinaldehyde semicarbazone[12], B-ionone thiosemicarbazone[13] 6-methyl-picolinaldehydeazine[14], picolinaldehyde thiosemicarbazone[15] and thiophene-2-aldehyde thiosemicarbazone[16]. Most of these react with Copper in alkaline medium and are highly sensitive but suffer from several interferences and required prolonged time of equilibration. Recently some important substituted thioureas reported for the determination of Copper include 1-p-tolyl-3-benzoyl-thiocarbamide[17], 1-phenyl-3-thiobenzoyl-2-thiourea[18], N-(4-hydroxy-3-methoxy-benzylidine) hydrazine carbothioamide[19]. Many metal interfere during determination and in case of some e.g. 1-phenyl-3-thiobenzoyl-2-thiourea 10 min heating on boiling water bath is necessary. Several new hydrazones reported as reagents for copper are benzothiazole-2-carboxyldehyde-2-quinolyl hydrazone[20], diacetyl monoquinolyl hydrazone[21] They react with copper in alkaline medium and are highly sensitive but suffer from several interferences and prolonged time of heating required for full complexation. eg. benzothiazole-2-carboxyldehyde-2-quinolhydrazone (15 min). Recently thiosemicarbazones are reported for the determination of copper as they are selective and sensitive reagents for Cu(II). These include furoin thiosemicarbazone[22], biacetyl bis-(4-phenyl)-3-thiosemicarbazone[23], di(2-pyridyl) gloxal bis-(4-phenyl-thiosemicarbazone)[24]. Only few are used to determine copper in highly acidic medium. Extractive procedure have been developed for determination of copper with numerous oximes. The reaction with copper are generally carried out mostly in weakly acidic media are less sensitive. Newly reported oximes are 2-hydroxy acetophenone oxime[25], 5-bromo salicylaloxime[26], 3'-bromo-

2'-hydroxyl-5'-methyl acetophenone oxime[27], nioxime[28], Michler's thioketone[29], furfural oxime[30], phenanthrequinone monoxime[31]. However, the rate of extraction of the Copper complex is slow e.g. 5-bromosalicylaldoxime (10min). Numerous azodyes have been investigated as sensitive reagents for Copper. These include 2-hydroxy-5-methyl acetophenone ethylene diamineanil(HMAEA)[32], bromopyrogallol red and benzyl dimethyl phenyl ammonium chloride[33], ferron[34], 4-nitrosoresorcinol[35], 4-(2-quinolyl azo) phenol[37], 6-(6-bromo-2-benzothiozolylazo)2,4-xylenol[38]. Many metal ions interfere in addition to the observed low tolerence limit for platinum metals.

It is possible to determine Copper with 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene[39], carboxylic acid[40], sodium 1-amidinoazo-2-hydroxynaphthalene-4-sulphonate[41], 2,6-pyridinediol[42]. These methods suffer from serious interferences due to phosphate, cyanide, Ni, Co, V, etc. and complex has low stability.

Pyridinethiols are also known as cyclicthioureas which proved to be analytically useful reagents. Singh et al. reviewed the analytical aspects of substituted pyrimidinethiols[43]. Mercaptopyrimidines react with Cu(II) to form extractable complex in presence of pyridine.

In present work the reagent 4'-bromo-PTPT is used for extractive photometric determination of Cu(II). This method is simple, selective and reproducible. Quantitative separation and determination of Cu(II) in presence of other metals is possible with this method.

A summary of the some selected reagents used for the extractive spectrophotometric determination of Cu(II) is represented in Table No. 1 describing the optimum conditions for the method, spectral properties of the complex, interferences due to foreign ions and remarks.

TABLE NO. 1 :- SUMMARY OF THE REAGENTS REPORTED FOR Cu(II).

Reagent	Conditions	λmax, Beer's range, Molar extinction coefficient	Interference	Remarks	Ref No.
1	2	3	4	5	6
4.7-Dihydroxy-2,9-dimethyl-1-10-phenanthroline	1.0 - 7.0M NaOH	λmax=400nm ϵ = 11500	CN^-, S^{2-}, CO^{++}, Fe^{++}	—	2
1,5-Diphenyl 3-thiocarnajudrazide	2.5	λmax=455nm upto 1.5ppm ϵ = 20600	—	—	4
Bis.(2-aminoethyl) dithiocarbamic acid	4 - 5	λmax=437nm upto 93.8µg ϵ = 13,200	—	Stability 40 min Only, 1:2 complex in excess reagent	5
1-(2-pyridylazo)-2-phenanthrone	2.2 - 8	λmax=560nm upto 3.2ppm ϵ = 30000 S = 2ng	$S_2O_3^{--}$, F^- Ni, Co, Zn	—	6
1-Benzoyl-3-(2-pyridyl) thiourea	2 to 6	λmax=430nm 2.0 to 20ppm	Many metals Ions	—	7
6-Methylpicolinaldehyde hydrazone	8.6	λmax=425nm 1 to 7 ppm	Numerous Cations	Complex stable for 1 hr.	8
2,4-Dinitroresorcinol Acetate buffer	5.0	λmax= 370nm	—	$NaClO_4$ Salting out effect	9

1	2	3	4	5	6
Dithioxamide	H_2SO_4	λmax=525nm upto 20ppm ϵ = 70000	Numerous Cations order of the addition of reagent is critical	—	10
1-(2-pyridylmethyl-eneamino)-2-naphthol	Acetate buffer 3-4	λmax = 482nm 0.2 to 6ppm	CO^{++}	Waiting time 30 to 60 min	11
Picolinaldehyde Semicarbazone	H_3PO_3+NaOH	λmax=350nm upto 1.5 ppm	—	—	12
B-Iononethiosemicarbazone	4.7, $CHCl_3$	λmax=380nm upto 6.0 ppm	Several Cations	—	13
6-Methylpicolinaldehyde azine	H_3PO_3 + NaOH 6 - 10	λmax=480nm upto 12 ppm	—	—	14
Piconilaldehyde thiosemicarbazone	8.9 - 10.7	λmax = 360 - 400nm upto 7	Many ions at 415	reagent blank is necessary	15
Thiophene-2-aldehyde-thiosemicarbazone	$CHCl_3$, 4.7	λmax = 372nm upto 1.2 ppm	Hg, Pt, Pd and other ions	—	16
N-(4-Hydroxy-3-Methoxy-benzylidine hydrazine Carbothioamide	pH=9.3-11.6	λmax=410nm upto 3.1ppm S=5.154µg/cm^2 ϵ = 12300	CO, Fe, Ni, Pb, Ag, Zn, Al	Determination of Cu possible in syntheic mixture	19
Furfural Oxime	—	λmax=394 nm upto 70µg	—	—	30

1	2	3	4	5	6
Phenanthrequinone monoxime	$CHCl_3$	λmax=400nm ε - 8300 S=0.0075μg/cm^2	—	—	31
Bromopyrogallol red and Benzyldimethyl phenyl ammonium chloride	pH = 7 isobutanol	λmax=625nm upto 5 ppm ε = 12860 S = 0.0049	Cd(II), Bi(III), Cr(III), Mn(II), Ni(II)	Determination of sample from Gunmetal Aluminium alloy, Cupronickel alloy.	33
Ferron	Chloroform low acidity	λmax=410nm upto 8 μg/cm^2	Mo, Ti, Zr	—	34
4-Nitrosoresorcinol	pH = 2.5 $CHCl_3$	λmax=365nm upto 10 ppm ε = 7100 S = 0.009	Hg, Thiocyanate, thiosulphate, EDTA, Oxalate, tartrate, citrate, fluoride,	—	35
4-(2-pyridylazo)-resorcinol	Mesityl Oxide	—	—	—	36
1-(2-Quinolylazo)-2,4,5-trihydroxybenzene	—	λmax=550nm ε = 25400	Fe, Cu, CN^- EDTA, Ni,	Determination of Cu in milk & body tissue	39
Carboxylic acid	pH = 6-9 benzene	—	—	—	40
Sodium 1-Amidineazohydroxynaphthalene-4-sulphonate		λmax=560nm upto 37.2μg /10ml S = 0.00792 ε = 1600	Various ions	—	41
2-6-pyridinediol	7 - 10.8	λmax = 535 ε = 14200	—	Reagent blank necessary	42

EXPERIMENTAL

Standard Copper Solution :-

A standard stock solution (1mg/ml) of Cu was prepared by dissolving 1.965 gm of Copper sulphate pentahydrate (AR) in double distilled water containing a few drops of sulphuric acid. The solution was diluted to 500ml. The Copper content of the solution was determined by volumetric method . It was found that the solution contains 1mg 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 0.5M pyridine and 0.01M thiol were prepared by dissolving 4.05M and 0.311gm of pyridine and thiol respectively in chloroform. The solution was diluted to 100ml. Equal volume (5ml) 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.

Apparatus :-

A Carl-Zeiss (JENA) spectrophotometer (speko equipped with 1cm quartz cells was used for all the absorbance measurements. For pH measurements the ELICO pH meter, Model L1-120 equipped with glass electrode was used.

General Procedure :-

An aliquot of sample solution containing 5-70ug of copper was taken and the pH of the solution was adjusted to 5.0 in a 25ml volume with 0.1M HCl and NaOH solutions. The solution was transferred into a 100ml separating funnel and shaken with 10ml of extracting solution for 1min. The layers were allowed to separate, removed in 25ml dry beaker, dried over anhydrous sodium sulphate. Volume of organic phase make up to 10ml and then the absorbance of organic phase was measured against chloroform as a blank at 410nm. The amount of copper was calculated from the calibration curve.

RESULTS AND DISCUSSION

Spectral Characteristics :-

The absorbance spectra of Cu(II) pyrimidine thiol complex in chloroform extract resulting from different amounts of Cu(II) solution (3,5,7 and 10ppm) are shown in Fig. 1. The yellow Cu(II) pyrimidinethiol complex exhibits an absorption maxima at 410nm. The solution of the reagent pyrimidinethiol in chloroform is colourless and hence does not absorb significantly in the visible-

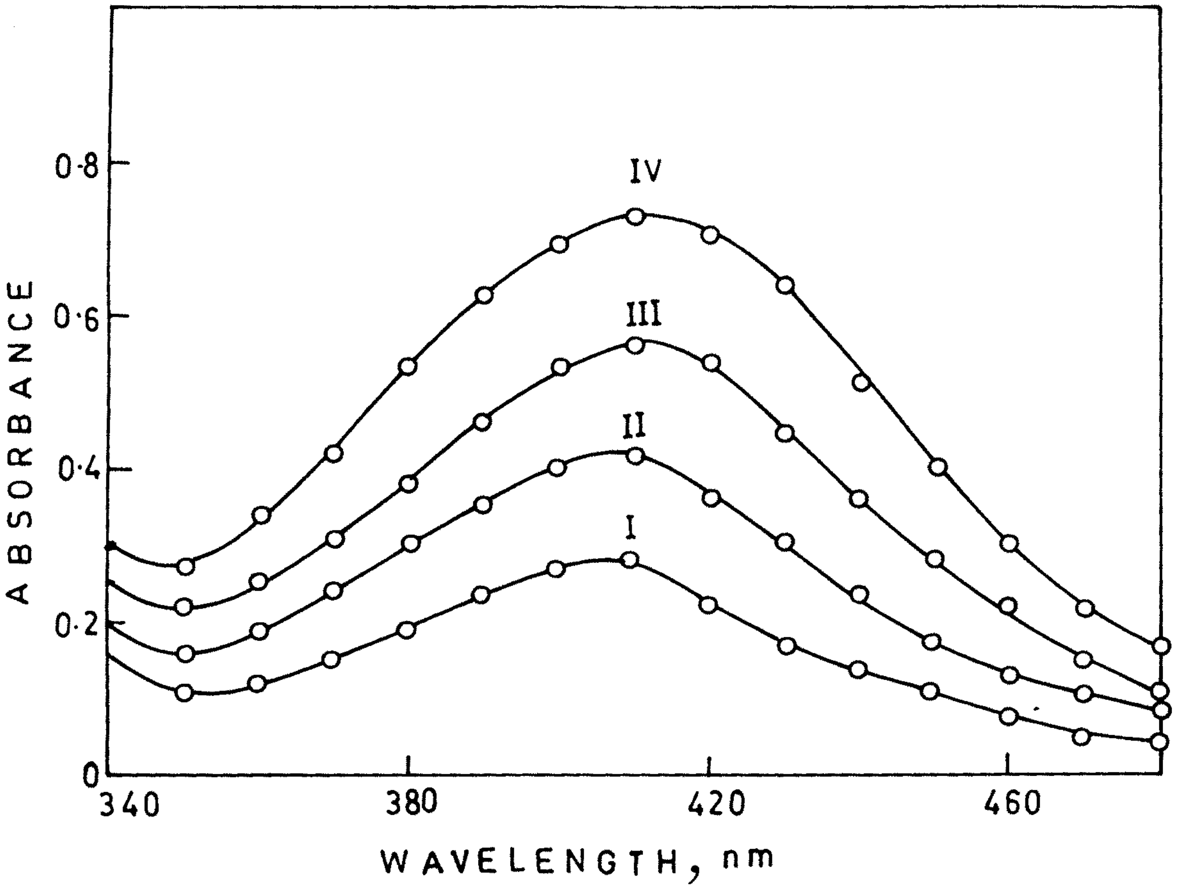


FIG. 1 — ABSORBANCE CURVES OF Cu (II) PYRIMIDINETHIOL COMPLEX.

Cu(II)— I, 3 ppm; II, 5 ppm;
III, 7 ppm; IV, 10 ppm.

region. The molar absorptivity of the complex Cu(II) + pyrimidinethiol as determined from Beer's law plot is 5.084×10^{3} L $mole^{-1}$ cm^{-1}. The Sandell sensitivity of the reagent was found to be 12.5 ng/cm^{2} at 410nm.

Effect of pH :-

In order to study the effect of pH on the Cu(II) pyrimidinethiol complex, a series of solutions were prepared containing fixed amount of Cu(II). Then the Cu(II) complex was extracted in fixed volume of extracting solution at various pH in presence and absence of pyridine. In the absence of pyridine extraction of Copper(II)-pyrimidine thiol complex commences at pH 7 but the extraction of Cu(II) was quantitative at pH 10 with 5 min shaking. However, in the presence of pyridine extraction of Cu(II) starts at pH 3 and becomes quantitative at pH 4.5. After extraction of the pH of the aqueous extract was found to be approximately 6.5. Thus, pyrimidine shows a synergetic effect on extraction of Cu(II)-pyrimidinethiol complex from acidic medium. Further absorption measurement studies were made at pH 5 by adjusting the pH of the solution with 0.1M HCl and NaOH solutions. The results of extraction of Cu(II)-pyrimidinethiol complex in presence and absence of pyridine as a function of pH are shown in Fig. 2.

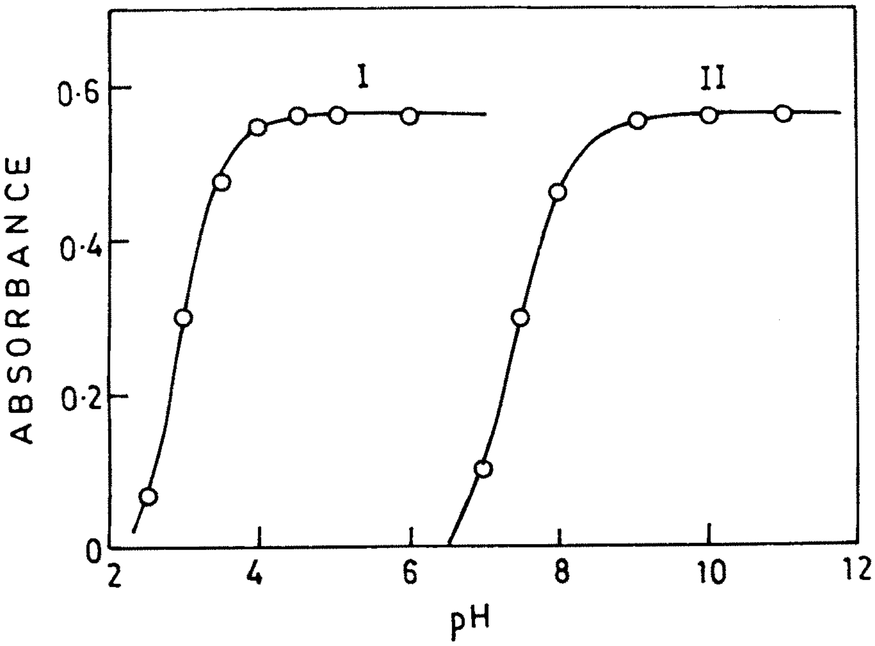
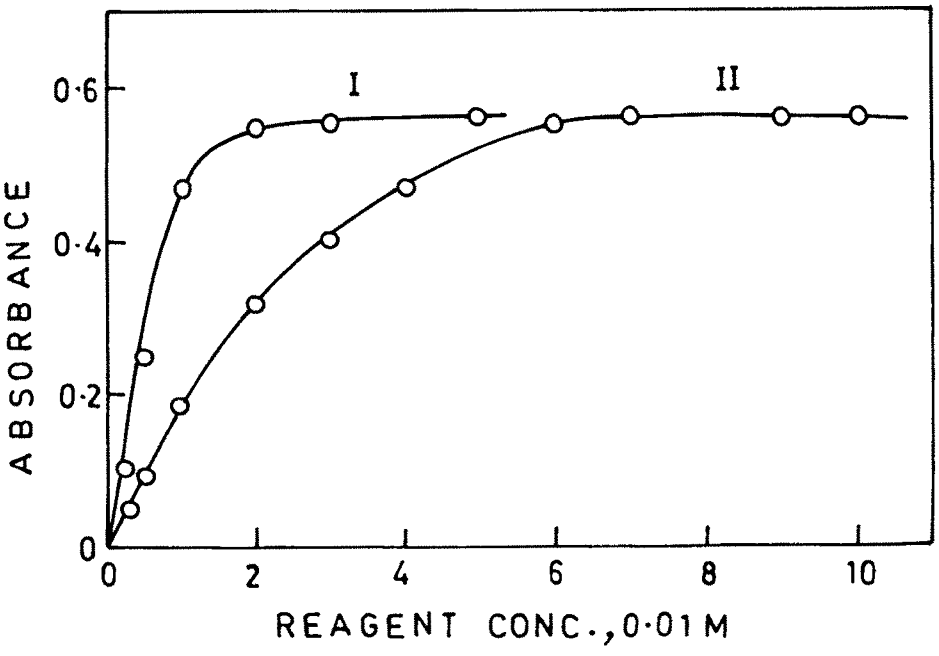


FIG. 2

EXTRACTION OF Cu (II) PYRIMIDINE-THIOL COMPLEX WITH PYRIDINE (I) AND WITHOUT PYRIDINE (II) AS A FUNCTION OF pH. Cu (II) = 7 ppm

FIG. 3

EFFECT OF REAGENT CONC. WITH PYRIDINE (I) pH = 5 AND WITHOUT PYRIDINE (II) pH = 10 Cu(II) = 7 ppm



Effect of Reagent Concentration :-

To study the effect of reagent concentration on colour intensity of the Cu(II)-pyrimidinethiol complex, the solutions containing same amount of Cu(II) 7ppm were taken. The complex of Cu(II) was extracted by using different amounts of the reagent varying from 1-10ml of 0.01M reagent solution. The colour of the Cu(II) complex was developed as per the general procedure and the absorbance of the complex was measured at 410nm against chloroform as a blank. The results of the studies are shown in Fig. 3 which indicate that in absence of pyridine 54 fold molar excess of reagent is required for full colour development of Cu(II) where as 27 fold molar excess of reagent is sufficient in presence of pyridine. There is no significant change in the absorbance of the Cu(II) pyrimidinethiol complex when large excess of the reagent is used.

Effect of Time of Shaking and Stability of the Complex -

In order to establish the optimum time for quantitative extraction of Cu(II) pyrimidine complex, the time of shaking was varied from 5sec.-10min. By following the recommeded procedure extraction of Cu(II) was carried out and absorbance of the chloroform extract of Cu(II) complex was measured at 410nm against chloroform as a blank. The plot of the % extraction versus shaking time indicates that, shaking for 2min and

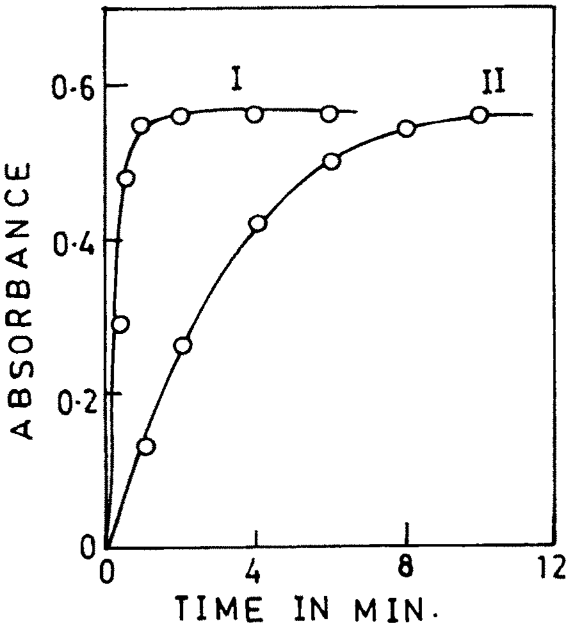


FIG. 4

EFFECT OF TIME OF SHAKING

Cu(II) = 7 ppm

I. WITH PYRIDINE, pH=5.

II. WITHOUT PYRIDINE, pH=10.

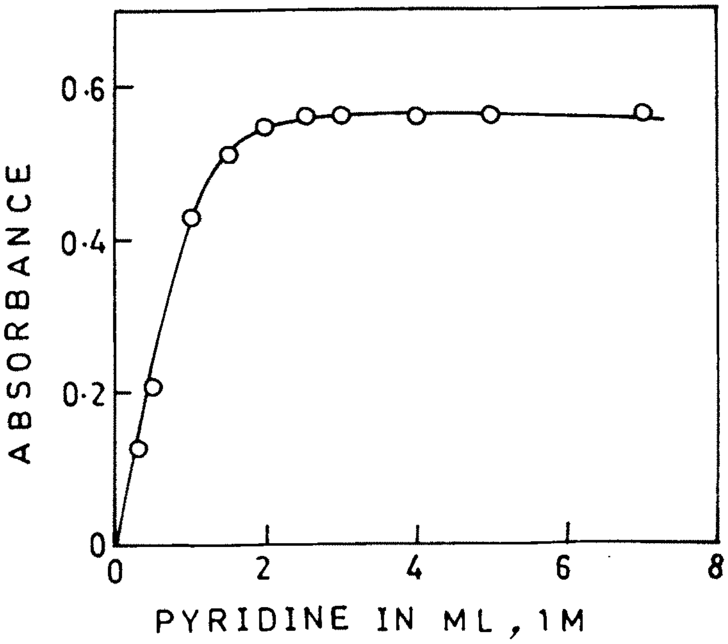
FIG. 5

EFFECT OF

PYRIDINE CONC.
(1M)

Cu(II)-PYRIMIDINE-

THIOL COMPLEX.
Cu(II) = 7 ppm



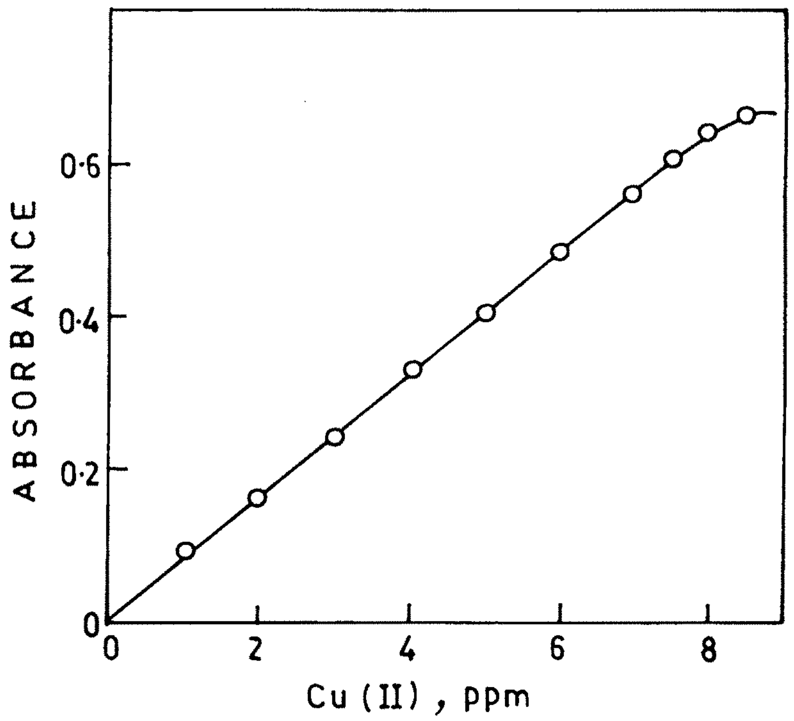


FIG. 6 — VALIDITY OF BEER'S LAW FOR Cu (II) PYRIMIDINETHIOL COMPLEX.

pH = 5·0

10min was sufficient for quantitative extraction of 7ppm of Cu(II) in presence and absence of pyridine respectively (Fig. 4). In order to ensure complete extraction of Cu(II) the mixture was shaken for 2min. At regular intervals of time the absorbance of yellow complex of Cu(II) pyrimidinethiol was measured at 410nm using chloroform as a blank. It was observed that the absorbance of the complex was stable for more than 12hrs.

Effect of Pyridine Concentration :-

To study the effect of pyridine concentration a series of solutions were prepared containing fixed amount of Cu(II) (7ppm). The complex of Cu(II) was extracted by using different amounts of the pyridine varying from 1-7ml of 1M pyridine. The colour of Cu(II) complex was developed as per the general procedure and the absorbance was measured at 410nm against chloroform as a blank. The results of studies are shown in Fig. 5 which indicate that 3ml of pyridine is sufficient for full colour development. But for all subsequent measurements 5ml of pyridine solution was used.

Validity of Beer's Law :-

The solution containing Cu upto the concentration range upto 10ppm were used for the 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 the equal volume of (5ml) 0.5M pyridine and 0.01M pyrimidinethiol in chloroform. The extracted yellow complex was measured at 410nm against solvent blank. From the plot in Fig. 6 it is clear that there is rectilinear relationship between the absorbance and the concentration of Cu(II) in the range 0.5 to 8ppm. However, the optimal concentration range was found to be 1.5-7.0ppm.

Composition of the Complex :-

The composition of the complex Cu(II) with pyrimidinethiol 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 measeured at 410nm against solvent blank. Job's plots shown in Fig.7 and 8 indicate formation of 2:1 (L:Cu) or (Py:Cu) complex in both the cases. The Cu(II) thiol complex is extractable into chloroform hence the probable composition of the uncharged complex is CuL_2Py_2 (1:2:2).

Effect of Diverse Ions :-

The effect of large number of diverse ions on the determination of 0.24mg of Cu with the reagent was investigated 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

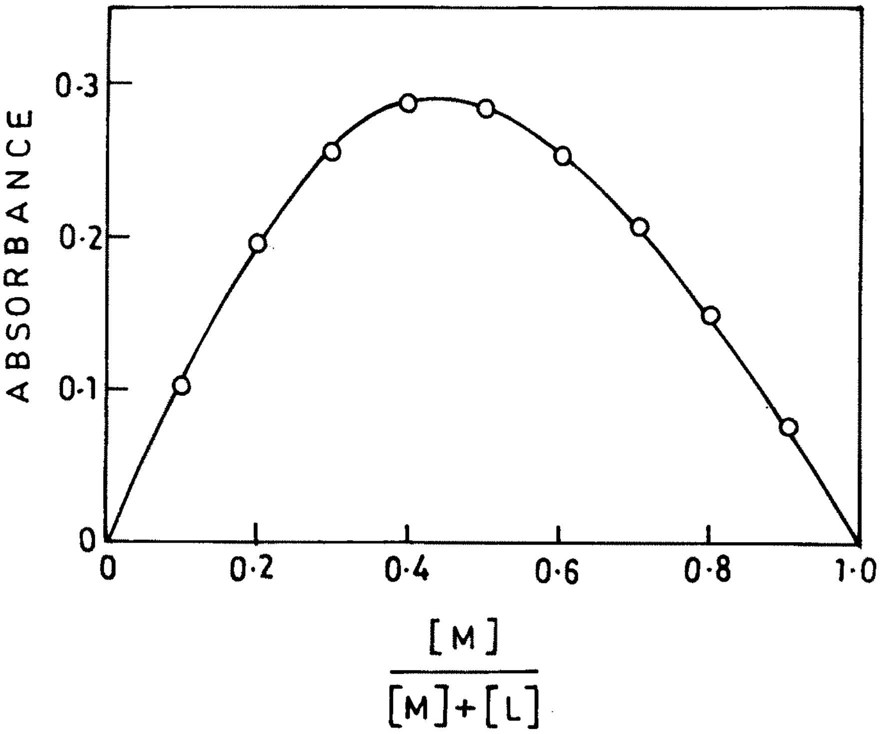


FIG. 7

JOB'S PLOT

[Cu]=PYRIMIDINETHIOL

$= 4{\cdot}70 \times 10^{-4}$ M

[PYRIDINE] = 0·5 M

FIG. 8

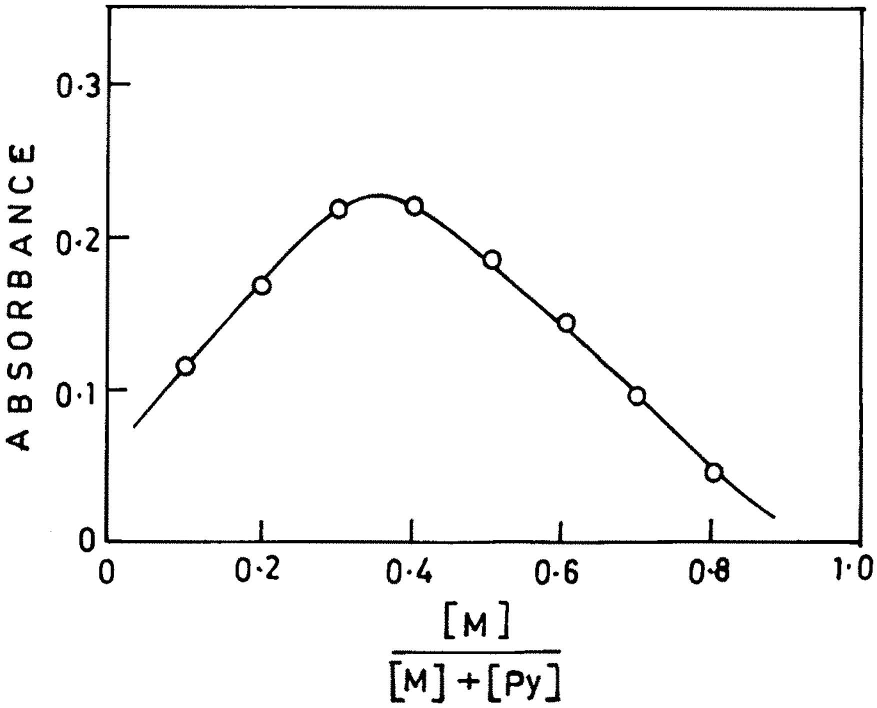
JOB'S PLOT

[Cu] = [PYRIDINE]

$= 7{\cdot}90 \times 10^{-4}$ M

PYRIMIDINETHIOL

= 0·01 M



foreign ion which gave error less than 2% in absorbance of the complex at 410nm. The tolerance limit of ions tested were shown in Table No. 2.

Reproducibility Accuracy and Sensitivity Data :-

For the study of reproducibility and accuracy of the method, absorbance measurements with ten different identical solutions containing 7.0 ppm of Cu(II) were performed as outlined in the procedure and concentration determined using calibration curve. The results are shown in Table No. 3. 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 Sandell sensitivity of the reaction as calculated from Beer's plot was found out to be 12.5ng/cm^2.

TABLE NO. 2 :- EFFECT OF DIVERSE IONS.

Cu(II) = 0.24 mg,

pyrimidinethiol = 0.01M in DMF, λmax = 410nm.

FOREIGN ION	TOLERANCE LIMIT in mg
V(V)	20
Cr(VI)	10
Mn(II)	5
Fe(II)	Interfere
Co(II)	5
Ni(II)	5
W(VI)	5
Zr(II)	2
Fe(III)	Interfere
Mo(VI)	Interfere
Ga(III)	1
Ru(III)	10
Rh(III)	2
Cd(II)	15
Sn(II)	Interfere
Te(IV)	Interfere
Ir(III)	10
Au(III)	0.2
Th(IV)	2
Se(IV)	10
Ag(I)	5
Hg(II)	1
Al(III)	2
Ti(IV)	Interfere
Re(VI)	1
U(VI)	10
Mg(II)	10
Pb(II)	5

TABLE NO. 3 :- PRECISION AND ACCURACY OF THE METHOD.

Amount of Cu = 7.0 ppm.

Sr. No.	Absorbance observed	ppm of Cu found ,(x)	$x - \bar{x}$	$(x - \bar{x})^2$
1	0.560	7.00	0.012	0.000144
2	0.565	7.06	0.048	0.002304
3	0.565	7.06	0.048	0.002304
4	0.555	6.94	0.072	0.005184
5	0.560	7.00	0.012	0.000144
6	0.555	6.94	0.072	0.005184
7	0.565	7.06	0.048	0.002304
8	0.560	7.00	0.012	0.000144
9	0.565	7.06	0.048	0.002304
10	0.560	7.00	0.012	0.000144
TOTAL		70.12		0.020190

$$\text{Average value } (\bar{x}) = \frac{70.12}{10}$$

$$= 7.012$$

Standard deviation (δ)

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

$$= \sqrt{\frac{0.02019}{10 - 1}}$$

$$= 0.05$$

Error (E) = Observed reading - Actual reading

$= 7.012 - 7.0$

$= 0.012$

Relative error Percent(accuracy) $= \frac{0.012 \times 100}{7.0}$

$= 0.17$

% coefficient of variation

$$c.v. = \frac{\delta \times 100}{\overline{x}}$$

where δ - standard deviation.

$$= \frac{0.05 \times 100}{7.012}$$

$= 0.7$

Molar Extinction coefficient

$$\epsilon = \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{Atomic Weight}$$

$= \text{slope} \times 1000 \times \text{Atomic Weight}$

$= 0.08 \times 1000 \times 63.546$

$= 50840 \text{ L Mole}^{-1}\text{cm}^{-1}$

$= 5.0840 \times 10^{3} \text{ L Mol}^{-1}\text{cm}^{-1}$.

Sandell's Sensitivity (S)

$$S = 10^3 \times \text{Atomic Weight} \times \text{Cmin}$$

$$\text{Where Cmin} = \frac{\text{Dmin}}{\epsilon \times b}$$

$$= 10^3 \times 63.546 \times \frac{0.001}{5.0840 \times 10^3 \times 1}$$

$$= 0.0125$$

$$= 12.5 \text{ ng/cm}^2$$

Reproducibility with 95% confidence

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

$$= 7.012 \pm 2.26 \times \frac{0.05}{\sqrt{10}}$$

$$= 7.012 \pm 0.036$$

REFERENCES

1. Charlot, G. and Denise Bezler; "Quantitative Analysis", Methuen London, 1947, 416.
2. Dunbar, N. E. and Schifl, A. A.; Talanta, 1972, 19, 1025.
3. Iwantscheff, G; Das Dithiozone and Seine Anwendung in der Mikro und spurenanalyse, Springer verlag, Weinheim (1958).
4. Hainberger, L.; Kebello, A.; Microchim. Acta, 1974, 5, 885.
5. Sugawar, M., Itoh Yarso and Kambara, T.; Japan Analyst., 1974, 23, 1161.
6. Rishi, A. K.; Trikha, K. C. and Singh, R. P.; Curr. Sci., 1975, 44, 122.
7. Das, M. K. and Majumdar, A. K.; Mikrochem. J., 1970, 15, 540.
8. Valcarcel, M. and Pino, F., Infeion Quim. Analit, pura apl. Ind., 1972, 26, 116.
9. Zayan, S. E.; ISSG, R. M. and Maghrabi, Jacquicline, Y.; Michrochim J. 1973, 18, 662.
10. Williams, Dale, A. and Boltz, D. F.; Analyst, Lett., 1975, 8, 103.
11. Isagai, Kazuyo; Isagai, Kiyoharu and Morisachiya; Banseki kagaku 1975, 24, 414.
12. Martinez, M. P.; Bendito, D. P. and Pino, F. P.; Ann. Quim., 1973, 63, 747.

13. Gurman, M.; Bendito, D. P.; Pino, F. P.; Infcion Quim, analit. pura apl. Ind. 1973, 27, 209.

14. Valcarcel, M.; Bendito, D. P.; Pino, F. P.; Infcion Quim, analit. pura apl. Ind. 1971, 25, 39.

15. Cano, Pavon, J. M.; Vazguez, Allev, J.; Bendito, D. P. and Pino, F. P.; Infcion. Quim. analit. pura apl., Ind., 1971, 25, 149.

16. Munoz, Leyva, J. A.; Cano. Pavon, J. M. and Pino, F. P.; An. Quim, 1973, 69, 251.

17. Patil, V. R.; Khasat, R. B. and Deshmukh, B. K.; J. Iorg. nucl. Chem., 1981, 43, 3397.

18. Ilyas, S. Q. R. and Joshi, A. P.; Mikro. Chim. Acta., 1980, II, 263.

19. H. Sanke Gowda; S. Maqbool Ahmed and Jagadeesh, K. S.; J. Indian Chem. Soc., 1989, 66, 915.

20. Otomo, Makota and Noda, Hidemasa; Microchem, J., 1978, 23, 297.

21. Anipindi, A. R.; Jain P. and Singh, R. P.; J. Chin. Chem, Soc., 1981, 29, 165.

22. Bhaskare, C. K. and Devi Sureka; Talanta, 1978, 25, 544.

23. Asuero, A. C. and Cano Pavon, J. M.; Analyst. (London), 1978, 103, 140.

24. Gonzalez Balarion M.; Cano Pavon, J. M. and Pino Perez, F.; An Quim Ser. B. 1980, 76, 106.

25. Reddy, T.; Sreenivasulu and Rao, S. Brahmaji; Curr. Sci., 1979, 48, 439.

26. Yamaguchi, Shegeroku and Uesugi, Katsurya; Banseki Kagaku, 1982, 31, 338.

27. Lal, Keemti and Malhotra, Sita Rani; J. Ind. Chem. Soc., 1980, 57, 233.

28. Bosch Reig, F.; Martinez, Calatayud, J and Marin Saez R. M.; An. Quim. Ser. B. 1981, 77, 349.

29. Matsibura, G. S.; Ryabushko, O. P. and Pilipenko, A. T.; Zh. Anal. Khim. 1981, 36, 449.

30. Rodsiguez, J. J.; Hernandez, G.; Silva, J. A.; Chacon, E.; Mocelo, R.; Rev. Cubana Quim. 1985, 1(3), 89.

31. Miss Purabisarkar, P. K. Paria and Majumdar, S. K.; Indian J. Chemistry, 1987, 26, 987.

32. Deshmukh, B. K.; Fert. Technol., 1980, 17, 200.

33. Bayan, K. C. and Das, H. K., J. Indian Chem. Soc. 1987, 64, 198.

34. Arya, S. P.; Malla, J. L. Veena Slathia; Talanta, 1987, 34(2), 293.

35. Sarkar, A.; Thokdar, T. K.; Paria, P. K. and Majumdar, S. K.; J. Indian Chem. Soc., 1988, 65, 742.

36. Shinde, V. M.; Indian J. Chem., 1988, 27A, 921.

37. Barva, S.; Varma, Y. S.; Garg, B. S.; Singh, R. P. and Singh, Ishwar, Analyst (London), 1981, 106, 799.

38. Perez Trujillo, J. P.; Anal. Quim. Ser. B., 1981, 77, 379.

39. Ishwar Singh, Mrs. Poonam and Kadyan P. S.; Talanta, 1985, 32(5), 387.

40. Ray. U. S.; Pradhan, B. D. and Kar, S. B.; J. Indian. Chem. Soc., 1986, 63, 326.

41. Pradhan, V. and Singh, R. P.; Indian J. Chem., 1988, 274, 1114.

42. Bansal, S. K.; Tikku Shiella, Shrey Suman and Sindhu R. S.; J. Indian Chem. Soc., 1989, 66, 917.

43. Singh, A. K.; Mukherjee, D; Singh, R. P. and Katyal, M.; Talanta, 1982, 29, 95.