CHAPTER - III

SPECTROPHOTOMETRIC DETERMINATION OF COPPER (II) WITH 2'-CHLORO-PTPT

C H A P T E R - I I I

1-(2'-CHLOROPHENYL)-4, 4, 6-TRIMETHYL (1H, 4H)-2-PYRIMIDINETHIOL AS AN EFFECTIVE REAGENT FOR RAPID DETERMINATION OF COPPER AFTER SYNERGIC EXTRACTION

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 alloys forms. However, one of the features of copper is its ability to form a great number and 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 increase 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 develop 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 vitriol 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 carbon dioxide, water and nitrogen. 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 amounts of copper. The most sensitive reagents are diethylthiocarbamate[2], dibenzyldithiocarbamate[3] and neocuproine[4]. However, diethyldithiocarbamic acid decomposes rapidly in solutions of low pH and therefore, extractions at low pH should be performed immediately, preferably with excess of reagent present. Its sodium salt reacts with large number of metal ions but can affect selective separation in the presence of masking agent 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 N i(II), Co(II), Bi(III), 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. Dithizone[8] has the advantages of very high sensitivity and mineral acid reaction medium for extraction. However, its strong colour and the mediocre stability of its solutions are

disadvantages. Biscyclohexanone oxalyldihydrazone[9] and oxylhydrazide[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 $CHCl_3$ having an absorption maximum in UV range and many metal ions interfere. The substituted thioureas, which are recommended are 1-benzoyl-3-methyl-2-thiourea[11], 1-p-tolyl-3-benzoyl-2-thiocarbamide[12], 1-phenyl-3-thiobenzoyl-2-thiourea[13], 1-benzoyl-3-(2-pyridyl)-2-thiourea[14] and diphenylthiourea[15]. In case of 1-phenyl-3-thiobenzoyl-2-thiourea. 10 min heating on boiling water bath is necessary for full colour development. Bis-cyclohexanone-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.[16] Hydrazones recently investigated include N N' oxalybis (salicylaldehyde hydrazone[17]) 2-furaldehyde benzothiazol-2-hydrazone (ε=44000)[18], thiophen-2-aldehyde--2-benzothiazolylhydrazone (ε=44000)[19], diacetylmonoquinolyhydrazone (ε=14500)[20] benzothiazole-2-carbaldehyde-2-quinolylhydrazone[21], substituted thiophen-2-aldehyde-2-benzothiazolylhydrazone ($\varepsilon=4.5-4.9\times10^4$)[22] biacetyl bis(2-quinolyhydrazone)[23] 2-hydroxy-1-naphthaldehyde-4-methoxy-benzoyl hydrazone[24]. Most of these reagents react with copper in alkaline medium and are highly sensitive but suffers from several interferences and prolonged time of equilibration e.g. Thiophen-2-aldehyde-2-benzothiazolylhydrazone (15 min) and benzothiazole-2-carboxalde-

hyde- carboxaldehyde-2-quinolylhydrazone (15 min). Thiosemicarbazones are selective and sensitive reagents for copper. Among the thiosemicarbazones reported recently for photometric determination of copper are di-2-pyridyl ketone thiosemicarbazone[25], furoin thiosemicarbazone[26], biacetyl-bis-(4-phenyl)-3-thiosemicarbazone[27], acetophenone-thiosemicarbazone[28], cyclohexane-1,2-dione-bis-thiosemicarbazone[29],di(2pyridyl) glyoxal bis (4-phenyl-3-thiosemicarbazone[30], 5,5'-dimethyl cyclohexane-1,2,3 trione 1,2 dioxime 3-thiosemicarbazone,[31] salicyladehyde thiosemicarbazone[32], 2,4-dihydroxy benzophenone thiosemicarbazone[33], 5-nitro-salicylaldehyde-4-phenyl-3-thiosemicarbazone[34] and 2'4'-dihydroxyacetophenone 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 2'-hydroxy-4-methoxy-5'-methylchalcone oxime[37], 1,10-phenanthroline phloxime[38], 5'-chloro-2'-hydroxy-4'-methylacetophenoneoxime[39], phenanthrenequinone monoxime[40], 2-hydroxyacetophenone oxime[41], phenylpyruvic acid oxime[42], salicylaldoxime[43], 3'-bromo-2'-hydroxy-5'-methylacetophenone oxime[44], 5-bromosalicylaldoxime[45], Nioxime[46] acetylacetone

oxime,[47] α-benzoin oximi[48], indane 1,2,3-trione trioxime[49], 2-hydroxy-4-n-propoxyacetophenone oxime[50], 3'5'-dibromo-2',4'-dihydroxyacetophenone oxime[51], 2-hydroxy-1-aceto-phenone oxime[52], 2-methoxy salicylaldoxime[53], phenanthrene quinone monoxime[54], and picolinamide oxime[55]. However, the rate of extraction of the copper complex is slow e.g. 5-bromosalicylal oxime (10 min) and phenan-threnequinone oxime (2 min):α-benzoin oxime method suffers from low stability of the complexes. In addition reagent blank is required. Some β-diketones form the coloured complexes in the pH range 3-6, which are extractable into nonpolar solvent, these include benzoyltrifluoroacetone[56], 1,1,1-trifluoro-3-(2-phenyl) acetone[57], thiobenzoylacetone,[58] thiothenoyltrifluoro acetone[59]. Michler's thioketone[60], thio-tropolone[61], acetyl-acetone[62] and iso-nitroso-acetylacetone[63]. Copper is determined spectrophotometrically by extracting copper-benzoyl-trifluoro-acetone complex from aqueous solution of pH 3 into amyl alcohol 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) interferes. Numerous azodyes have been investigated as the sensitive reagents for copper. In 1-(2-pyridylazo)-2-phenan-

throl[64], eriochrome azurol G[66], chlorsulphonenol S[66], 6-(benzothiazol-2-ylazo)-2,4-xylenol[67], 5'-amino-3-(3-carboxy-1,2,4-triazol-5-ylazo)-4-hydroxynaphthalene-4,5-disulphonic acid[68], 5'-dimethyl azobenzene-4-sulphonic acid (DMHAS)[69], 2-hydroxy-5-methyl acetophenone ethylene diamineanil (HMAEA)[70], 4-)2-quinolylazo)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-dimethyl-4,5,6,7-tetrahydrobenzothiazol-2-ylazo) phenol and 5-diethylamino) 2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzo-thiazol-2-ylazo) phenol[74], Eriochrome cyanine R[75], 3,5-diamino-2-(2-thiazolylazo) benzoic and 3,5-diamino-2-(4,5-dimethyl-2-thiazolylazo) benzoic acid[76], chromal blue G[77], 4-(2-pyridylazo) resorcinol[78], 3-(4-antipyrinylazo)-6-(2-arsonophenylazo) chromotropic acid[79], ferron[80], 2-(3,5,-dibromo-2-pyridylazo)-5-diethylaminophenol[81], 1-(4-nitrophenyl) 3-(2-benzothiazolyl) triazene[82], 5-(4-arsonic phenylazo)-8-aminoquinoline[83], 1-(2-imidazolylazo)-2-naphthol-4-sulphonic acid[84], 4-(4,5-dimethyl-2-thiazolylazo)-2-methyl resorcinol[85] and 2-(4-hydroxy-6-methyl pyrimidin-2-ylazo)-1-naphthol[86] methods, many ions interfere. In disodium 3-hydroxy-4-(6-methyl-2-pyridylazo)-naphthalene[87], N-(2-aminoethyl) N-2-pyridylmethylene amino ethyl-dithio-carbamic acid[88] and pyridine-2-aldehyde-2'-hydroxynaphthyl-imine[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^{o} for salicylic acid[90], 30 min heating at 50^{o} for N-phenyl-glycine[91], while 40 min.heating at 50^{o} for bis (2,4-diaminophenyl)

phosphonate[92] is required. In photometric determination of copper with 2-salicylideneamino benzoic acid[93] Al(III), Cr(III), Ti(IV), V(V) tartrate, citrate,while for dicyclohexyl dithiophosphinic acid[94], tervalent Bi, Pd(II), Pt(IV) and Au(III) interfere. The ethanolic solution of thiovioluric acid[95] reacts 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 the copper complex with piperidine-1-carbothionate[96] exhibits absorption maximum at 440 nm but method suffers from interference of Fe(III), V(V), As(III), Sb(III), Hg(II), Cr(III), Sn(II), Mo(VI), SCN^- and NO_3^-. 2-methyl -3-chloro-5-hydroxy-4-naphthaquinone[97] forms red complex with copper(II) in 70% ethanol in the pH range 6.5 to 8.0 it was measured at 520 nm. Zinc(II) did not interfere if present upto 100 fold excess. Copper-4-(2-quinolyl-methylene amino)-1-phenyl -2,3-dimethyl-5-pyrazolone[98] complex 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 $\geq$ 30 min.

The proposed method describes synergetic solvent extraction of copper(II) with 1-(2'-chlorophenyl) 4,4,6-trimethyl (1H, 4H)-2-pyrimidinethiol (2'-chloro PTPT) in combination with a neutral base containing an electron donor such as pyridine from an aqueous solution of pH 4.5. The extracted yellow complex is quite stable and hence suitable for the

spectrophotometric determination of copper(II) at 400 nm. The method is rapid, extremely simple, sensitive and reproducible. The reagent is colourless and used for determination of microgram amount of copper in alloys and drug samples.

EXPERIMENTAL

Standard Cu(II) Solution :

A stock solution (1 mg/ml of Cu) was prepared by dissolving 1.965 g of copper sulphate pentahydrate (AR) in double distilled water containing a few drops of sulphuric acid and by diluting to 500 ml. The solution on standardisation by volumetric method[99] was found to contain 1.00 mg of Cu(II)/ml. Working solution of lower concentration were made from it by diluting the stock solution.

Extracting Solution :

A 0.5 M pyridine and 0.01 M pyrimidinethiol I solutions were prepared by dissolving 4.05 ml and 0.266 g respectively in chloroform diluting to 100 ml. Equal volume (5 ml) of the base and pyrimidinethiol I solution in chloroform were mixed before the extraction experiments.

Chloroform, pyridine and all other materials used in this work were of guaranteed grade. Distilled water was used throughout.

Apparatus :

A Elico digital spectrophotometer model CL-27 with a set of 1 cm quartz cells was used for absorbance measurements. The pH was measured with Toshniwal, type CL 46.

Procedures :

Dissolution of Brass and Copper-Nickel Alloy :

About 0.5 g of alloy is taken in a 250 ml conical flask, covered with stem cut funnel and is treated with 20 ml of HNO_3 (1:1) when vigorous reaction occurs. The solution is boiled for 5 min, cooled thoroughly and treated with 4 ml of concentrated sulphuric acid. The boiling is continued till brown fumes of NO_2 disappears and white fumes of SO_3 ceases. The solution is cooled and made upto volume in 250 ml flask with distilled water.

Dissolution of Gun metal and Nickel-Silver alloy :

The sample about (0.500 g each) is dissolved in 10 ml of concentrated HNO_3 and tin is precipitated as metastannic acid. The filtrate is evaporated to dryness. The residue is leached with dilute hydrochloric acid, boiled to remove the oxide of nitrogen and is made upto volume in 250 ml flask with distilled water.

Dissolution of Gold-Copper-Silver Alloy :

About 0.100 g of sample is transferred into 250 ml conical flask covered with stem cut funnel and heated gently with 10 ml aqua regia to dissolve the alloy. The solution is treated with 10 ml of concentrated hydrochloric acid in 2 ml portions, the solution being evaporated almost to dryness on steam-bath after each addition. The residue is dissolved in dilute hydrochloric acid and precipitated silver chloride is removed by filtration. The precipitate is washed well with dilute hydrochloric acid. The filtrate and washings are transferred into 250 ml volumetric flask and made upto volume with distilled water.

General Procedure :

Take a aliquot of sample solution containing 5-60 μg of copper, adjust the pH of the solution to 5 in 25 ml volume with 0.1 M HCl and NaOH solution. Transfer the solution into a 125 ml separatory funnel and shake with 10 ml of extracting solution for 5 min. Allow the phase to separate and measure the absorbance of the organic phase against chloroform at 400 nm. Compute the copper content from the calibration graph.

RESULTS AND DISCUSSION

Spectral Characteristics :

The absorbance spectra of Cu(II)-pyrimidinethiol I -pyridine complex in chloroform resulting from taking 1,2,3,4,5

ppm of Cu(II) through the general procedure are shown in Fig.1. The absorption spectrum of the yellow Cu(II)-pyrimidinethiol I -pyridine complex has an absorption maxima at 400 nm. The solution of pyrimidinethiol I is colourless and hence does not absorb significantly in the visible region. The molar absorptivity of the complex is 7625 L $mole^{-1}$ cm^{-1}. The Sandell's sensitivity of the reaction was found to be 8.3 ng cm^{-2}.

Effect of pH :

The extraction of Cu(II) was studied at various pH (fig.2) In the absence of pyridine extraction of the Cu (II)-pyrimidinethiol I complex commences at pH 5 (in acidic medium), becomes quantitative at pH 8.0 (in basic medium) with 8 min shaking. In presence of pyridine, however, extraction starts at pH 1.0 and becomes quantitative at pH 4. There is increase of absorbance 10% in presence of pyridine. Pyridine thus shows a synergetic effect on the extraction of Cu(II)-pyrimidinethiol I 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 solutions. After extraction the pH of the aqueous phase was found to be approximately 6.8. The results of extraction Cu(II)-pyrimidinethiol I complex in presence of pyridine as a function of pH is shown in Table 1.

Effect of Reagent Concentration :

Effect of reagent concentration on colour intensity of the

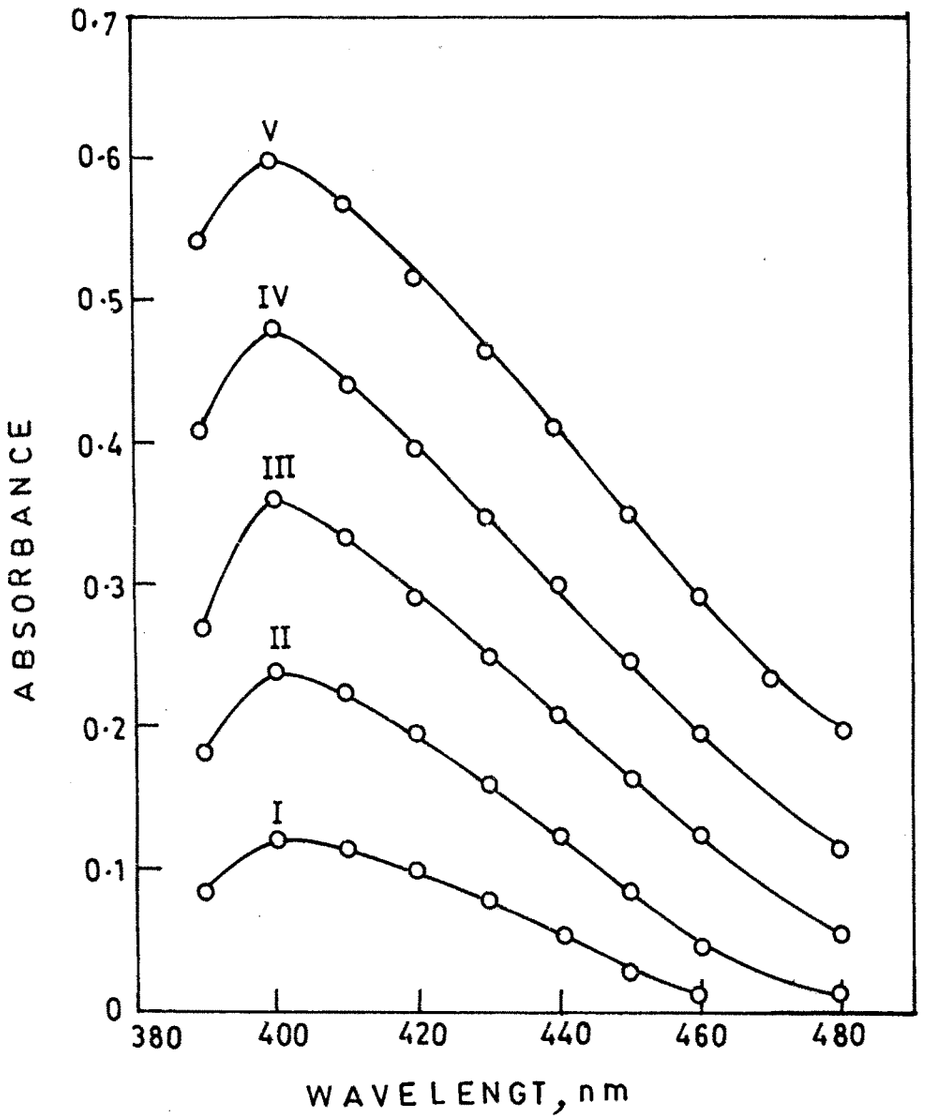


FIG. 1:— ABSORBANCE CURVES OF Cu(II)-PYRIMIDINETHIOL I COMPLEX.

Cu(II) : I, 1 ppm ; II, 2 ppm ; III, 3 ppm ; IV, 4 ppm ; V, 5 ppm.

Table - 1 : Extraction of Cu(II) Pyrimidinethiol I complex with pyridine as a function of pH

Cu(II) = 3 ppm; λ max = 400 nm

pH	Absorbance	% Extraction, E	Distribution Ratio, D
1.0	0.070	19.00	0.58
1.5	0.113	31.38	1.14
2.0	0.245	68.05	5.32
2.5	0.305	84.72	13.86
3.0	0.335	93.05	33.47
4.0	0.355	98.60	176.07
5.0	0.360	100.00	∞
6.0	0.360	100.00	∞
7.0	0.360	100.00	∞
8.0	0.360	100.00	∞
9.0	0.360	100.00	∞
10.0	0.360	100.00	∞

Cu(II)-pyrimidinethiol I complex at pH 5 was studied by varying amount of reagent, while Cu(II) concentration was kept constant at 3 ppm. The colour of the Cu(II)-pyrimidinethiol I complex was developed as per the recommended procedure. In absence of pyridine 127 fold molar excess of reagent is required for full colour development for 3 ppm of Cu (II) only. Whereas 85 fold molar excess of reagent is sufficient in presence of pyridine (Fig.3). There was increase of absorbance in presence of pyridine to 10%. There was no significant change in the absorbance with large excess of the reagent. Table 2 shows the effect of reagent concentration on extraction of Cu(II) pyrimidinethiol I complex in the presence and absence of pyridine.

Effect of time of shaking and stability of the complex :

In order to establish the optimum time for quantitative extraction of Cu(II)-pyrimidinethiol I 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 4 min and 7 min was sufficient for quantitative recovery of 3 ppm of Cu(II) in presence of pyridine and absence of pyridine respectively . There was also increase of absorbance by 10% (Table 3).

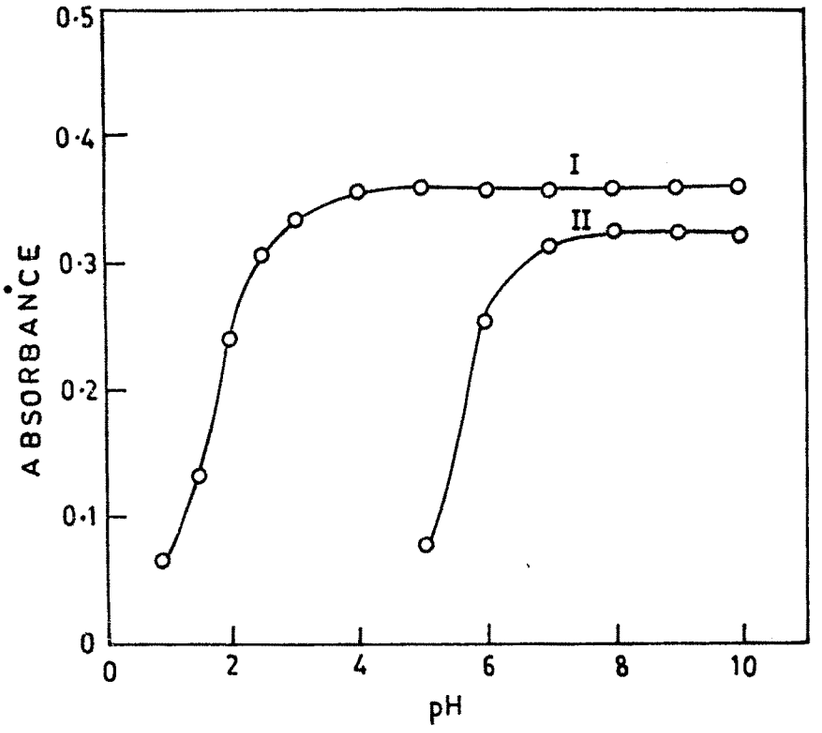
The yellow complex of Cu(II) was measured at 400 nm at regular intervals of time. Absorbance of the complex remained

Table - 2 : Effect of Reagent Concentration on Extraction of Cu(II) Pyrimidinethiol I complex in presence of Pyridine.

Cu(II) = 3 ppm, λ max = 400 nm

Pyrimidinethiol I = 0.01 M

Pyrimidine-thiol conc. 0.01 M (ml)	Absorbance	% Extraction, E	Distribution Ratio, D
0.25	0.085	23.61	0.79
0.50	0.140	38.88	1.59
1.00	0.215	59.72	3.70
2.00	0.295	81.94	11.34
3.00	0.342	95.00	47.5
4.00	0.360	100.00	∞
5.00	0.360	100.00	∞
6.00	0.360	100.00	∞
8.00	0.362	100.00	∞
10.00	0.360	100.00	∞



FIG·2 — EXTRACTION OF Cu-PYRIMIDINETHIOL I COMPLEX WITH PYRIDINE(I) AND WITHOUT PYRIDINE(II) AS A FUNCTION OF pH. Cu(II) = 3 ppm

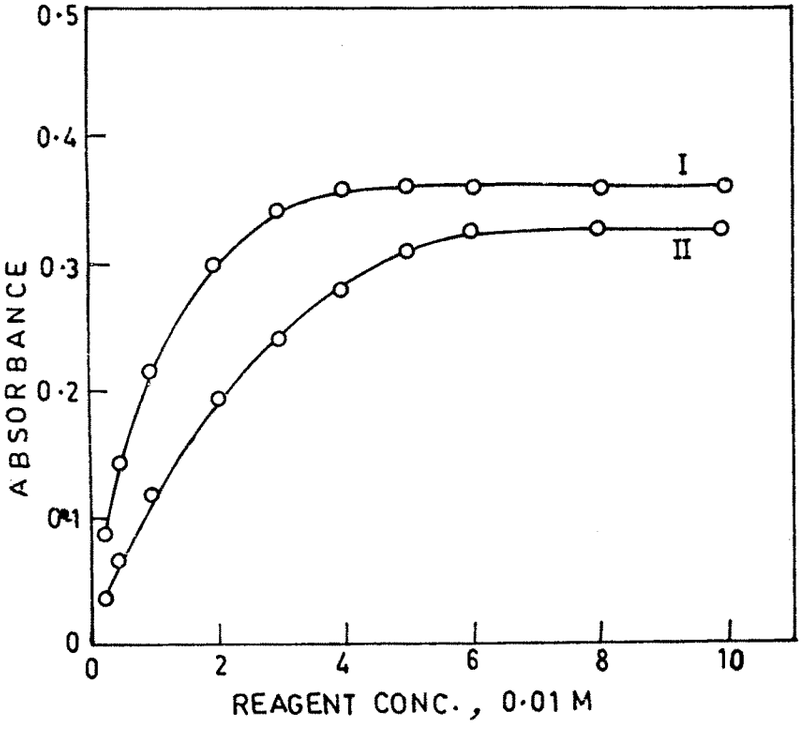


FIG. 3 — EFFECT OF REAGENT CONC. WITH PYRIDINE(I) pH=5 AND WITHOUT PYRIDINE(II) pH=9. Cu(II) = 3 ppm

Table - 3 : Effect of Time of Shaking with Pyridine

Cu(II) = 3 ppm, λ max = 400 nm

Pyrimidinethiol ± = 0.01 M

Time in min	Absorbance	% Extraction, E	Distribution Ratio, D
0.5	0.315	87.50	17.5
1.0	0.325	90.27	23.19
1.5	0.337	93.61	36.62
2.0	0.348	96.67	72.57
3.0	0.355	98.61	177.35
4.0	0.360	100.0	∞
5.0	0.360	100.0	∞
7.0	0.360	100.0	∞
10.0	0.360	100.0	∞
15.0	0.360	100.0	∞
20.0	0.360	100.0	∞

stable for more than 12 h. Hence the time of measurement of absorbance is not critical.

Effect of Solvent :

Of the various solvents examined as an extractants for Cu(II)-pyrimidinethiol I complex, it was observed that the complex was extractable into solvents such as chloroform, benzene, toluene, 4-methyl-2-pentanol, methyl-iso-butyl ketone, amyl alcohol, n-butanol, amyl acetate, carbontetrachloride. However chloroform was chosen as it offers a clear cut separation of phases and because of high distribution ratio of the complex in it.

Validity of Beer's Law :

The solution containing Cu(II) in the concentration range upto 8 ppm were used for the study of the validity of Beer's law. The colour of the copper-pyrimidinethiol I complex was developed as described in the general procedure using equal volume of (5 ml) 0.5 M pyridine and 0.01 M pyrimidinethiol I in chloroform. The extracted yellow complex was measured at 400 nm against chloroform. The absorbance was plotted versus the ppm of Cu(II) taken (Fig.5). The curve indicates that, there is a rectilinear relationship between the absorbance and the concentration of Cu(II) in the range 0.5 to 6 ppm. However, the optimal concentration range was found to be 1.75 to 5.80 ppm.

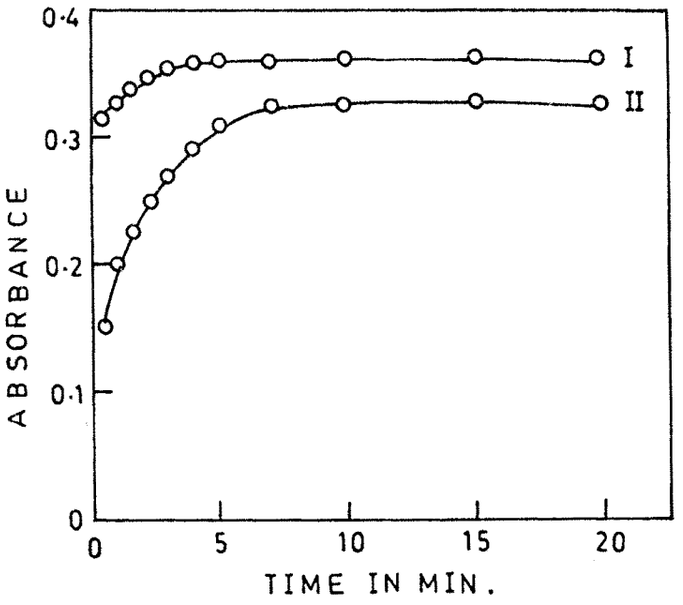
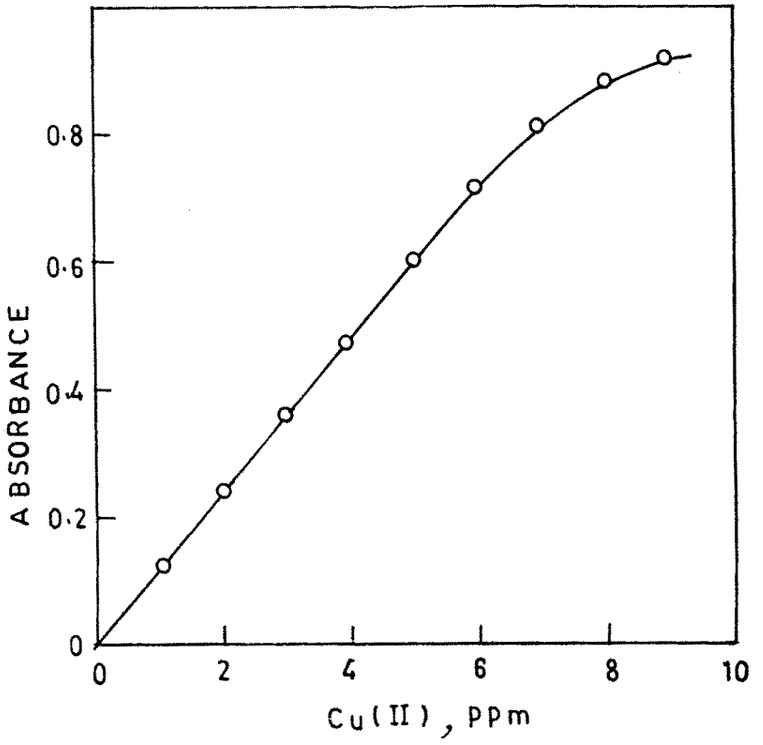


FIG. 4 —
EFFECT OF TIME OF SHAKING .
Cu (II) = 3 ppm
I, WITH PYRIDINE
pH=5
II, WITHOUT PYRIDINE
pH=9

FIG. 5 —
VALIDITY OF BEER'S LAW FOR Cu (II) PYRIMIDINETHIOL-(I) COMPLEX .
pH=5 .



Composition of the extracted species :

The Job's plots shown inFig.6 and 7 indicate formation of a 1:2 (Cu:L or Cu:Py) complex in both the cases as well as the 1:2 complexes. This explains the non-integral slopes of 1.43 in case of log D - log pyrimidinethiol I plot at constant pyridine concentration (Fig.8) and a slope of 1.41 in case of log D-log C pyridine plot at constant pyrimidinethiol I concentration (fig.9). In the presence of reducing agents like iron(II), tin(II) and ascorbic acid, the complex is not formed indicating that only copper(II) reacts with the reagent. The copper(II) pyrimidinethiol I complex is extractable into chloroform hence the probable composition of the uncharged complex is CuL_2Py_2 (1:2:2).

The synergic effect in the extraction is attributable to the formation of the readily extracted pyridine adduct as it is evident from the very high absorbance at 0.1 mole fraction of copper in fig.8 as against the low absorbance found at mole fractions of copper above 0.8 in fig.6.

Effect of Diverse Ions :

In order to assess the possible analytical applications of the copper-pyrimidinethiol-I complex the effect of some foreign ions that often accompany copper were studied. For these studies different amounts of ionic species were added to the sample solution containing 30 μg of copper(II) and above

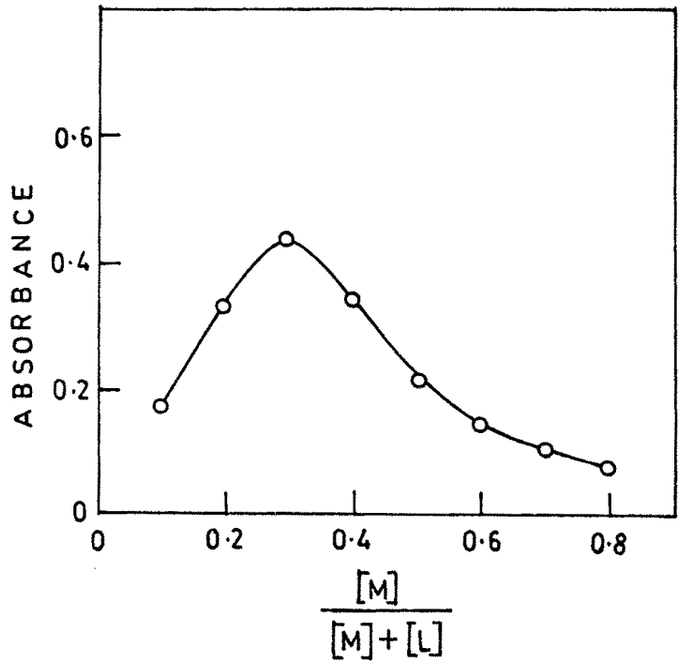
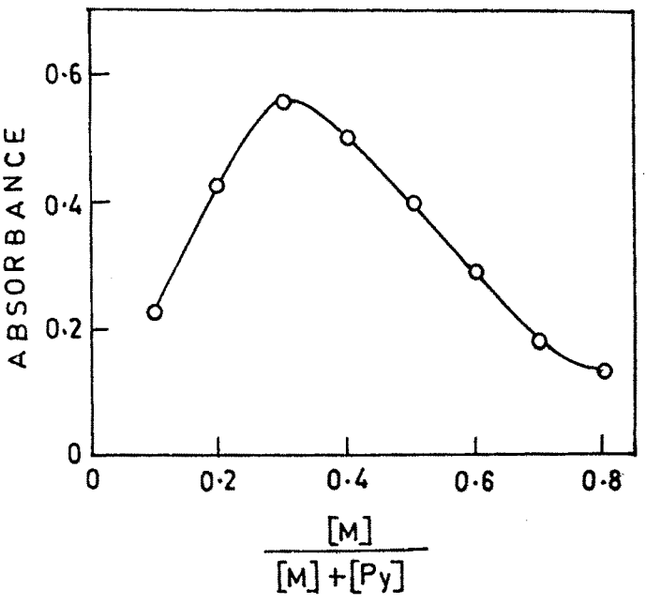


FIG. 6 —
JOB'S PLOT
[Cu] = [PYRIMIDINETHIOL-I]
$= 1{\cdot}25 \times 10^{-3}$ M
[PYRIDINE] = 0·5 M

FIG. 7 —
[Cu] = [PYRIDINE]
$= 2{\cdot}5 \times 10^{-3}$
[PYRIMIDINETHIOL-I]
= 0·01 M



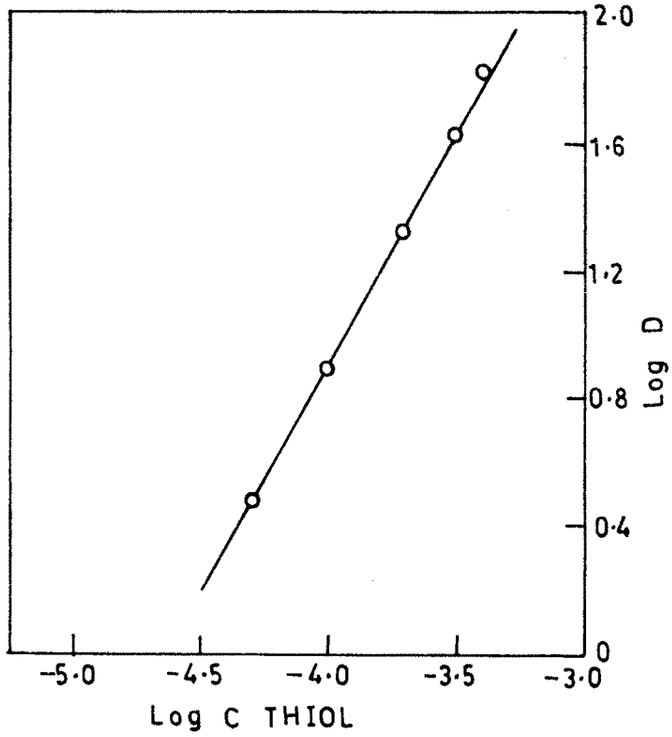


FIG. 8 —

Log D – Log $C_{Pyrimidinethiol-I}$

PLOT AT CONSTANT

PYPIRIDINE CONC.

[Pyrimidinethiol-I] = 0·01 M

pH = 5·0 .

FIG. 9 —

Log D – Log $C_{Pyridine}$

PLOT AT CONSTANT

THIOL CONC.

[Pyrimidinethiol-I] = 0·01 M

pH = 5·0

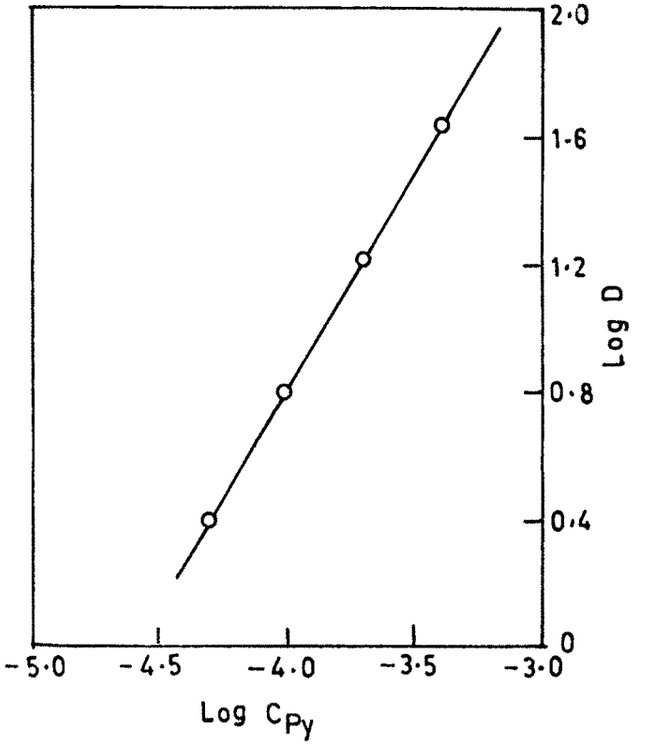


Table - 4 : Effect of foreign ions on the determination of copper(II) with pyrimidinethiol I

Cu(II) = 30 μg, pH = 5, λmax = 400 nm

Foreign ion added	Amount tolerated (mg) in the determination of Cu(II)
IrIIII)	5.0
Co(II)	5.0
Ni(II)	5.0
Mn(II)	5.0
Cr(VI)	5.0
V (V)	10.0
Zn(II)	5.0
Ru(III)	5.0
Rh(III)	5.0
Pt(IV)	5.0
Se(IV)	5.0
Ce(IV)	5.0
Mg(II)	5.0
Cd(II)	10.0
U (VI)	10.0
Pb(II)	10.0
W (VI)	10.0
Tl(I)	1.0
Th(IV)	1.0
Ga(III)	0.5
Hg(II)	0.5
Al(III)	0.5
Zr(IV)	0.5
Re(VI)	0.5
Pd*(II)	Coextract
Os*(VIII)	Coextract
Au*(III)	Coextract
Ag**(I)	5.0

* Prior extraction (100) ** AgCl centrifuge

general procedure was applied. An error of ± 2% in the absorbance readings was considered tolerable. The tolerance of various ions tested is shown in Table-4. The interference study showed that a few cations, namely Fe(II), Fe(III), Mo(VI) Sn(II), Te(IV), Ti(IV) and Bi(III) interfere in the determination of copper. There is no interference from 0.5 mg of Ga(III) Re(VI), Hg(II), Al(III) and Zr(IV); 1 mg of Tl(I), Th(IV) and W(VI), 5 mg of Ni(II), Co(II), Cr(VI), Mn(II), Mg(II), Zn(II), Se(IV), Ce(IV), Ru(III), Rh(III), Ir(III), Pt(IV) and Ag(I). The method could also tolerate 10 mg of Pb(II), Cd(II), U(VI), V(V). There was coextraction of Pd(II), Os(VIII) and Au(III). Complexing anions interfere severely and must be absent.

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 outlined in the procedure and concentration determined using calibration curve. The results are shown in Table-5. 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 were found out in each case and then standard deviation was calculated. From the standard deviation the reproducibility of the results with 95% confi-

Table - 5 : Precision and Accuracy of the Method

Amount of Cu(II) = 3.0 ppm

Sr. No.	Absorbance observed	ppm of Cu found	$X - \bar{X}$	$(X \quad \bar{X})^2$
1	0.360	3.00	0.012	0.000144
2	0.365	3.04	0.028	0.000784
3	0.355	2.96	0.052	0.002704
4	0.365	3.04	0.028	0.000784
5	0.365	3.04	0.028	0.000784
6	0.365	3.04	0.028	0.000784
7	0.360	3.00	0.012	0.000144
8	0.365	3.04	0.028	0.000784
9	0.360	3.00	0.012	0.000144
10	0.355	2.96	0.052	0.002704
	Total	30.12		0.009760

Average value ($\bar{X}$) = $\frac{30.12}{10}$

= 3.012

Standard deviation

$$S = \sqrt{\frac{(X_1-\bar{X})^2 + (X_2-\bar{X})^2 \ldots\ldots (X_n-\bar{X})^2}{n-1}}$$

$$= \sqrt{\frac{0.009760}{9}}$$

$$= \sqrt{0.0010844}$$

$$= 0.0329$$

Percentage coefficient of variation

$$C.V. = \frac{S \times 100}{\bar{X}}$$

$$= \frac{0.0329 \times 100}{3.012}$$

$$= 1.092$$

Error (E) = Observed reading - Actual reading

$$= 3.012 - 3.000$$

$$= 0.012$$

Relative error (Percent) $= \frac{0.012 \times 100}{3.0}$

$$= 0.4$$

Reproducibility with 95% confidence

$$= \bar{X} \pm 2.26 \times \frac{S}{\sqrt{n}}$$

$$= 3.012 \pm 2.26 \times \frac{0.0329}{\sqrt{10}}$$

$$= 3.012 \pm 2.26 \times \frac{0.0329}{\sqrt{3.162}}$$

$$= 3.012 \pm 0.0235$$

Molar Extinction Coefficient

$$\varepsilon = \frac{\text{Absorbance}}{\text{ppm}} \times 1000 \times \text{Atomic weight}$$

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

$$= 0.12 \times 1000 \times 63.545$$

$$= 7625 \text{ L mole}^{-1} \text{ cm}^{-1}$$

Sandell's sensitivity (S)

$$S = 10^3 \times \text{Atomic weight} \times C_{min}$$

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

$$S = 10^3 \times 63.545 \times \frac{0.001}{7625 \times 1}$$

$$= 0.0083 \ \mu g \text{ cm}^{-2}$$

$$= 8.3 \text{ ng cm}^{-2}$$

dence limit was calculated. The Sandell's sensitivity of the reaction as calculated from Beer's plot was found out to be 8.3 ng cm^2.

PRACTICAL APPLICATIONS

Analysis of Alloys of Copper :

Appropriate aliquots of sample solutions obtained as outlined in the dissolution procedure is taken and the pH of the solution is adjusted to 5.0 in 25 ml of volume with 0.1 M HCl and NaOH solutions. Copper was determined by proposed method. Results for analysis of some standard samples are reported in Table 6. The recovery of copper in alloys shows an agreement with the certified values.

Determination of Copper in Drugs :

The samples (1-2 tablets) were heated with minimum amount of concentrated hydrochloric acid followed by the addition of 2-3 drops of concentrated nitric acid. The organic matter was destroyed by treatment with 5 ml conc perchloric acid. The solution was slowly evaporated to moist dryness and the residue was dissolved in dilute hydrochloric acid. The solution was made 6 M with respect to hydrochloric acid and iron was extracted twice with 10 ml portions of isobutyl methyl ketone. The aqueous phase was slowly evaporated to dryness in order to remove excess hydrochloric acid. The residue was dissolved in

Table 6: Determination of copper in alloys

Alloy	Composition of alloy, %	Copper		Relative mean deviation %
		Certified value, %	Found %	
Brass[a]	Zn, 39.01	60.99	60.80	0.3
Copper-Nickel alloy[b]	Ni, 25.2; Mn,0.1; Fe,0.03	74.62	74.50	0.2
Gun metal alloy[c]	Sn, 4.49; Sb,0.31; Pb,2.31	84.95	84.82	0.7
Nickel-Silver alloy[d]	Ni,17.0; Pb,0.1; Sn,0.05; Mn,0.21	54.60	54.50	0.2
Gold-Copper-Silver alloy	Au,43.4; Ag,7.25	49.35	49.20	0.3

(Six determinations)

a - National Metallurgical Laboratory, India.

b - India Govt. Mint. Supplies.

c - Kamini Industries Standards, India.

d - ITA Laboratory, India.

hot dilute acid and made upto 100 ml with distilled water. Copper content was determined by the recommended procedure. The results were satisfactory and reported in Table-7.

Table - 7 : Determination of Copper in Drugs

Drug	Manufactured by	Copper, ppm		Relative mean deviation %
		Certified value	This method	
Aquamin[a]	Pfimex International Ltd., Hyderabad-500855.	7.64	7.61	0.4
Supradyn[b]	Roche Products Ltd.,India	13.50	13.47	0.2
MultivitefM[c]	Glaxo Laboratories Ltd., India.	2.54	2.52	0.8

Each tablet contains : (Six determinations)

a - Iron (as dried ferrous sulphate I.P.) 3.0 mg; magnesium (as magnesium sulphate) I.P. 35.0 mg; Zinc (as zinc sulphate) I.P. 1.5 mg; Iodine (as potassium iodide) I.P. 15 mcg; Copper (as copper sulphate) I.P. 300 mcg; Manganese (as manganese sulphate) B.P. 500 mcg; chromium (as chromium sulphate) 20 mcg; Selenium (as selenium dioxide) 20 mcg; Molybdenum (as molybdenum trioxide 50 mcg.

b - Trace elements - copper sulphate I.P. 3.39 mg; Zinc sulphate I.P. = 2.20 mg; Sodium molybdate = 0.25 mg; sodium borate I.P = 0.88 mg; Minerals - calcium phosphate I.P. 129.0 mg; Magnesium oxide light I.P. = 60.0 mg; Dried ferrous sulphate I.P. 32.04 mg Manganese sulphate I.P. 2.03 mg; Total phosphorous in the preparation = 25.80 mg.

c - Vit A I.P. 5000 IU; Vit D_3 (cholecalciferol) IP 200 IU; Vit E IP 7.5 mg; Vit B_1 IP 2.5 mg; Vit B_2 IP 2.5 mg; Nicotinamid IP 25 mg; Vit B_g IP 1 mg; bibasic calcium phosphate IP 2.5 mg; Vit C IP 40 mg; Folic acid IP 500 mcg, Vit B_{12} IP 2.5 mcg; Ferrous fumarate IP 25 mg; Dibasic calcium phosphate IP 35 mg; Copper sulphate IP 1966, 0.1 mg; Manganese sulphate 0.01 mg; Zinc sulphate IP 50 mg; potassium iodide IP 0.025 mg; Magnesium oxide IP 0.15 mg.

REFERENCES

1. Analytical Methods Committee,
   Analyst, 88, 253 (1963).
2. Chang, K.L. and Bray, R.H.,
   Analyt. Chem., 25, 655 (1953).
3. Abbott, D.C. and Polhill, R.D.A.;
   Analyst, 79, 547 (1954).
4. Smith, G.F. and Mocurdy, W.H.,
   Analyt. Chem., 24, 371 (1952).
5. Sdirec, V. and Vasak, V.,
   Collection Czech. Chem. Comm., 15, 260 (1950).
6. Bode, H.Z.,
   Anal. Chem., 143, 182 (1954).
7. Diehl, H. and Smith, G.F.,
   The Copper Reagents. The G. Frederick
   Smith Chemical Co., Columbus Ohio (1970).
8. Fischer, H.,
   Mikrochemie; 30, 38 (1942).
9. Wetlessen, C.U. and Gran, G.,
   Anal. Chem. Acta. 16, 268 (1957).
10. Gran, G.,
    Anal. Chem. Acta, 14, 150 (1956).
11. Kashikar, S.M. and Joshi, A.P.,
    Curr. Science, 45, 99 (1976).

12. Patil V.R., Kharat, R.B. and Deshmukh, B.K.,
J. Inorg. nucl. Chem; 43, 3397 (1981).

13. Ilyas. S.Q.R. and Joshi, A.P.,
Micro Chim Acta, II, 263 (1980).

14. Wandalkar, D.M. and Joshi, A.P.,
Z. Analyt. Chem, 280,220 (1976)

15. Petrukhin, O.M; Shevchnko, V.N. Zakharova, I.A. and
Prokhorov, V.A.;
Zh. Anal. Khim; 32, 897 (1977).

16. Singh, R.B; Jain, P. and Singh, R.P;
Talanta, 29,77 (1982).

17. Kim Y.N; Ohoi K.S., Lee I.H. , Bark K.M; Chung R.J;
J. Korean Chem. Soc. (36), 95 (1992).

18. Odashima; Tsugikatsu and Ishii Hajime;
Anal Chem. Acta; (83) 431. (1976).

19. Idem. Ibid (74) 61 (1975).

20. Anipindi A.R, Jain P, and Singh R.P.
J. Chin. Chem. Soc. (28) 165 (1981).

21. Otomo Makoto and Noda Hidemasa,
Microchem J; (23) 297 (1978).

22. Odashima Taugikatau Anzai F. and Ishii Hajime,
Anal. Chim. Acta, (86) 231 (1976).

23. Berger S.A., Rothchild R.,
Microchem. J. (37) 181 (1988).

24. Grischenko N.V., Kondratenok B.M., Brach B.Ya.
Anal. Khim. (5) 69 (1986).

25. Martinez M.P., Valcercel M. and Pino Perez F.,
Anal. Chem. Acta, (81) 157 (1976).

26. Bhaskare C.K. and Devi Surekha,
Talanta (25) 544 (1978).

27. Asuero A.G. and Cano Paron J.M.,
Analyst (London) (103) 140 (1978).

28. Calzolari Claudio, Coussini Lokar Laura, Benci Pietro and Favretto Luciano,
Annali. Chim. (63) 363 (1973).

29. Munoz Leyro J.A., Cano Pavon J.M. and Pino Perez,
An. Quim., (72) 392 (1976).

30. Gonzalez Balairon M., Cano Pavon J.M. and Pino Perez F.,
An. Quim Ser. B (76) 106 (1980).

31. Salim R., Laila A.H., Qumhieh A.,
Spectrosc. Lett. (21) 541 (1988).

32. Gao C., Sheng Z., Huaxlie Shijie (33) 28 (1992).

33. Reddy K.G., Reddy K.H., Reddy D.V.,
Indian J. Chem. Sect.A (25A) 982 (1986).

34. Yamaguchi S., Uesugi K.,
Anal. Sep. (2) 149 (1986).

35. Reddy A.V., Reddy Y.K.,
Talanta, (33) 617 (1986).

36. Uhlemann E., Maack B. and Raub M.,
Anal. Chim. Acta, (116) 403 (1980).

37. Deshmukh B.K., Gholse S.B. and Kharat R.B.
Z. Analit. Chem., (279) 363 (1976).

38. Popa, Grigore and Dumitrescu Nina,
Rev. Chim. (Bucharest) (28) 381 (1977).

39. Gupta S.P. and Lal Keemati,
Acta Cienc. Indica, (2) 119 (1976).

40. Akaiwa Hideo, Kawamoto Hirashi and Izumi Fujio,
Ann. Chim. (Rome) (68) 71 (1978).

41. Reddy T., Sreenivasula and Rao S. Brahmji,
Curr. Sci. (48) 439 (1979).

42. Katyal M., Trikha K.C. and Mehra H.C.,
Acta Cienc Indica (Ser) Chem. (5) 144 (1979).

43. Milosevic Radule and Hojman Jolanda,
Arh Farm, (29) 23 (1979).

44. Lal Keemti and Malhotra Sita Rani,
J. Ind. Chem. Soc., (57) 233 (1980).

45. Yamaguchi Shigeroku and Usesugi Katsuy,
Bunseki Kagaku (31) 338 (1982).

46. Bosch Reigf, Martinez Calalayud J. and Marin Saez, R.M.,
An. Quim. Ser. B, (77) 349 (1981).

47. Patil P.S. and Shinde V.M.,
Analyst (London) (103) 79 (1978).

48. Gawali S.B. and Shinde V.M.,
Separation Science, (9), 451 (1974).

49. Rao D.M., Reddy K.H., Reddy, D.V.,
Indian J. Chem., Sect A. (28A) 1122 (1989).

50. Desai A., Naik H.B.,
J. Inst. Chem. (India) (62) 165 (1990).

51. Bhuee G.S., Singh J. Rastogi S.H.,
J. Inst. Chem. (India) (56) 163 (1984).

52. Reddy K.V., Hussain R.C.,
Curr. Sci. (53) 798 (1984).

53. Uesugi K., Nagahiro T., Kumagai T., Yamaguchi S.,
Kenkyu Hokoku-Himeji Kogyo Daigaku (39A) 16 (1986).

54. Sarkar P., Pana P.k., Majumdar S.K.,
Indian J. Chem. Sect.A (26A) 987 (1987).

55. Lorenzo E., Losada, J., Vicente Perez S.,
Quim. Anal. (Barcelona) (6) 489 (1987).

56. Rao G.N. and Thakur J.S.,
Z. analyt. Chem. (271) 286 (1974).

57. Akaiwa Hideo, Kawamoto Hiroshi and Izumi Fujio,
Talanta (23), 403 (1976).

58. Murti M.V.R. and Khopakar S.M.,
Talanta, (25) 165 (1978).

59. Honjo Takaharu, Fujioka Yoshinori, Itoh Hitoshi and
Kiba Toshiyasu,
Anal. Chem., (49) 2241 (1977).

60. Matsibura G.S., Ryabushko O.P. and Pilipenko A.T.,
Zh. Anal. Khim, (136) 449 (1981).

61. Srivastava J.H. and Singh R.P.,
J. Chin. Chen. Soc., Taipai, (21) 275 (1974).

62. Irving H.M. N.H. and Al-Miaimi N.S.,
J. Inorg Nucl. Chem., (27) 717 (1965).

63. Patil P.S. and Shinde V.M.,
Analyst, (103) 79 (1978).

64. Rishi A.K., Trikha K.C. and Singh R.P.,
Curr. Sci., (44) 122 (1975).

65. Ishida Ryoel, Kikuchi Kohji and Tonosaki Koichi,
Sci. Rep. Hirosaki Univ., (23) 9 (1976).

66. Ishikura Fumiko and Tonosaki Kochi,
Sci. Rep. Hirosaki Univ., (23) 84 (1976).

67. Arias Leon J.J., Perez Trujillo J.P. and
Garcia Montelong P.,
An. Quim., (74) 606 (1978).

68. Pachadzhanov D.N., Inrailov M.A., Yusupov M. Yu.
and Tabarov A.,
Izv. Akad. Nauk. Tadzhik SSR, Oldel Fitmatem geol-khim
Nauk, (4) 42 (1972).

69. Golse S.B., Sharma O.P. and Kharat R.B.,
J. Ind. Chem. Soc., (55) 776 (1978).

70. Deshmukh B.K.,
Fert. Technol., (17) 200 (1980).

71. Barale S., Verma Y.G., Garg B.S., Singh R.P. and
Singh Ishwar,
Analyst (London), (106) 799 (1981).

72. Arias Leon J.J., Galvan Marrazo B., Perez Trujillo J.P.,
Anal. Quim. Ser., B, (77) 379 (1981).

73. Cacho Palomar J., Nerin de La Puerta C.,
Gonzalez Mateo P.,
Quim Se B. (79) 406 (1983).

74. Kundrac J., Szalo A., Uch. Zap-Yarosl.
Gos. Pedagog. Inst. im. K.D. Ushinskogo (205) 68 (1984).

75. Zou S., Liang W., Xu B., Wus S.,
Fenxi Huaxue (12) 525 (1984).

76. Francisco Ortega A., Garcia Montelonge F.,
Quim. Anal. (Barcelona), (4) 447 (1985).

77. Uesugi K., Miyawaki M., Nagahiro T.,
Microchem J., (32) 332 (1985).

78. Somoner L., Koethe J., Langova M., Ackermann G.,
Ser. Fac. Sci. Nat. Univ. Purkynianae Brun., (14)
135 (1984).

79. Aznarez Alduan J., Loper Molinero A.,
An. Quim. Ser. B, (82) 165 (1986).

80. Ayra S.P., Mulla J.L., Slathia V.,
Talanta, (34) 293 (1987).

81. Sai Y., Qing G.,
Fenxi Shiyanshi, (7) 34 (1988).

82. Long Y., Cao S.Y., Lin Z.,
Huaxue Shiji, (28) 195 (1992).

83. Zeng Z., Xu Q., Huang L.,
Yejin Fenxi, (13) 3 (1993).

84. Pan F.Y., Zhang S.W.,
Yaukuang Ceshi, (11) 330 (1992).

85. Pole Conde F.A., Lopez Cancio J.A.,
An. Quim. Ser. B., (84) 330 (1988).

86. Goto K., Furukawa M., Shibata S.,
Huaxue Shiji, (9) 135 (1987).

87. Beaupro P.W., Holland W.J., Zak B. and Thibert K.J.,
Microchim Acta ((II) 403 (1979)

88. Itoh Yasooi, Sugawora Masuo and Kambara Tornihito,
Bunseki Kagaku, (24) 571 (1975)

89. Isugai Kazuyo, Isagai Kiychara and Morisaehiko;
Bunseki Kagaku (24), 414 (1975).

90. Minzl Erich, and Hainberger Leopold; Mikrochim Acta,
(II) 353 (1975).

91. De Aranjo N.,
Electica Quim., (13) 101 (1988).

92. Mori Hidehiko Fujimura Yoshikazu and
Takugami Yoshinobu., Bunseki Kagaku, (31) 261 (1982)

93. Ishii Hajime, Eigna Hisaliko and Sarayo Tauguo,
Japan Analyst, (22) 546 (1975).

94. Al' Khatib D., Garifzyanov A.R., Toropova V.F.,
Zavod. Lab. (57) 9 (1991).

95. Sinha P.P., Chawala R.S., Sinlhwani S.K. and Kamil
Fasihaddin, Rev. Roum. Chim., (26) 917 (1981).

96. Vardarajula A. and Rao A.P.,
Ind. J. Chem. (13) 974 (1975).

97. Kulkarni P.L., Watve G.G., Kulkarni A.R., Kelkar V.D.,
Acta Cienc, India Chem.,(17)293 (1991).

98. Grabaric Z., Eskinja I., Koprivanac N., Mesinovic A.,
Microchem J., (46) 360 (1992).

99. Charlot G. and Denise Bezler,
"Quantitative Analysis", Methuen, London, P 416 (1957).

100. Anuse, M.A., And Chavan, M.B.,
Chem. Anal. (Warsaw), 29, 409 (1984).