C H A P T E R - I I

SPECTROPHOTOMETRIC DETERMINATION OF

COPPER(II) WITH 2CHLOROQUNOLINE

3-CARBALDEHYDE THIOSEMICARBAZONE

This chapter gives a detailed account of the use of 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (QAT) in photometric determination of copper(II). The method described is simple and rapid.

EXPERIMENTAL

Synthesis of 2-chloroquinoline-3-carbaldehyde thiosemicarbazone :

Preparation of 2-chloroquinoline-3-carbaldehyde :

2 chloroquinoline-3-carbaldehyde was prepared by standard method[68] using vilsmeier reagents (VR) as follows.

Dimethyl formamide (9.6 ml, 0.125 mol.) was cooled to $0^{o}C$ in a flask equipped with a drying tube and phosphoryl chloride (32.2 ml, 0.35 mol.) was added dropwise with stirring. To this solution was added the acetanilide (0.05 mol.) and after 5 min. the solution was heated at $75^{o}C$ under reflux for 16.5 hours. Then the reaction mixture was worked up as below.

The reaction mixture was poured into ice water (300 ml) and stirred for 30 min at $0 - 10^{o}C$. The product was filtered off and washed well with water (100 ml), dried (68 %, 6.5 gm). Then the product was recrystallised from ethyl acetate m.p. $147^{o}C$ (reported m.p. $148^{o}-9^{o}c$). Due to the lack of reactivity of 2chlorogroup[69], it does not interfere with the derivative formed.

Synthesis of 2chloroquinoline 3-carbaldehyde thiosemicarbazone

The 2chloroquinoline-3-carbaldehyde thiosemicarbazone (QAT) was synthesised by refluxing equimolar quantity of 2chloro-quinoline-3-carbaldehyde and thiosemicarbazide in minimum amount of ethanol for one hour. The white crystalline product was obtained, washed with distilled water, ether and finally with ethanol. It was recrystallised from ethanol m.p.225° - 226°C.

Structure of QAT

$$CH = N - NH - \underset{\underset{S}{\|}}{C} - NH_2$$

Cl
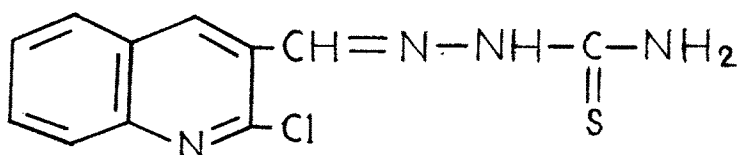
Reagent Solution :

0.055 gm QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the solution is 2.07×10^{-3}. The solution was found to be stable for more than a week.

Standard copper(II) solution

Standard copper(II) solution (1 mg/ml) was prepared by dissolving copper sulphate pentahydrate in distilled water containing a drop of sulphuric acid. The solution was standard-ised by volumetrically[70]. Further dilution for experimental purposes were made by diluting the stock solution with distilled water.
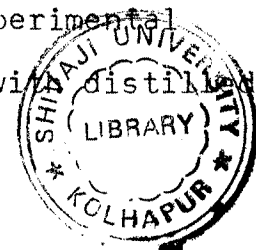
Other reagents :

Reagent grade chemicals were used for preparing the solutions required for the study of various diverse ions. The common cations were used as either chlorides or nitrates and the anions used were either sodium or ammonium salts solutions.

Preparation of buffer solutions :

The buffer solutions of pH 1 to 10 were parpared by the following procedure.

pH	Composition of the mixture
1	47.5 ml of $\frac{N}{5}$ HCl + 25 ml $\frac{N}{5}$ KCl and dilute to 100 ml
2	5.3 ml $\frac{N}{5}$ HCl + 25 ml $\frac{N}{5}$ KCl, dilute to 100 ml.
3	20.55 ml of Na_2HPO_4 $(\frac{N}{5})$ + 79.45 ml of $(\frac{N}{10})$ citric acid
4	41.0 ml of 0.2 M CH_3COOH + 9 ml of 0.2 M CH_3COONa
5	14.75 ml 0.2 M CH_3COOH + 35.26 ml CH_3COONa
6	9 ml of 0.2 M CH_3COOH + 191.0 ml 0.2 M CH_3COONa
7	12 ml 0.05 M borax + 188 ml solution containing 12.40 g boric acid and 2.93 g of NaCl in 1 lit.
8	11 ml 0.05 M borax + 29 ml solution containing 12.40 g of boric acid and 2.93 g of NaCl in 1 lit.
9	40 ml 0.05 M borax + 10 ml solution containing 12.40 g of boric acid + 2.93 g of NaCl in 1 lit.

10   equal parts of 0.025 N $NaHCO_3$ and 0.025 N Na_2CO_3

5.5 51.4 ml of 1 N CH_3COOH + 50 ml of 1 N NaOH and
        dilute to 500 ml

6.5 31.3 ml of $(1/15)$ M NaH_2PO_4 and dilute to 100 ml
        with $(1/15)$M KH_2PO_4 .

In addition to these buffer solutions standard buffer
of pH 4 was prepared by dissolving 10.21 g of potassium
hydrogen phthalate in 1 lit.

Apparatus :

All the spectral measurements over visible region were
done on a Carl Zeiss grating spectrophotometer spekol by using
10 mm matched pair of glass cuvettes. For the measurement of pH
values Philips pH meter PR 9405 L was used. A glass calamel
combination electrode Philips PV 9014 was used. Standard
phthalate buffer (0.05 M) was used for the standardization of
the pH meter.

SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II)

INTRODUCTION

Copper was probably the first metal known to man it and it
is associated with the development of human civilization. It is
less abundant in the earth crust than any other metals, for ages

it has served mankind as metal, alloys and salts. Analytical chemistry of copper covers macrolevels. Studies to traces in biological samples and is one of the widely studied subject.

The industrially important alloys of copper are brass, bronze and gun metals. Copper is one of the trace metals of greatest interest in the petroleum analysis. It is also associated with iron, sulphur etc. in the principal minerals. Copper plays an important role in living organism. It is one of the important micronutrients for crops. Also large number of copper compounds are used as insecticides. The trace determination of copper in foods, beverages, feeds, soils and biological materials is of great interest and also in research industries and in quality control. Trace amounts of copper in various substances may be vital and objectionable.

Copper is an element which gives sensitive colour reactions with innumerable organic compounds. Many colourimetric reagents have been proposed for the determination of copper, but few are sensitive and selective. A well known reagents for copper is diethyl dithiocarbamate[1-3] but suffers from several interferences. Other classic reagents for copper are derivatives of bipyridines and phenanthroline, cuproin[4-6] and neocuproin[7,8] and bathocupron[9] suffer from interferences and are not selective. Also hydroxy substituted 1,10-phenanthroline[10] and termethylthiurams[11] are not selective and in the latter case the rate of formation of complex is slow and so heating is necessary.

Among other Dithiozone[12] is also one of the most sensitive
copper reagent but it is not specific because of its strong
colour and low stability of its solutions, are disadvantages of
its. The methods involving phenyl thiosemicarbazide[13], catechol
sulphonephthalein[14], neocuproin[15], T-sulphonamidine[16], stilbazo[17],
biacetyl monoxime thiosemicarbazone[18], 3-5-dimethyl pyrazole[19],
pentyl-2-pyridyl ketoxime[20] form complexes of copper very
slowly and require a time period of 15 minutes to 2 hours.
Complex of 6-amino-4-hydroxy-2-mercapto-5-nitrosopyrimidine[21]
is unstable. Sensitivity of 2,2'-biqunoline[22] and 2,9-dimethyl-1,
10-phenanthroline[22] is much less (0.01 and 0.008 $\mu g/cm^2$ resply).
Sensitive reagents nitroso-R-salt[23], orotic acid[24], Zephiramine[25],
calichrome[26] and ammonium pyrophosphate[27] are not selective.

Different thiosemicarbazones[28-33] of aldehydes and ketones
can effectively be used in the estimation of copper, such as
1,3-cyclohexanedione bithiosemicarbazone monohydrochloride[54],
has been used for the determination of copper ion in milk,
vegetable oils and sheep liver samples. Another classic
sensitive and selective reagents for copper determinations are
2,4-dihydroxy acetophenone thiosemicarbazone[55], furoin thiosemi-
carbazone[56], p-Anisaldehyde thiosemicarbazone[59]. Quinoline-2-
aldehyde thiosemicarbazone required extraction while the proposed
method is in aqueous medium. Biacetyl monoxime-4-phenyl-3-thio-
semicarbazone[66], di-2-pyridyl ketone thiosemicarbazone[67] are
sensitive reagents for copper determination.

The detailed summary of reported photometric methods for
copper determination is given in table 2.1.

Table 2.1   Review of the methods for the photometric determination of copper(II).

Reagent	pH	λmax nm	Molar extinction coefficient, sensitivity, range, ppm.	Interference and remarks	Ref.
1	2	3	4	5	6
3-Methyl-1-thiocarbamoyl-2-pyrozoline-5-one	3.7 to 9.6	410	0.5 to 80 μg	Fe(III),Co(II),Zn,Hg,Bi SCN⁻ interfere	34
2'-hydroxy-3'-5-dimethyl azobenzene-4-sulphonic acid	8	480	Sensitivity is 0.013 μg/cm	Cr(III),Fe(II),Fe(III) and Zn interfere	35
1-Hydroxy-3-methyl-1-phenyl-2-thiourea	5.4 to 8.9 aq.EtOH	430	$\epsilon = 24,600$	Cations and anions do not interfere	36
Oximidobenzotetronic acid (4-hydroxy-3-nitroso coumarin)	5.3 to 7.5	427	—	Bi(III),Sb(III),Sn(II),Sn(IV) & W are masked with tartrate.	37
1-benzoyl benzimidazole-2-aldoxime	6.8 to 8.0	337	$\epsilon = 14,500$	Selective	38
Quinoline aldehyde 2-quinolyl hydrazone	6 to 7	540	—	Cd, Zn, Fe, Hg interfere	39
6-(benzothiazol-2-ylazo)-2-4-xylenol.	5.5	635	$\epsilon = 16,000$	Ni(II),Co(II) & Fe(II) interfere.	40
1-benzoyl-3-methyl-2-thiourea	6	355	—	Fe(III),Co(II),Ni(II),V(V) & Zn interfere.	41
1-benzoyl-3-(2-pyridyl)-2-thiourea	5	340	—	Cr(II),Mn(II),V(V),Th(IV) & Ce(IV) interfere.	42

24

Table 2.1 (contd.)

1	2	3	4	5	6
Pyridoin phenyl hydrazone	-	450	$\epsilon = 2.1 \times 10^4$	-	43
2-quinoline aldehyde-2-quinolyl hydrazone	10	536	$\epsilon = 47300$	Many cations and anions	44
2-Thioquinalidinanilide	1.5 - 3.8	550	$\epsilon = 8.1 \times 10^3$ Sensitivity 0.0017 μg cm^{-2}	Ag(I),Cr(VI),Os(VI) interfere highly selective method.	45
Phenanthraquinone monoxime	6.2 to 8.5	460	$\epsilon = 8700$	-	46
Pyrrolidine-1-carbodithioate	4.7 to 6.1	440	$\epsilon = 15700$	Cd,Fe(III),Mn(II),Co(II) & CN$^-$ interfere.	47
Phenylpyruvic acid 2-quinolyl hydrazone.	9.5 to 12.5	450	$\epsilon = 31,500$	-	48
Chlorosulphophenols	2 - 4.3	645	$\epsilon = 22,000$	Al,Bi,Ga,Th & EDTA strongly interfere	49
Alzarin maroon	5 - 5.6	585	$\epsilon = 1400$	CN$^-$ interfere seriously	50
4-hydroxy-3-(Salicylidene-amino)benzene sulphonic acid	5.2	406	$\epsilon = 14,500$	Fe(III),Mo(VI), Al & V(V) interfere.	51
Acenophthene quinone monoxime	8.5	430	Sensitivyty is 0.0047 μg cm^{-2}	-	52
Nitroxaminazo[4-amino-3-(2-hydroxy-5-nitro-3-sulpho-phenylazo)-naphthalene-2,7-disulphonic acid]	3 to 5	542	$\epsilon = 36300$	-	53

Table 2.1 (contd.)

1	2	3	4	5	6
1,3-Cyclohexanedione bis thiosemicarbazone mono hydro-chloride	6.0 to 7.0	390	Sensitivity is 0.00127 $\mu g/cm^2$	–	54
2-4-Dihydroxy acetophenone thiosemicarbazone	3 to 6	360	$\epsilon = 1.4 \times 10^4$	Better sensitivity	55
Furoin thiosemicarbazone	3	355	–	–	56
Thenoyl trifluoro acetone	5.4 with acetate buffer	344	$\epsilon = 49000$	Al,Fe(II),Cr(III) interfere	57
Thiobenzoyl acetone	6	410	$\epsilon = 34600$	–	58
p-Anisaldehyde thiosemi-carbazone	0.1-0.75 M NaOH	402	$\epsilon = 6.1 \times 10^3$	–	59
2-phenyl aceto hydroxamic acid	3.7	730-750	–	Ni(II),Th(IV),Zn(IV) interfere severely.	60
3-(O-Acetophenyl)-1-phenyl triazene-N-oxide	7.5	435	0.4-4.0 ppm $\epsilon = 1.09 \times 10^4$	Co(II),Ce(IV),Pd(II),V(VI), Fe(III),EDTA,oxalate, thiophosphate interfere.	61
3-hydroxy-3-methyl-1-o-chloro phenyl triazine	4.4 to 5.0	415	Sensitivity is 0.0605 $\mu g\ cm^{-2}$	–	62
1-(2-Quinolylazo)-2,4,5-trihydroxy benzene	7.0 to 9.0	550	$\epsilon = 2.54 \times 10^4$	Sb(II),Sn(III),Ni,Ce,Th,V(V), Cl^-,I^-,Br^-,F^-,thiocyarate interfere.	63
Pivaloyl acetyl methane 5,5'-dimethyl hexane-2-4-dion	4.5 to 5.0	436	$\epsilon = 13700$	Fe(III),Pd(II),EDTA, citrate interfere.	64

The present work accounts for the spectrophotometric determination of copper(II) by 2-chloroquinoline-3-carbaldehyde thiosemicarbazone. Copper forms yellow coloured complex with 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (QAT) at pH 6. Beer's law is obeyed upto 3.5 ppm of copper(II) at 415 nm. The effect of pH, reagent concentration and diverse ions have been studied. The molar absorptivity and Sandell sensitivity are 1.144×10^4 L mole^{-1} cm^{-1} and 0.0055 µg cm^{-2} respectively. The dissociation constant of the complex is 4.80×10^{-6}. Cations like Zn(II), Pd(II) and Fe(II) while anions like tartrate, and fluoride strongly interfere but Pb(II), Mn(II) and Ni(II) tolerated at tracer concentration in the determination of copper(II).

Recommended Procedure :

To an aliquot of the solution containing upto 3.5 ppm of copper, add 1 ml of 2.07×10^{-3} M reagent solution and a buffer solution of pH 6 (sodium acetate acetic acid). Dilute this to 10 ml with DMF and water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

Spectral characteristics :

Fig.2.1 shows the absorption spectrum of the copper(II) QAT complex containing 5.509×10^{-5} M of copper(II) and 2.07×10^{-4} M reagent at pH 6 using reagent blank. Absorption
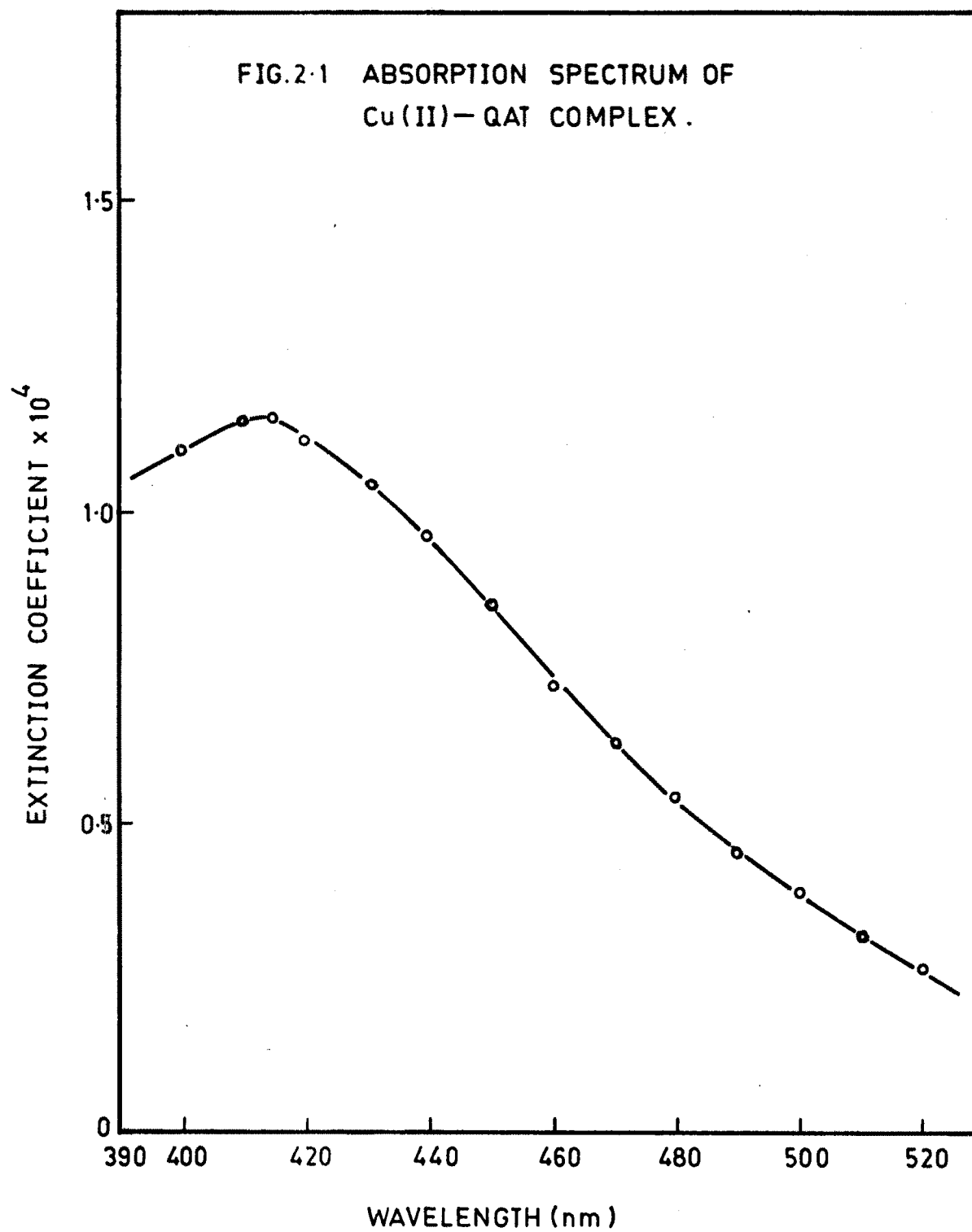
measurement were made in the spectral region 395 to 520 nm and recorded in Table 2.2. From the graph, it was found that 415 nm will be suitable wavelength for the copper determination. The molar absorptivity of the complex is to 1.44×10^4 L mole^{-1} cm^{-1} at 415 nm.

Table 2.2   Molar extinction coefficients of Cu(II)-QAT complex
$(QAT) = 2.07 \times 10^{-4}$ M,   pH = 6
$Cu(II) = 5.509 \times 10^{-5}$ M.

Wave length nm	Molar extinction coefficients of the complex x 10^4 L mole^{-1} cm^{-1}
395	1.0620
400	1.1000
405	1.1181
410	1.1363
415	1.1434
420	1.1090
425	1.0818
430	1.0363
435	1.000
440	0.9636
445	0.9000
450	0.8363
460	0.7181
470	0.6272
480	0.5363
490	0.4545
500	0.3909
510	0.3181
520	0.2545

FIG.2·1   ABSORPTION SPECTRUM OF
Cu(II) — QAT COMPLEX.

Effect of time on absorbance :

In order to study effect of time on the absorbance of copper(II)-QAT complex containing 5.509×10^{-5} M Cu(II) at pH 6, the absorbance measurements were recorded at different time intervals at 415 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 1 hour and decreases after that. Hence the complex is stable for 1 hr.

Effect of reagent concentration :

Solutions containing the same amount of copper $(5.509 \times 10^{-5}$ M) but different amounts of reagent varying from 0.1 to 1.2 ml of 2.07×10^{-3} M reagent solutions were prepared. The pH 6 buffer was added and the solution was made upto 10 ml with DMF:water (3:2). Absorbance measurements were recorded at 415 nm against the simultaneously prepared reagent blank. The data given in Table 2.2, Fig.2.3 show that 5.509×10^{-5} M copper solution required minimum 0.6 ml of 2.07×10^{-3} M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in absorbance. However, 1 ml of 2.07×10^{-3} M reagent solution was employed for further studies to ensure maximum colour intensity of the copper complex.

Table 2.3 : Effect of reagent concentration on the
absorbance of Cu – QAT complex.

$(Cu) = 5.509 \times 10^{-5}$ M, $(QAT) = 2.07 \times 10^{-3}$ M

pH = 6

Reagent ml	Absorbance at 415 nm
0.1	0.315
0.2	0.390
0.3	0.450
0.4	0.525
0.5	0.580
0.6	0.625
0.8	0.630
1.0	0.630
1.2	0.635

Effect of pH :

A series of solutions containing 5.509×10^{-5} M Cu(II)
and 2.07×10^{-4} M of the reagent but varying in pH from 3 to 9
were prepared and the absorption measurements were recorded at
415 nm. The results are summarised in Table 2.4. It was
observed that maximum absorbance was obtained at the pH 6. The
absorbance of the solutions decreases at higher or lower pH
values than this which is shown in Fig.2.3. Hence the pH 6
was maintained in further studies.

Table 2.4 : Effect of pH on the absorbance of

Cu – QAT complex

$(Cu) = 5.509 \times 10^{-5}$ M $(QAT) = 2.07 \times 10^{-4}$ M

pH	Absorbance at 415
3.0	0.340
4.0	0.480
5.0	0.590
5.5	0.625
6.0	0.635
6.5	0.620
7.0	0.580
8.0	0.440
9.0	0.300

Validity of Beer's law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of Copper (range of final concentration 1.5738×10^{-5}M to 1.1016×10^{-4} M) and the same amounts of reagents (final concentration 2.07×10^{-4} M) with the pH maintained at 6 were used for the study. The absorption measurements were recorded against the reagent blank at 415 nm (Table 2.5, Fig. 2.4). Beer's law is obeyed upto a concentration of 3.5 ppm of Cu(II). The Sandell sensitivity[71] of the reaction is 0.0055 µg cm^{-2} of copper(II) at 415 nm for $\log \frac{I_o}{I} = 0.001$. The Ringbom's plot[72] (Fig.2.5) indicated that the optimum range is 1 to 3 ppm of Cu(II).

FIG. 2·2
EFFECT OF REAGENT CONC. ON
Cu (II) – QAT COMPLEX.

λ = 415 nm

FIG. 2·3
EFFECT OF pH ON THE
Cu(II) – GAT COMPLEX.

λ = 415 nm

FIG. 2·4
VALIDITY OF
BEER'S LAW.
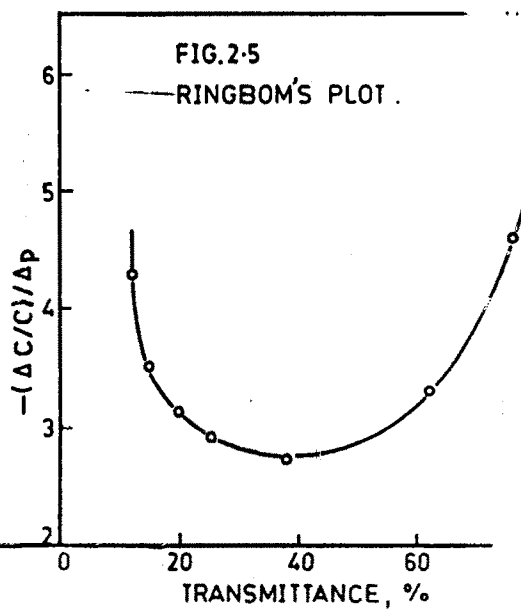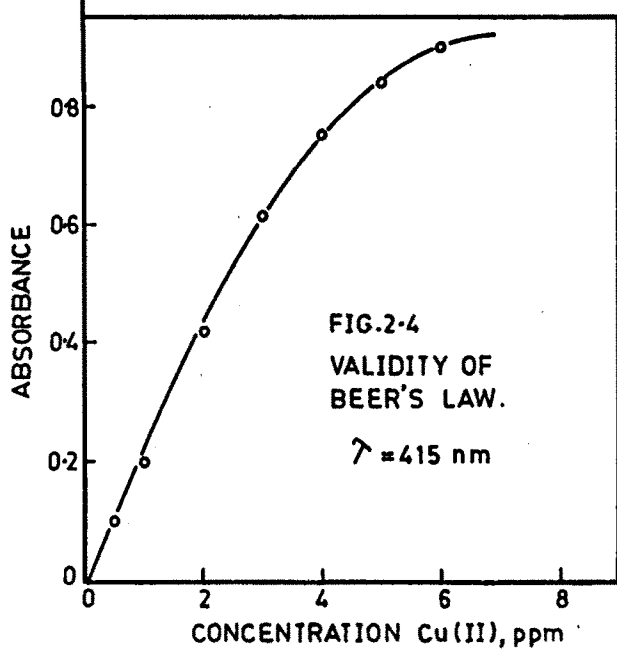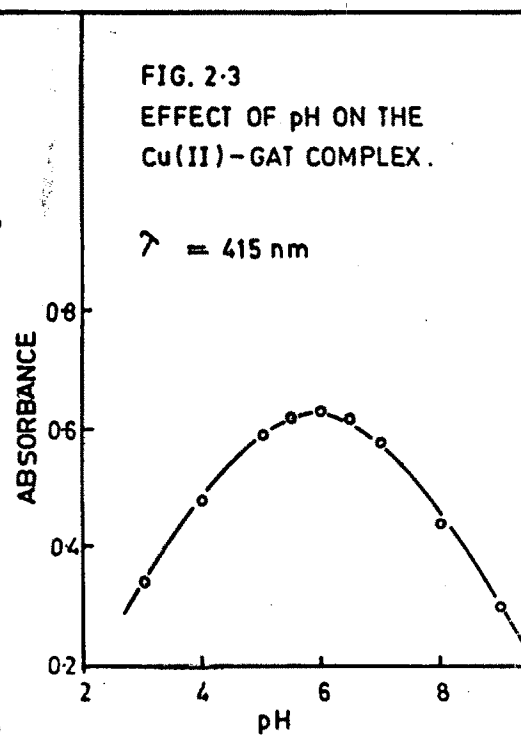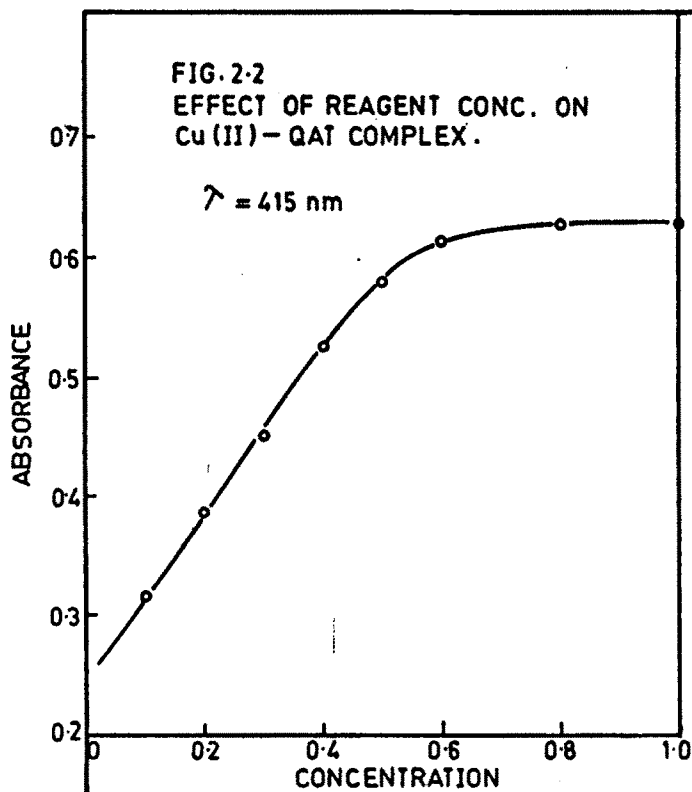
λ = 415 nm

FIG. 2·5
— RINGBOM'S PLOT.

Table 2.5 : Varification of validity of Beer's law
              for Cu-QAT complex.
              $(QAT) = 2.07 \times 10^{-4}$ M, pH = 6.

Copper taken ppm	Absorbance at 415 nm
0.5	0.100
1.0	0.195
2.0	0.410
3.0	0.605
4.0	0.750
5.0	0.840
6.0	0.900

Composition of the complex :

The combining ratio of metal to reagent was ascertained
by Job's method of continuous variations[73] and Mole ratio
method[74]. For Job's method of continuous variation, a series
of solutions were prepared by mixing equimolar solutions cf
copper(II) and the reagent (1.57×10^{-4} M). The pH of the
solution was adjusted to 6. The absorbances of the solutions
after diluting to 10 ml in volumetric flask were recorded at
415 nm against simultaneously prepared reagent blank (Fig.2.6,
Table 2.6). The plot indicates the existance of 1:1 complex
with respect to metal and reagent represented as ML.

Table 2.6 : Determination of the fomula of the Cu-QAT

complex by Job's method of continuous variation.

$(Cu) = (QAT) = 1.57 \times 10^{-4}$ M,   pH = 6.

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 415 nm
0.1	0.9	0.1	0.275
0.2	0.8	0.2	0.420
0.3	0.7	0.3	0.560
0.4	0.6	0.4	0.680
0.5	0.5	0.5	0.710
0.6	0.4	0.6	0.585
0.7	0.3	0.7	0.550
0.8	0.2	0.8	0.430
0.9	0.1	0.9	0.325

For mole ratio method, solutions containing the same final
metal concentration (3.75×10^{-5} M) and different amounts of the
reagent ranging from 1.775×10^{-6} to 1.50×10^{-4} M concentration
were prepared keeping the pH 6. Absorbances of the solutions
were measured at 415 nm against the reagent blank. The curve
showed break at the metal to ligand ratio 1:1, confirming the
results obtained by the application of Job's method of
continuous variations (Fig.2.7, Table 2.7).

The dissociation constant of the complex K, is calculated from the mole ratio plot by using following equation:

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

where n = 1

    c = molarity of the solution of the complex and

    α = degree of dissociation defined by

$$\alpha = \frac{A_m - A_s}{A_m}$$

A_m is the maximum absorption obtained from horizontal portion of the curve and A_s is the absorbance at stoichiometric molar ratio of reagent to copper in the complex. The value of K comes out to be 4.80×10^{-6}.

Table 2.7 : Determination of the formula of Cu-QAT complex by mole ratio method

(Cu) = (QAT) = 3.75×10^{-4} M.

Metal ion ml	Reagent ml	Reagent to metal ratio	Absorbance at at 415 nm
1	0.5	0.5	0.275
1	0.65	0.65	0.350
1	1.0	1.0	0.460
1	1.5	1.5	0.510
1	2.0	2.0	0.540
1	3.0	3.0	0.580
1	4.0	4.0	0.590

$\lambda = 415$ nm

ABSORBANCE

0·8

0·7

0·6

0·5

0·4

0·3

0·2

0·1

0   0·2   0·4   0·6   0·8

MOLE FRACTION OF METAL
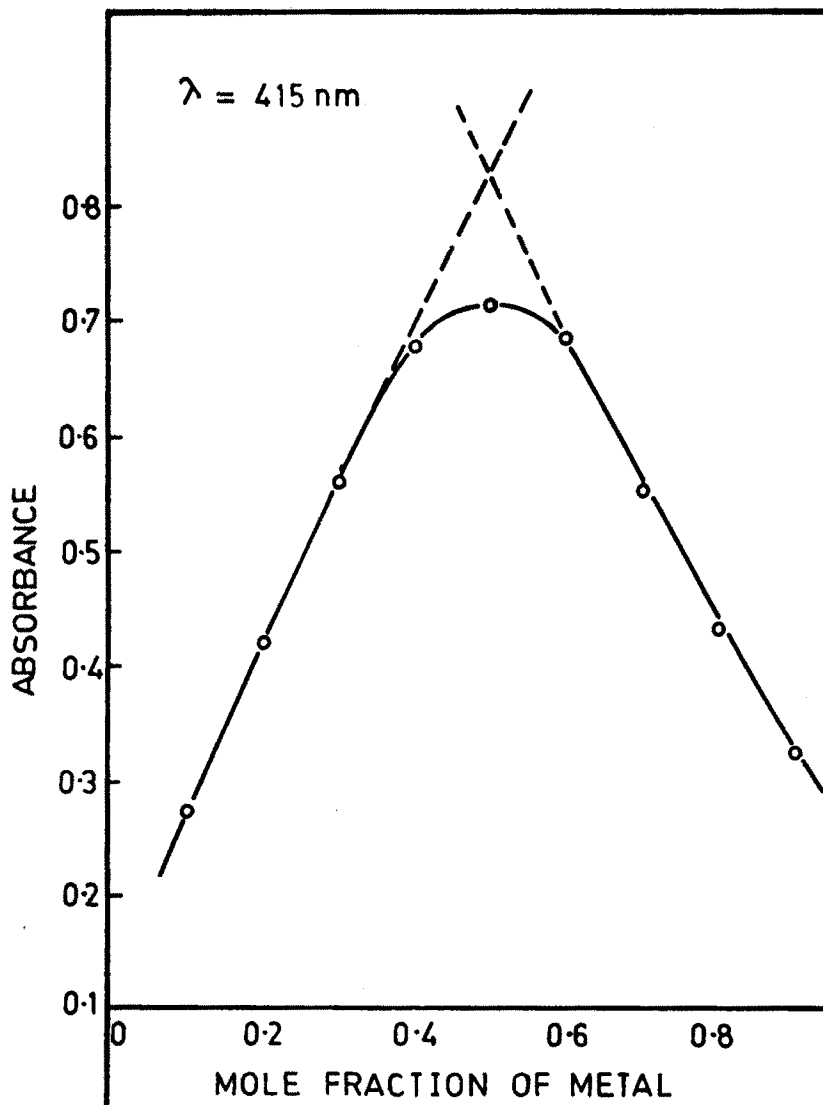
FIG. 2·6
JOB'S PLOT FOR
Cu(II)-QAT
COMPEX.
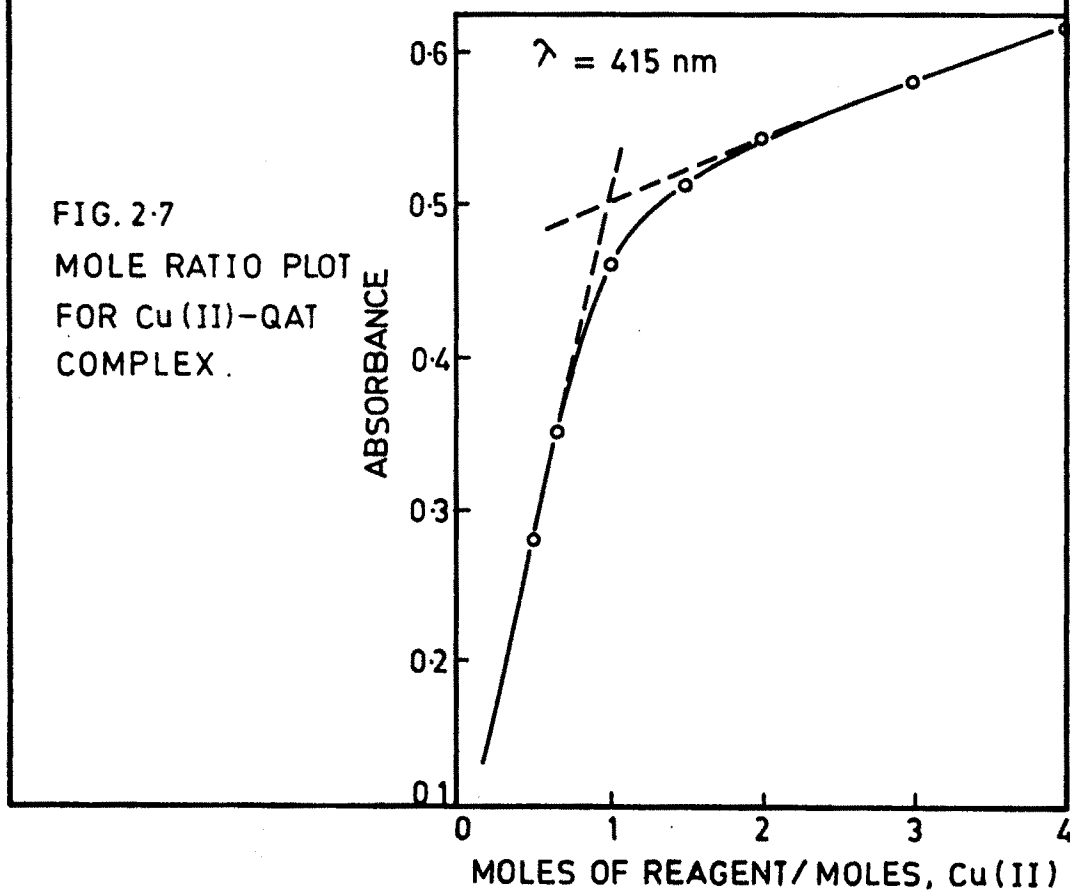
FIG. 2·7
MOLE RATIO PLOT
FOR Cu(II)-QAT
COMPLEX.

$\lambda = 415$ nm

0·6

0·5

0·4

0·3

0·2

0·1

ABSORBANCE

0   1   2   3   4

MOLES OF REAGENT/MOLES, Cu(II)

Effect of diverse ions :

The effect of diverse ions was studied using $5.50\textrm{\foreignlanguage}0 \times 10^{-5}$ M of copper and 2.07×10^{-4} M reagent in a final volume of 10 ml at pH 6. An error of less than 2 % in absorbance was considered to be tolerable. The results indicated that zinc, iron and palladium and anions like tartarate, fluoride interfere strongly. The tolerance for various foreign ions tested has been shown in table 2.8.

Table 2.8 : Effect of diverse ions.

$$[\ Cu(II)\ ] \ = \ 5.5 \times 10^{-5} \ M$$
$$[\ QAT\ ] \ = \ 2.07 \times 10^{-4} \ M$$

| Metal ion	Added as	Tolerance limit,ppm	Metal ion	Added as	Tolerance limit,ppm
Zn(II)	$ZnSO_4\ 7H_2O$	none	V(V)	$NH_4VO_3H_2O$	15
Ca(II)	$CaCl_2$	100	Ce(IV)	$Ce(SO_4)_2$	50
Mn(II)	$MnCl_2\ 6H_2O$	5	W(VI)	$Na_2WO_42H_2O$	200
Co(II)	$CoCl_2\ 6H_2O$	15	Ti(IV)	Titanium oxalate	20
Al(III)	$AlCl_3\ 6H_2O$	10			
Pb(II)	$Pb(NO_3)_2$	5	Mo(VI)	$(NH_4)_6Mo_7O_{24}$	15
Sn(II)	$SnCl_2\ 2H_2O$	200	EDTA	Na–EDTA	30
Pd(II)	$PdCl_2\ 2H_2O$	none	Tartrate	Tartaric acid	none
Bi(III)	$Bi(NO_3)_3$	15			
Ni(II)	$NiCl_2\ 6H_2O$	5	Acetate	CH_3COONa	100
Fe(III)	$FeCl_3\ 6H_2O$	2	Fluoride	NaF	none
Cr(VI)	$K_2Cr_2O_7$	15	Chloride	KCl	100
Mg(II)	$MgSO_47H_2O$	20	Citrate	Citric acid	10
Ba(II)	$BaCl_22H_2O$	10	HPO_4^{-2}	Na_2HPO_4	50
U(VI)	$UO_2(NO_3)_26H_2O$	30	$C_2O_4^{-2}$	$H_2C_2O_4$	30

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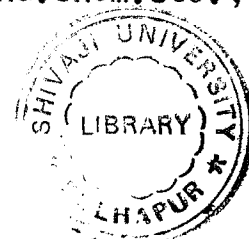
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