
CHAPTER - IV

SPECTROPHOTOMETRIC DETERMINATION OF
IRON(II) WITH 2CHLOROQUINOLINE
3-CARBALDEHYDE THIOSEMICARBAZONE

PHOTOMETRIC DETERMINATION OF IRON(II)

INTRODUCTION

Iron has industrial importance which exceeds that of any other element. It is a key element in industries and plays a vital role in science, technology, metallurgy and also plays an important role in the functioning of red corpuscles of blood (haemoglobin) and of the respiratory ferment porphyrins and also of plant tissues. The analytical chemists are concerned with iron in the samples ranging from food materials, medicinal preparations, ores and minerals, metals and alloys, blood and other body fluids etc.

Numerous colorimetric reagents are reported for tracer determination of iron. Phenolic compounds give purple or violet coloured complexes with iron(III). In the case of reagents like α -pyridyl hydrazone¹, pyridil- β -monoxime², glycine cresol red³, and 2-benzoyl pyridine hydrazone⁴, heating is necessary due to slow rate of formation of the complex. Reagents like o-dianisidine⁵, 2-pyridyl glyoxime⁶, formaldoxime⁷, dimethyl triketone⁸, catechol⁹; quinisatin oxime¹⁰, colour formation is very slow and requires longer duration of time.

Methods involving 2-thenoyl trifluoroacetone¹¹, dinitroso-resorcinol¹², phenyl-2-pyridyl ketoxime¹³, O-hydroxy acetophenone oxime¹⁴, and chromotope 2R¹⁵, as reagents are not selective where sensitivity of the methods is very low in case of o-hydroxy

acetophenone oxime¹⁴ and chromotope 2R¹⁵. Among the other reagents that have been proposed or used for photometric determination of iron, the following may be mentioned: pyramidone¹⁶, salicylaldoxime¹⁷, cuferron¹⁸, Rhodamine B¹⁹, 2-formyl pyridine-2-hydroxy benzoyl hydrazone²⁰, Bis-(2-9-dimethyl-1, 10 phenanthroline)²¹, Thiodibenzoyl methane²², Di-2-pyridyl ketone azine²³, di(2-pyridyl) ketone-2-furoyl hydrazone²⁴, Brilliant cresyl blue²⁵, 2,2'-Dipyridyl-2-quinolyl hydrazone²⁶, phenanthraquinone monoxime²⁷, α -furyl-dioxime²⁸, 2,2'-Dipyridyl-ketoxime²⁹, Erichrome cyanine R³⁰, 1-phenyl-3-quinolyl-2-thiourea³¹, syn-phenyl-2-pyridyl ketoxime³², complexes of p-amino-NH-dimethyl aniline³³, 5-sulpho- β -resorcylic acid³⁴, 8-hydroxy-7-nitroquinoline-5-sulphonic acid³⁵, are stable for atleast 10-20 minutes. Reagents such as 2-formyl pyridine azine³⁶, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol³⁷, 2'-hydroxy-5'-methyl propiophenone oxime³⁸, 1(2-quinolylazo)-2,4,5-trihydroxy benzene³⁹, are reported for determination of iron.

Recently for trace determination of iron, some thiosemicarbazones are reported. But most of them are affected by one or the other drawback discussed earlier. Such are Biacetyl monoxime 4-phenyl-3-thiosemicarbazone⁴⁰, 2-Benzol pyridine-4-phenyl-3-thiosemicarbazone⁴¹, 2'-hydroxy-5'-methyl acetophenone thiosemicarbazone⁴², salicylaldehyde thiosemicarbazone⁴³, Di-2-pyridyl ketone thiosemicarbazone⁴⁴, 2-Acetyl-pyridine-4-phenyl-3-thiosemicarbazone⁴⁵, Quinoline-2-aldehyde thiosemicarbazone⁴⁶, Bipyridyl glyoxal dithiosemicarbazone⁴⁷.

Table 4.1 : Reviews of the methods for photometric determination of iron(II)

Reagents	pH	λ max	Sensitivity, molar extinction coefficient range ppm	Interference and remark	Ref.
1	2	3	4	5	6
2-thenoyl trifluoro acetone	pH 1.0	500	$\epsilon = 4600$	SO_4^{2-} , NO_3^- , Cu, Mo, W, Co(II), interfere.	11
Phenyl-2-pyridyl ketoxime	4.5 to 5.0	596	-	aqueous solution should be heated.	13
O-Hydroxy acetophenone oxime	3.7 to 8.5	420	Sensitivity is $0.013 \mu\text{g cm}^{-2}$	Na, K, NH_4^+ , Cl^- , I^- , NO_3^- do not interfere.	14
Rhodamine B	4.3 to 5.3	558	$\epsilon = 9 \times 10^4$	Determined in water	19
2-Formyl pyridine-2-hydroxy benzoyl hydrazone	4.0 to 4.7	640	$\epsilon = 0.3 \times 10^4$	-	20
Bis-(2-g-dimethyl-1,10-phenanthroline)	4.5 to 5.0	596	-	Fe determined in sea water and tap water.	21
Thiodibenzoyl methane	6.5	480	-	Cu(II), Co(II), Zn, Ni, Cd, EDTA interfere.	22
Di-2-pyridyl ketone azine	6.5 to 7.5	460	$\epsilon = 9.299 \times 10^3$	Ni(II), Bi(III), Sb(III), Au(II), tartrate interfere.	23
Di(2-pyridyl)ketone 2-formyl hydrazone	5.3 to 11.3	620	$\epsilon = 8.4 \times 10^3$	Determination of iron in cement.	24
Brilliant cresyl blue	4.0 to 6.0	630	$\epsilon = 24600$	Ga, Bi(III), Au, Tl(III) interfere.	25

Table 4.1 (contd..)

1	2	3	4	5	6
2,2'-Dipyridyl-2-quinolyl hydrazone	3.4 to 4.5	605	$\epsilon = 3.11 \times 10^4$	-	26
Phenanthraquinone monoxime	2.5 to 9.0	470	-	Many cations and anions do not interfere.	27
α -furyl-dioxime	pH 2.4	570	-	Cu, Ni, Mn & Co interfere	28
2,2'-Dipyridyl ketoxime	4.5 to 5.8	335	$\epsilon = 1.9 \times 10^4$	-	29
Erichrome cyanine R	pH 6	613	$\epsilon = 17300$	Pb, Hg(II), Sn(II), Cr(III), I^- , SCN^- , NO_3^- interfere.	30
1-phenyl-3-quinolyl-2-thiourea	4.2 to 9.8	425	-	Cu, Bi, Sb, Ag, EDTA, borate & oxalate interfere.	31
Syn-phenyl-2-pyridyl ketoxime	Ascorbic acid	475 & 550	-	Co and Ni strongly interfere.	32
8-Hydroxy-7-nitroso quinoline-5-sulphonic acid	4.5 to 6.0	705	$\epsilon = 1.8 \times 10^4$ sensitivity is 0.003 $\mu\text{g cm}^{-2}$	Co(II) masked with citrate, tartrate, nitrite and thiosulphate.	35
2-formyl pyridine azine	4.0 to 5.0	660	$\epsilon = 0.29 \times 10^4$	-	36
2-(5-bromo-2-pyridyl azo)-5-diethylamino phenol.	4.0	552	$\epsilon = 4.5 \times 10^4$	K, Mg, Na, Ca, Ni, I^- , F^- , Cl^- , $S_2O_3^{2-}$, SO_4^{2-} interfere.	37
2'-hydroxy-5'-methyl propiophenone oxime	8.5 to 9.5	500	-	MoO_4^{2-} , WO_4^{2-} , EDTA, Mn, Cr(III), Al, interfere.	38

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Table 4.1 (contd..)

1	2	3	4	5	6
1-(2-Quinolylazo)-2,4,5-trihydroxy benzene	8.0 to 10	510	$\epsilon = 1.86 \times 10^4$	Ce, Th, V(V), Cl^- , I^- , Br^- thiocyanate interfere.	39
Biacetyl monoxime, 4-phenyl-3-thiosemicarbazone	4.0 to 9.3	350	$\epsilon = 17600$	-	40
2-Benzoyl pyridine-4-phenyl-3-thiosemicarbazone	pH 4.7	670	0.5 to 5 ppm $\epsilon = 11.4 \times 10^3$	Pd, Cd, Ti(IV), Cu(II), Pd(II), V(V), Cr(III) interfere.	41
2'-hydroxy-5'-methyl acetophenone thiosemicarbazone.	2.2	645	-	V(IV) & Cu(II) seriously interfere.	42
Salicylaldehyde thiosemicarbazone	10	510	$\epsilon = 1.7 \times 10^3$	-	43
Di-2-pyridyl ketone thiosemicarbazone.	pH 3.0	620	$\epsilon = 9.3 \times 10^3$	Complex is stable for at least 2 hrs.	44
2-Acetyl-pyridine-4-phenyl-3-thiosemicarbazone.	6.0	650	$\epsilon = 6.8 \times 10^3$	Cu(II), Ni(II), Co(II), Pd(II), EDTA, Cd(II) interfere.	45
Bipyridyl glyoxal dithiosemicarbazone	2.5	550	2.0 to 9.0 ppm $\epsilon = 5.58 \times 10^3$	$\text{UO}_2(\text{II})$ & V(V) strongly interfere.	47
1-(2-pyridyl methylidene amine)-5-(salicylidene amine)	4.8	635	0 to 8 ppm	1:3 complex, Fe determined in alloys & ores.	48

The summary of the reported methods for photometric determination of iron is given in Table 4.1. The present work accounts for the spectrophotometric determination of iron(II) by 2-chloroquinoline-3-carbaldehyde thiosemicarbazone(QAT). Iron(II) gives yellow coloured complex with 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (pH 6, λ_{\max} 418 nm). Beer's law is obeyed upto 5 ppm of iron(II) at 418 nm. The effect of pH, reagent concentration and diverse ions have been studied. The molar absorptivity and Sandell sensitivity are 0.3463×10^4 L mole⁻¹ cm⁻¹ and $0.016 \mu\text{g cm}^{-2}$ respectively. Iron estimation is interfered seriously by tin(II) while Ni(II), Ce(IV) and Cu(II) tolerate to tracer concentration. The dissociation constant of the complex is 6.092×10^{-11} .

EXPERIMENTAL

All the chemicals used were of A.R. grade.

Standard iron solution :

A stock solution of iron(II) (1 mg/ml) was prepared by dissolving A.R. grade ammonium ferrous sulphate hexahydrate in distilled water followed by 2-3 drop of conc. sulphuric acid and the solution was standardised volumetrically by using literature procedure⁴⁹. Further dilutions for experimental purposes were made by diluting the stock solution with distilled water.

Reagent solution

0.027 g of QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the resulting solution is 1.02×10^{-3} .

Buffer solution

Buffer solutions required were prepared as described in Chapter II.

A 2 % (w/v) solution of ascorbic acid was prepared and used for the reduction of iron(III).

Recommended procedure

To an aliquot of the solution containing upto 10 ppm of iron, add 1.5 ml of 1.02×10^{-3} M reagent solution, add 1 ml of 2 % ascorbic acid solution to prevent atmospheric oxidation of iron and a buffer solution of pH 6 (sodium acetate-acetic acid). Dilute this to 10 ml with DMF and water (3:2) in volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

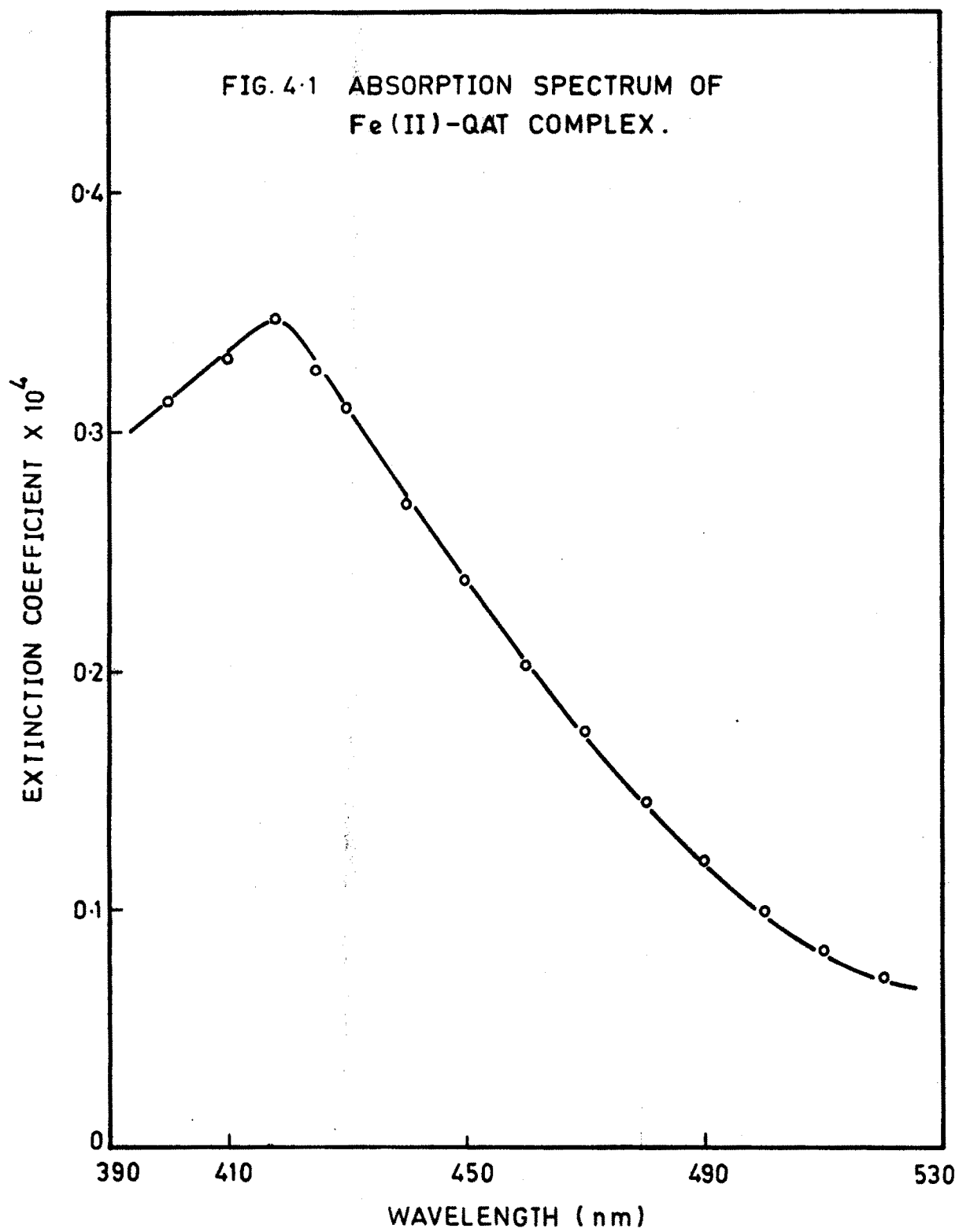
Spectral characteristics

The absorption spectrum of the iron(II)-QAT complex containing 1.7905×10^{-4} M of iron(II) and 1.02×10^{-3} M reagent at pH 6 using reagent blank is shown in fig.4.1. Absorption measurements were made in the spectral region 400 to 520 nm and recorded in Table 4.2. From the graph, it was found that

418 nm will be suitable wavelength for the determination of iron. The molar absorptivity of the complex is $0.3463 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 418 nm. Table 4.2 gives the observation traced in Fig. 4.1.

Table 4.2 : Molar extinction coefficients of Fe(II)-QAT complex
(QAT) = $1.02 \times 10^{-3} \text{ M}$ Fe(II) = $1.790 \times 10^{-4} \text{ M}$

Wave length nm	Molar extinction coefficient of complex $\times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$
400	0.3128
405	0.3212
410	0.3296
412	0.3351
415	0.3435
418	0.3463
420	0.3407
425	0.3240
430	0.3100
435	0.2877
440	0.2681
445	0.2513
450	0.2402
460	0.2011
470	0.1759
480	0.1452
490	0.1173
500	0.1005
510	0.0837
520	0.0726



Effect of time on absorbance

In order to study the effect of time on the absorbance of iron(II)-QAT complex containing 1.79×10^{-4} M iron(II) at pH 6, the absorbance measurements were recorded at different time intervals at 418 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 45 minutes and decreases after that.

Effect of Reagent Concentration

Solutions containing the same amount of iron (1.7905×10^{-4}) but different amounts of reagents varying from 0.1 ml to 1.4 ml of 1.02×10^{-3} M reagent solutions were prepared. The pH 6 buffer (1 ml) and 1ml 2 % ascorbic acid solution were added and the solution was made upto 10 ml with DMF:water (3:2). Absorbance measurements were recorded at 418 nm against the simultaneously prepared reagent blank. The data given in the Table 4.3, Fig.4.2 show that 1.7905×10^{-4} M iron(II) solution required minimum 0.8 ml of 1×10^{-3} M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in the absorbance. However 1.5 ml of 1.02×10^{-3} M reagent solution was employed for the further studies to ensure maximum colour intensity of the iron complex.

Table 4.3 : Effect of reagent concentration on the absorbance of Fe-QAT complex.

$$(\text{Fe}) = 1.790 \times 10^{-4} \text{ M} \quad \text{QAT} = 1.02 \times 10^{-3} \text{ M}$$

Reagent ml	Absorbance at 418 nm
0.1	0.195
0.2	0.270
0.3	0.340
0.4	0.405
0.6	0.500
0.8	0.615
1.0	0.620
1.2	0.620
1.4	0.615

Effect of pH :

A series of solutions containing 1.79×10^{-4} M iron(II) and 1.02×10^{-3} M of the reagent but varying in the pH from 3 to 9 were prepared and the absorption measurements were recorded at 418 nm. The results are summarised in Table 4.4. It was observed that maximum absorbance was obtained at pH 6. The absorbance of the solutions decreases at higher or lower pH values than this which is shown in Fig.4.3. Hence the pH 6 was maintained in the further studies.

Table 4.4 : Effect of pH on the absorbance of
iron(II) - QAT complex

$$(\text{Fe}) = 1.790 \times 10^{-4} \text{ M} \quad (\text{QAT}) = 1.02 \times 10^{-3} \text{ M}$$

pH	Absorbance at 418 nm
3.0	0.380
4.0	0.470
5.0	0.570
5.5	0.600
6.0	0.615
6.5	0.600
7.0	0.560
8.0	0.440
9.0	0.310

Validity of Beer's Law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of iron(II) (range of final concentration $1.790 \times 10^{-5} \text{ M}$ to $1.4324 \times 10^{-4} \text{ M}$) and the same amounts of reagents (final concentration $1.02 \times 10^{-3} \text{ M}$) with the pH maintained at 6 were used for the study. The absorption measurements were recorded against the reagent blank at 418 nm (Table 4.5, Fig.4.4).

Beer's law is obeyed upto a concentration of 5 ppm of iron(II). The Sandell sensitivity⁵⁰ of the reaction is $0.016 \mu\text{g}/\text{cm}^2$ of Fe(II) at 418 nm for $\log \frac{I_0}{I} = 0.001$. The Ringbom's plot⁵¹ (Fig. 4.5) indicated that optimum range is 3 to 8 ppm of Fe(II).

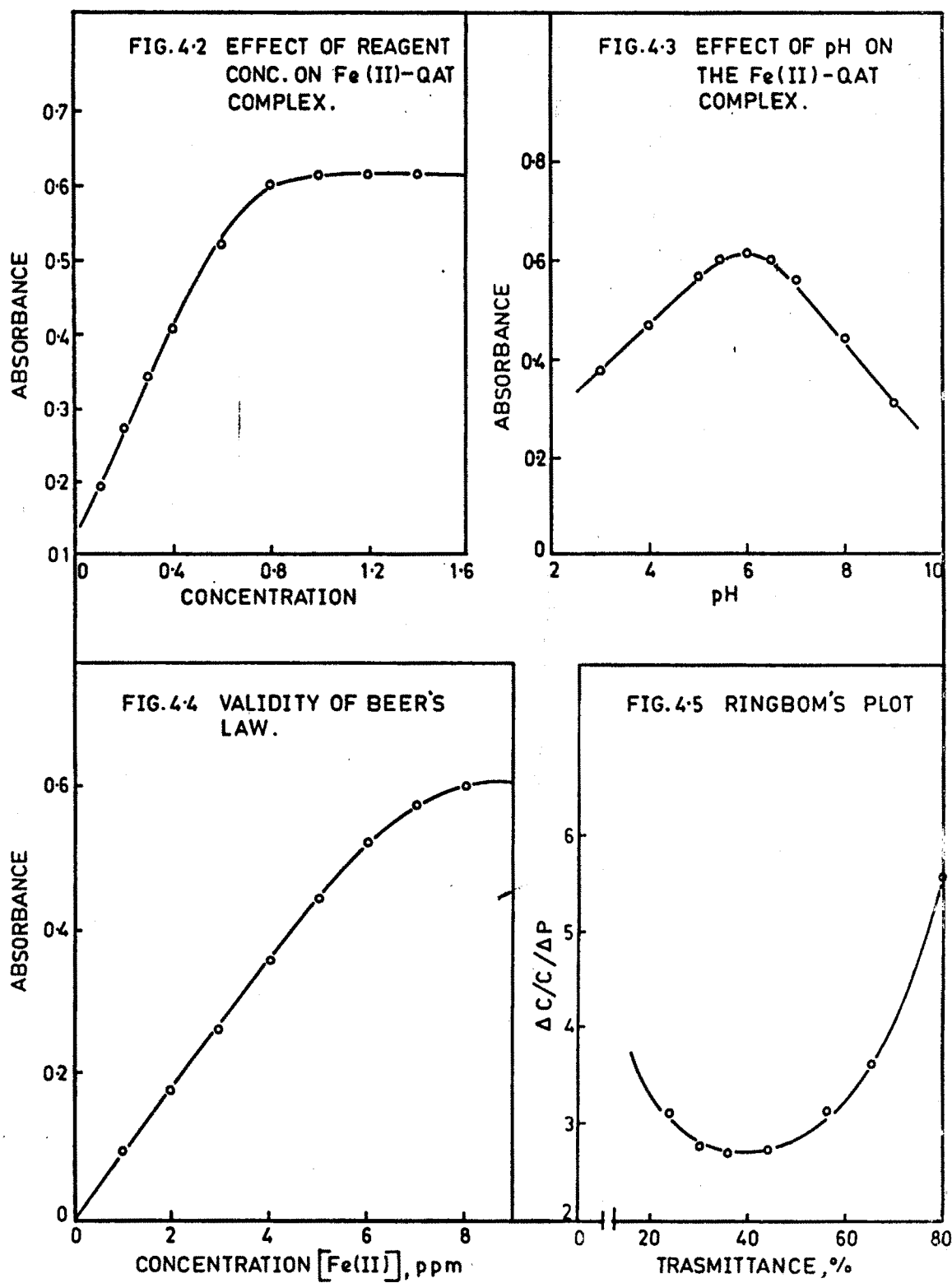


Table 4.5 : Varification of validity of Beer's law for
Fe - QAT complex.

$$(\text{QAT}) = 1.02 \times 10^{-3} \text{ M}$$

Iron taken in ppm	Absorbance at 418 nm
1	0.095
2	0.175
3	0.260
4	0.355
5	0.440
6	0.525
7	0.565
8	0.605

Composition of the complex :

The combining ratio of metal to ligand (reagent) was ascertained by Job's method of continuous variations⁵² and Mole ratio method⁵³. For Job's method of continuous variation, a series of solutions were prepared by mixing equimolar-solutions of iron(II) and the reagent ($2.69 \times 10^{-4} \text{ M}$). 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 418 nm against simultaneously prepared reagent blank (Fig.4.6, Table 4.6). The plot indicates the existence of 1:2 complex with respect to metal and reagent represented as ML_2 .

Table 4.6 : Determination of the formula of iron-QAT complex by Job's method of continuous variation.
 $(\text{Fe}) = (\text{QAT}) = 2.690 \times 10^{-4} \text{ M}$

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 418 nm
0.1	0.9	0.1	0.330
0.2	0.8	0.2	0.410
0.3	0.7	0.3	0.460
0.4	0.6	0.4	0.435
0.5	0.5	0.5	0.385
0.6	0.4	0.6	0.320
0.7	0.3	0.7	0.260
0.8	0.2	0.8	0.210
0.9	0.1	0.9	0.170

For mole ratio method, solutions containing the same final metal concentration ($2.69 \times 10^{-4} \text{ M}$) and different amounts of the reagent ranging from 5.380×10^{-6} to $3.766 \times 10^{-5} \text{ M}$ concentration were prepared keeping the pH 6. Absorbances of the solutions were measured at 418 nm against the reagent blank. The curve showed break at the metal to reagent ratio 1:2, confirming the results obtained by the application of Job's method of continuous variation (Fig.4.7 Table 4.7). The dissociation constant is calculated from mole ratio plot and comes out to be 6.092×10^{-11} .

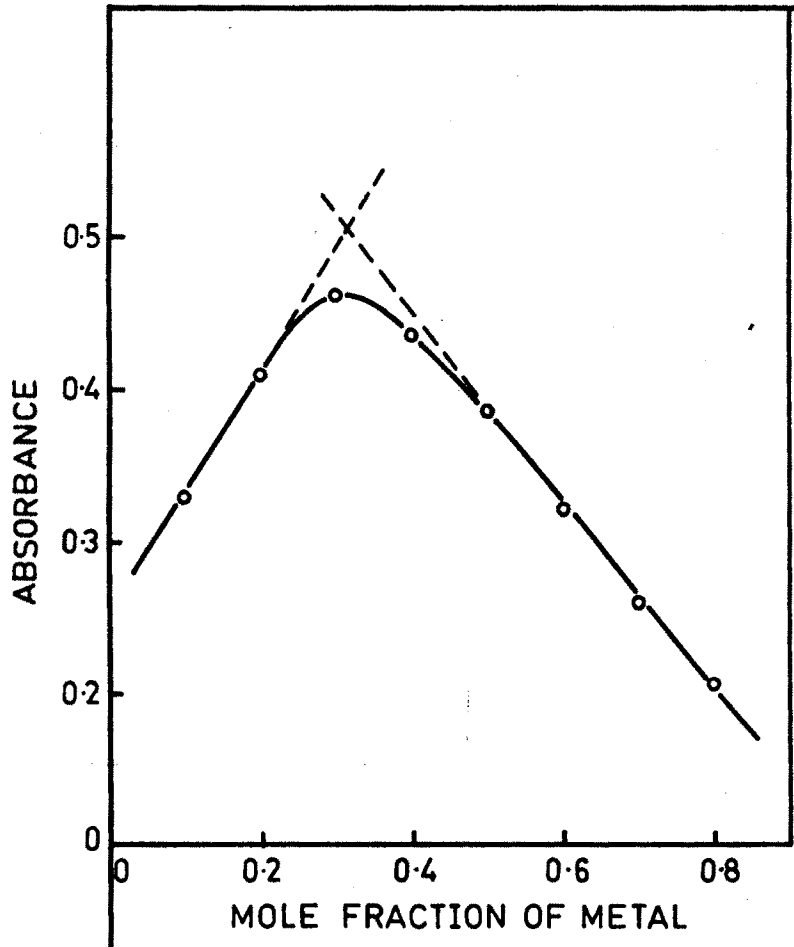


FIG.4-6
JOB'S PLOT FOR Fe(II)-
QAT COMPLEX.

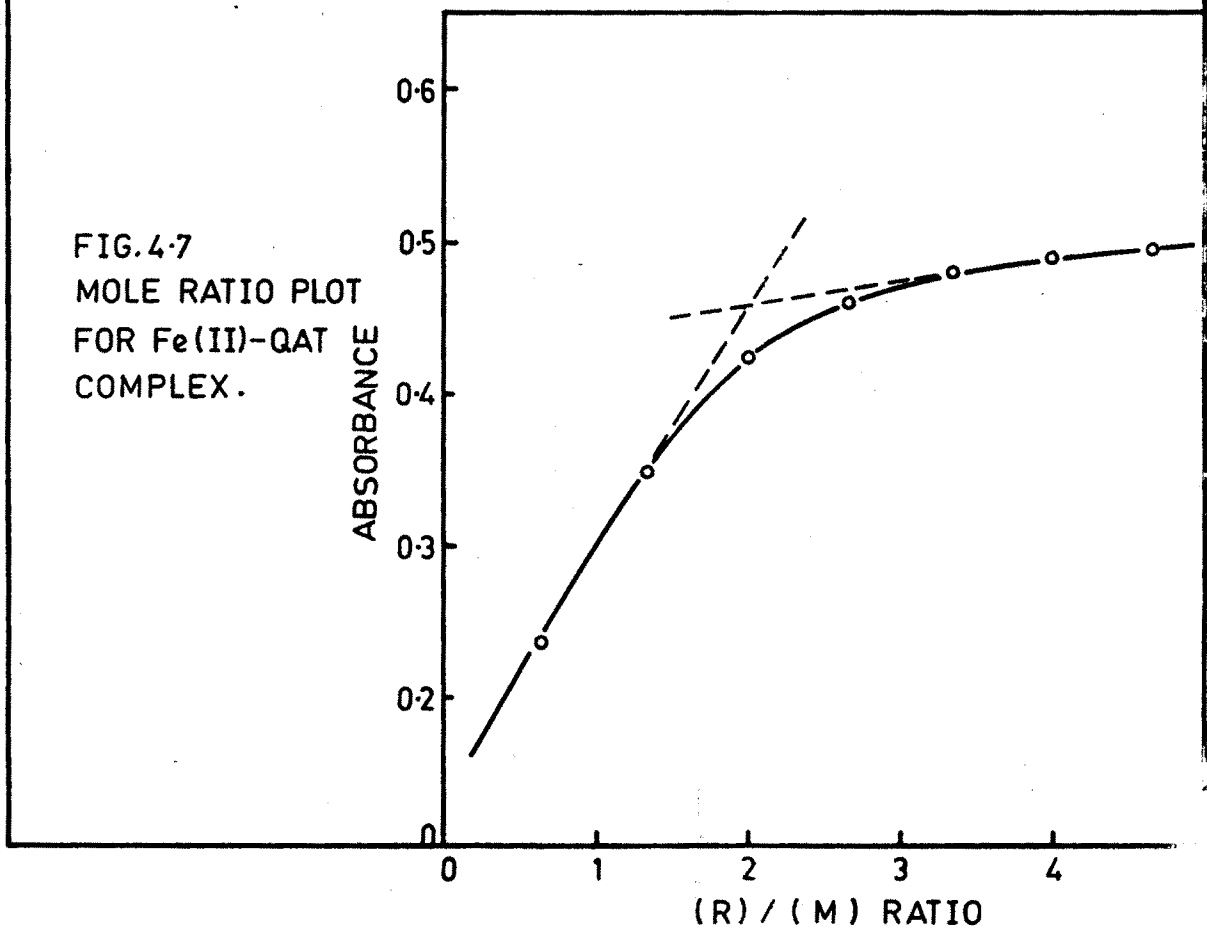


FIG.4-7
MOLE RATIO PLOT
FOR Fe(II)-QAT
COMPLEX.

Table 4.7 : Determination of the formula of iron-QAT complex by mole ratio method.

$$(\text{QAT}) = (\text{Fe}) = 2.69 \times 10^{-4} \text{ M}$$

Metal ion ml	Reagent ml	Reagent metal ratio	Absorbance at 418 nm
0.3	0.2	0.66	0.235
0.3	0.4	1.33	0.345
0.3	0.6	2.0	0.425
0.3	0.8	2.66	0.460
0.3	1.0	3.33	0.480
0.3	1.2	4.0	0.490
0.3	1.4	4.66	0.495

Effect of diverse ion :

A number of representative ions were examined for their interference in the determination of iron as per the recommended procedure. The tolerance limit was assumed to be caused less than 2 % error. Iron estimation is interfered seriously by tin(II) where as Nickel, cerium and copper tolerate at tracer concentrations. The tolerance for the various foreign ions tested has been shown in Table 4.8.

Table 4.8 : Effect of diverse ions

$$[\text{Fe(II)}] = 1.79 \times 10^{-4} \text{ M}, [\text{QAT}] = 1.02 \times 10^{-3} \text{ M}$$

Metal ion	Added as	Tolerance limit, ppm	Metal ion	Added as	Tolerance limit, ppm
Zn(II)	ZnSO ₄ ·7H ₂ O	15	Cr(VI)	K ₂ Cr ₂ O ₇	10
Co(II)	CoCl ₂ ·6H ₂ O	10	V(V)	NH ₄ VO ₃ ·H ₂ O	200
Ni(II)	NiCl ₂ ·6H ₂ O	5	Ce(IV)	Ce(SO ₄) ₂	5
Mn(II)	MnCl ₂ ·6H ₂ O	15	U(VI)	UO ₂ (NO ₃) ₂ ·6H ₂ O	50
Ba(II)	BaCl ₂ ·2H ₂ O	30	Ti(IV)	Titanium oxalate	10
Sn(II)	SnCl ₂ ·2H ₂ O	none			
Pb(II)	Pb(NO ₃) ₂	80	W(VI)	Na ₂ WO ₄ ·2H ₂ O	25
Ca(II)	CaCl ₂	20	Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ ·12H ₂ O	10
Cu(II)	CuCl ₂ ·2H ₂ O	5	EDTA	Na-EDTA	50
Mg(II)	MgSO ₄ ·7H ₂ O	10	tartarate	Na-tartarate	150
Bi(III)	Bi(NO ₃) ₃ ·5H ₂ O	200	Citrate	Citric acid	25
Al(III)	AlCl ₃ ·6H ₂ O	15	HPO ₄ ⁻²	Na ₂ HPO ₄	100
Cd(II)	CdCl ₂ ·6H ₂ O	20	Chloride	KCl	250
Pd(II)	PdCl ₂ ·2H ₂ O	15	Acetate	CH ₃ COONa	30
Os(VIII)	OsO ₄	10	Fluoride	NaF	50
Th(IV)	Th(NO ₃) ₄ ·6H ₂ O	15			

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