

CHAPTER - III

DETERMINATION OF IRON

3.1 INTRODUCTION

Among those elements, essential for life, iron enjoys a status of extra-ordinary importance. It is a very important element in industry and plays a prominent role in technology, science, health science, metallurgy and in the development of living forms. The analytical chemists are concerned with iron medicinal preparations, blood and other body fluids, food materials, ores and minerals, metals and alloys etc.

Iron is a major constituent of whole earth (35 %). Earth crust contains 5 % iron. It is universally distributed throughout the solar system and commonly occurs in meteorites.

Several techniques were applied for the determination of very low to high percentage of iron. Although several reagents such as 2,2'-bipyridine¹ and 1,10-phenanthroline² are known as colourimetric reagents, the search for new reagents continues. Thiophene-2-aldehyde guanylhydrazone (TAG) has distinct advantage over the previous methods. The present chapter deals with application of TAG for photometric determination of iron.

Several reagents including ammonium sulphocyanide, protocatechuric acid,³ cupferron,⁴ pyramidone,⁵ salicylaldoxime,⁶ salicylic acid⁷ and sulphosalicylic acid⁸ are used in the estimation of iron. In case of reagents like O-dianisidine,⁹ catechol,¹⁰ formaldoxime,¹¹

quinisatin oxime,¹² 2-pyridyl glyoxime¹³ and dimethyl triketone,¹⁴ colour formation is very slow and requires longer duration of time. Methods involving violuric acid,¹⁵ 2-thenoyl trifluoro acetone,¹⁶ dinitrosoresorcinol,¹⁷, α -hydroxy acetophenone oxime¹⁸ and morin¹⁹ as reagents are not selective. In case of α -pyridyl hydrazone,²⁰ glycine cresol red,²¹ pyridyl- β -monoxime²² and 2-benzoyl pyridine hydrazone²³ heating is necessary due to slow rate of formation of complex. The sensitivity of the methods is very low in case of α -hydroxy acetophenone oxime¹⁸ and chromotrope 2R.²⁴ Whereas complexes of *p*-amino-NH-dimethylaniline,²⁵ 5-sulpho- β -resorcylic acid²⁶ and 8-hydroxy-7-nitrosoquinoline-5-sulphonic acid²⁷ are only stable for 10-20 minutes. Recently, some thiosemicarbazones²⁸⁻³⁵ are reported for the determination of iron at tracer level. Iron is determined in synthetic fatty acids by sodium salts of diethyldithiocarbamate.³⁶ Some other reagents like pyrazinyl methyl ketone,³⁷ 1-(2-pyridylazo)-2-naphthol³⁸ are also used.

The proposed reagent, thiophene-2-aldehyde guanylhydrazone (TAG) forms a yellow complex with iron at pH 10.0. The method has the desired sensitivity for colorimetric determination of iron in micro quantities.

3.2 EXPERIMENTAL

3.2.1 Standard Solutions :

Standard Iron (II) Solution :

A stock solution of Fe(II) (1 mg/ml = 0.01790 M) was prepared by dissolving A.R. grade ferrous ammonium sulphate hexahydrate in distilled water followed by 2-3 drops of concentrated sulphuric acid and was standardised volumetrically³⁹ by using literature procedure.

Reagent Solution :

A stock solution of 0.01 M reagent (TAG) was prepared by dissolving 0.168 gms of TAG in 100 ml ethyl alcohol (1.68 mg/ml).

Buffer Solution :

Buffer solution of pH 11 was prepared by dissolving appropriate amount of sodium carbonate in distilled water.

3.2.2 Recommended Procedure :

An aliquot of the solution containing about 10 μ g of iron (II) was taken in a 10 ml volumetric flask. Then 3.0 ml of 1.0×10^{-2} M reagent (TAG) solution was added which provides desired excess quantity to complete the complex formation. The pH of the solution was adjusted to 10 by adding 0.6 ml of sodium carbonate buffer solution of pH 11 and was adjusted upto the mark with distilled ethanol.

The absorbance of the complex was measured at 360 nm against reagent blank. The concentration of iron was read out from a calibration curve.

3.3 RESULTS AND DISCUSSION

3.3.1 Spectral Characteristics :

The absorption spectrum of Iron (II)-TAG complex of the solution containing 10 µg Fe (II) [1 ml of 0.01 mg/ml i.e. $1.790 \times 10^{-4} \text{ M}$] and 3.0 ml of $1.0 \times 10^{-2} \text{ M}$ of the reagent (TAG) was recorded at pH 10.0 against reagent blank. The complex shows absorption maximum at 360 nm. The molar extinction coefficient at 360 nm is $7.262 \times 10^3 \text{ l mole}^{-1} \text{ cm}^{-1}$. The reagent does not absorb in this region. Absorption spectra of the complex and the reagent are shown in figure 3.1. Observations are given in table 3.1.

Table 3.1 : Molar extinction coefficients of the Fe(II)-TAG Complex and the reagent (TAG)

Wavelength λ , nm	Molar extinction coefficients, ϵ	
	Fe(II)-TAG complex $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	Reagent, TAG $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$
340	0.5586	0.0280
350	0.6739	0.0180
360	0.7262	0.0120
365	0.6608	0.0105
370	0.5307	0.0086
380	0.3296	0.0068
390	0.1899	0.0055
400	0.1229	0.0045
410	0.0977	0.0038
420	0.0810	0.0030
430	0.0754	0.0028
440	0.0726	0.0028
450	0.0642	0.0025
460	0.0558	0.0023
470	0.0530	0.0020
480	0.0502	0.0016
490	0.0391	0.0016
500	0.0391	0.0015
520	0.0335	0.0010
540	0.0312	0.0006
560	0.0308	0.0005
580	0.0306	0.0005
600	0.0300	0.0003

3.3.2 Effect of pH :

To study the effect of pH of the solution on the absorbance of the complex, a series of solutions containing 1.0 ml of 0.01 mg/ml of Fe (II) [1.790×10^{-4} M] and 3.0 ml of 0.01 M reagent (TAG) was prepared as per the recommended procedure over a range of pH 2.0 to 13.0. The absorbances were measured against corresponding reagent blank. It was found that the complex has maximum and constant absorbance over the pH range 9.0 to 11.0. Therefore, pH 10.0 was selected as the optimum pH for further studies. The observations are given in table 3.2 (Fig. 3.2).

Table 3.2 : Effect of pH

pH	Absorbance at 360 nm
2.0	0.04
4.0	0.14
5.0	0.40
6.0	0.90
7.0	0.94
8.0	1.00
9.0	1.20
10.0	1.20
11.0	1.20
12.0	1.00
13.0	0.82

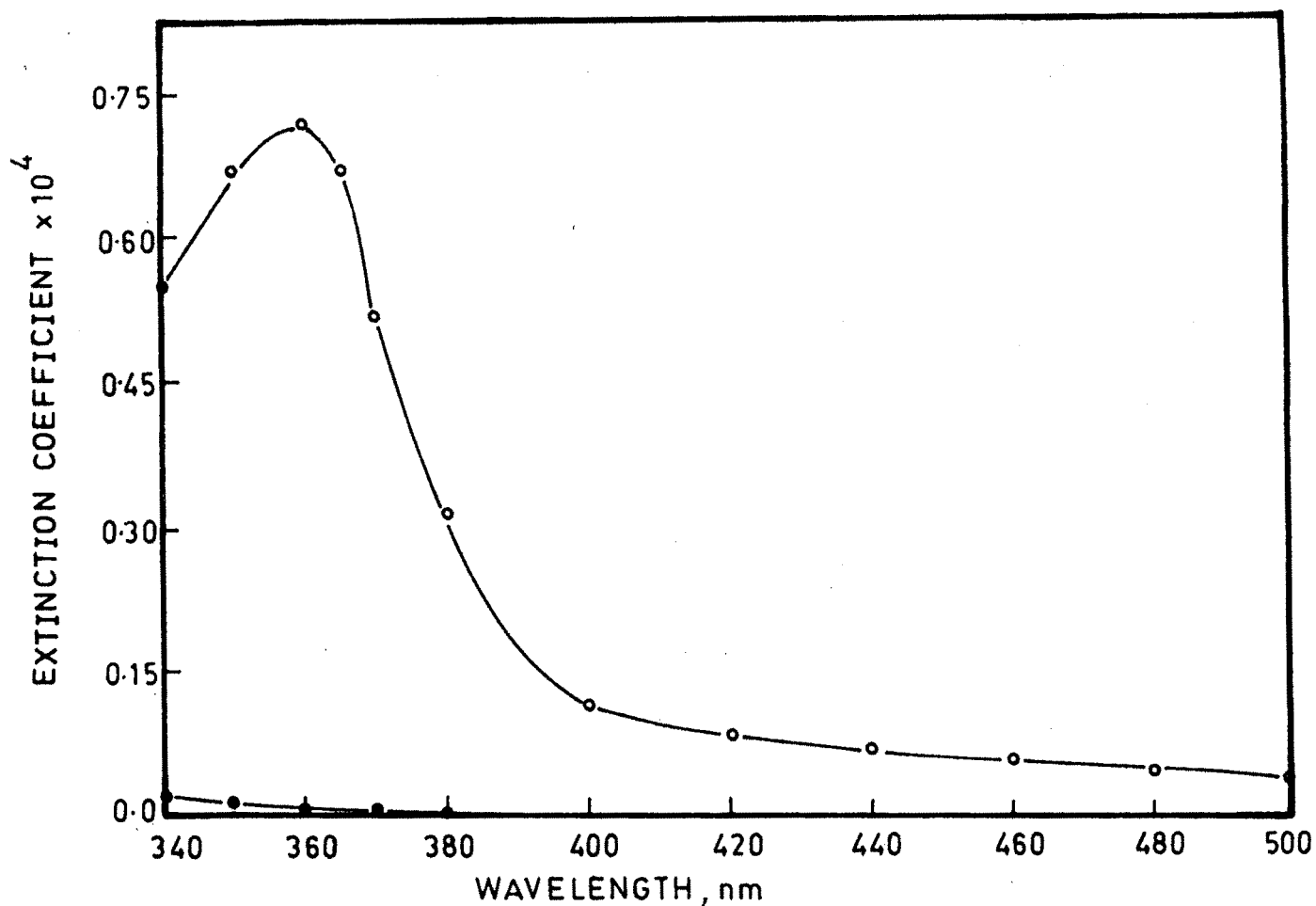


FIG. 3.1— ○—○ ABSORPTION SPECTRUM OF IRON (II) -TAG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (TAG).

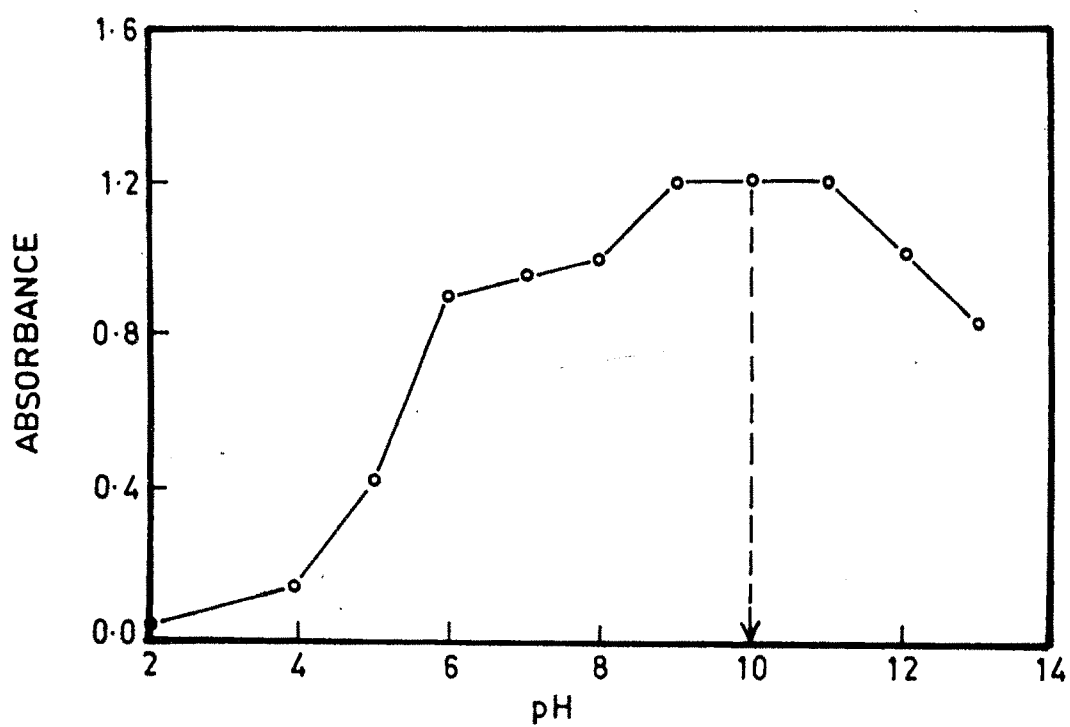


FIG. 3.2 — EFFECT OF pH.

3.3.3 Effect of reagent concentration :

A series of solutions containing same amount of iron ($1.790 \times 10^{-4} \text{M}$) and different amounts of reagent ($5.0 \times 10^{-3} \text{M}$ to $4.0 \times 10^{-2} \text{M}$) were prepared at pH 10.0. The complex was developed as per the recommended procedure. Results in the table 3.3 show that three fold molar excess of the reagent is sufficient for full colour development.

Table 3.3 : Effect of reagent concentration

$$[\text{Fe(II)}] = 10 \text{ ppm}; [\text{TAG}] = 1.0 \times 10^{-2} \text{M}$$

ml of reagent	Absorbance at 360 nm
0.5	0.61
1.0	0.90
1.5	1.10
2.0	1.20
2.5	1.25
3.0	1.30
3.5	1.30
4.0	1.30

3.3.4 Stability and reaction rate :

Iron(II) - TAG complex is stable for several hours and complex formation is instantaneous.

3.3.5 Validity of Beer's Law :

For the study of validity of Beer's law, the solutions containing different amounts of iron and the same amount of reagent (TAG) 3.0 ml of 1.0×10^{-2} M were taken. The absorbance measurements were recorded at 360 nm against corresponding reagent blank. It was found that Beer's law is valid upto 8.0 ppm (Table 3.4; Fig. 3.3). The Ringbom plot⁴⁰ indicated that optimum concentration range is 1.5 to 5.8 ppm of Fe(II) at 360 nm (Fig. 3.4).

Table 3.4 : Validity of Beer's Law

Amount of Iron (II) ppm	Absorbance at 360 nm
2.0	0.28
4.0	0.55
6.0	0.83
8.0	1.10
10.0	1.30
12.0	1.40

3.3.6 Composition of the complex :

The composition of the complex Fe(II)-TAG was determined by Job's continuous variation method,⁴¹ mole ratio method⁴² and slope ratio method.⁴³ The complexes were developed as per the recommended procedure and absorbances were measured (Table 3.5). The plot of absorbances against the mole fraction

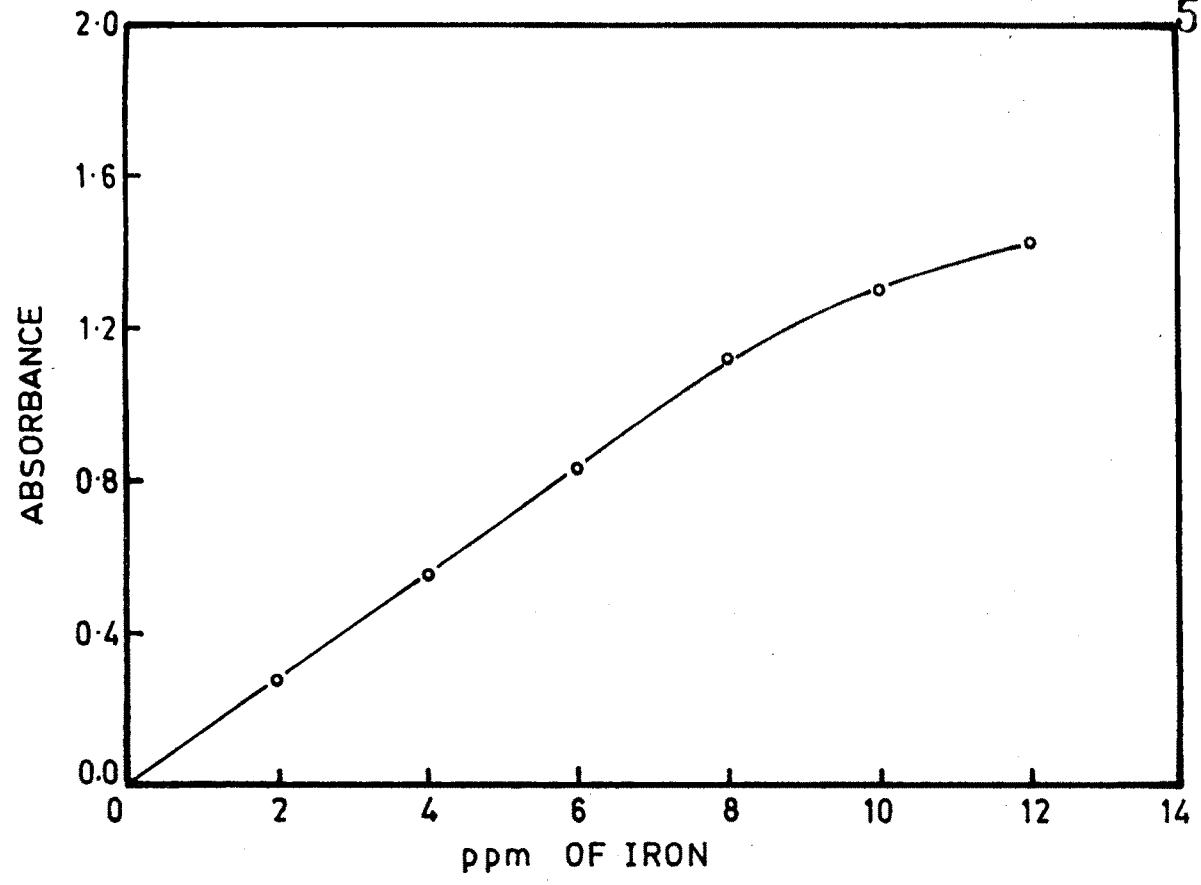


FIG.3-3 VALIDITY OF BEER'S LAW.

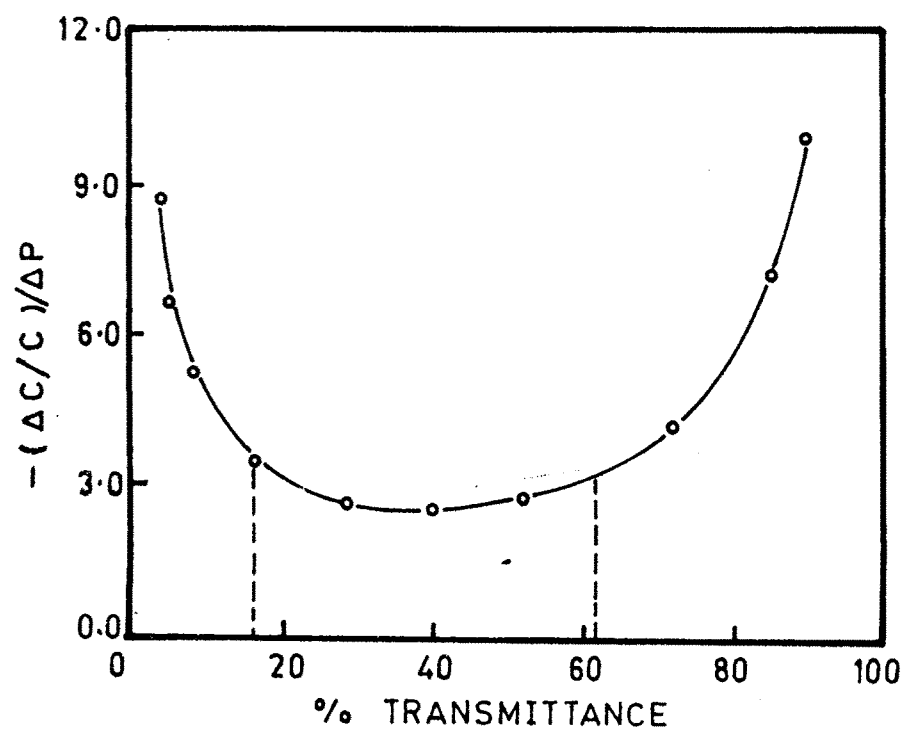


FIG.3-4 RINGBOM PLOT.

of the reagent indicated the existence of 1:2 complex with respect to metal and ligand (Fig. 3.5). For mole ratio method, solutions containing same concentration of reagent ($1.790 \times 10^{-4} \text{ M}$) and varying amounts of iron ranging from $3.58 \times 10^{-5} \text{ M}$ to $3.58 \times 10^{-4} \text{ M}$ were prepared and absorbances of solutions were measured (Table 3.6). The plot of absorbance against metal to reagent ratio (Fig. 3.6) shows the formation of 1:2 complex which confirms the results of Job's method. Slope ratio method also confirms the 1:2 complex of Fe(II)-TAG.

Table 3.5 : Job's continuous variation method

$$[\text{Fe(II)}] = [\text{TAG}] = 1.790 \times 10^{-4} \text{ M}$$

Iron (II) ml	Reagent (TAG) ml	Molar ratio M:L	Absorbances at λ			
			350 nm	360 nm	380 nm	410 nm
0.0	1.8	-	-	-	-	-
0.2	1.6	1:8	0.195	0.270	0.120	0.060
0.4	1.4	2:7	0.320	0.390	0.175	0.100
0.6	1.2	1:2	0.365	0.455	0.200	0.125
0.8	1.0	4:5	0.325	0.410	0.180	0.115
1.0	0.8	5:4	0.270	0.335	0.145	0.090
1.2	0.6	2:1	0.200	0.260	0.100	0.065
1.4	0.4	7:2	0.130	0.175	0.060	0.035
1.6	0.2	8:1	0.050	0.076	0.025	0.010
1.8	0.0	-	-	-	-	-

Table 3.6 : Molar ratio method

$$[\text{Fe(II)}] = [\text{TAG}] = 1.790 \times 10^{-4} \text{ M}$$

Iron (II) ml	Reagent (TAG) ml	Molar ratio M:L	Absorbances at λ	
			360 nm	380 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.100	0.080
0.4	2.0	1:5	0.200	0.150
0.6	2.0	3:10	0.295	0.235
0.66	2.0	1:3	0.390	0.300
0.8	2.0	2:5	0.480	0.370
1.0	2.0	1:2	0.540	0.410
1.2	2.0	3:5	0.570	0.440
1.33	2.0	2:3	0.585	0.455
1.4	2.0	7:10	0.590	0.460
1.6	2.0	4:5	0.590	0.460
1.8	2.0	9:10	0.595	0.470
2.0	2.0	1:1	0.595	0.475

3.3.7 Sensitivity of the method :

The photometric sensitivity of the method was calculated by Sandell's method⁴⁴ and was found to $0.05397 \mu\text{g}/\text{cm}^2$ at 360 nm.

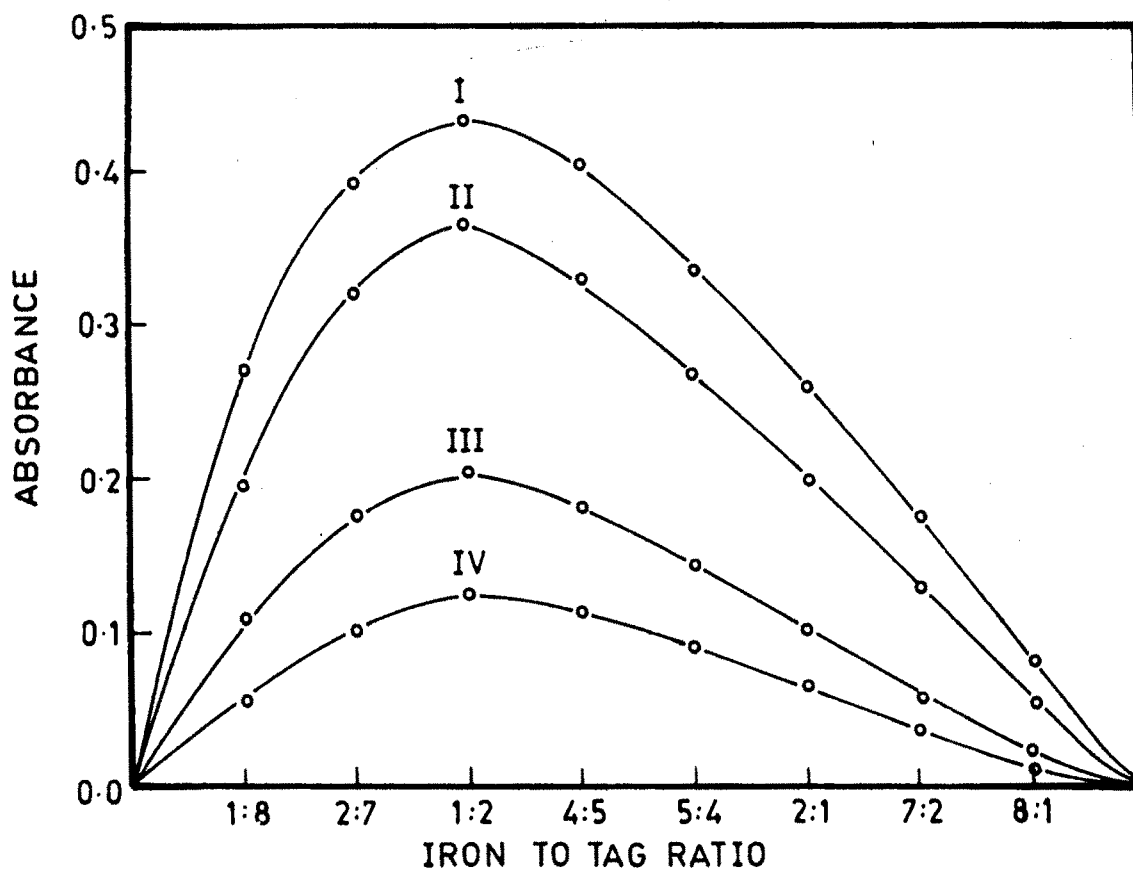


FIG. 3-5 - JOB'S CONTINUOUS VARIATION METHOD.
I - 360 nm, II - 350 nm, III - 380 nm, IV - 410 nm.

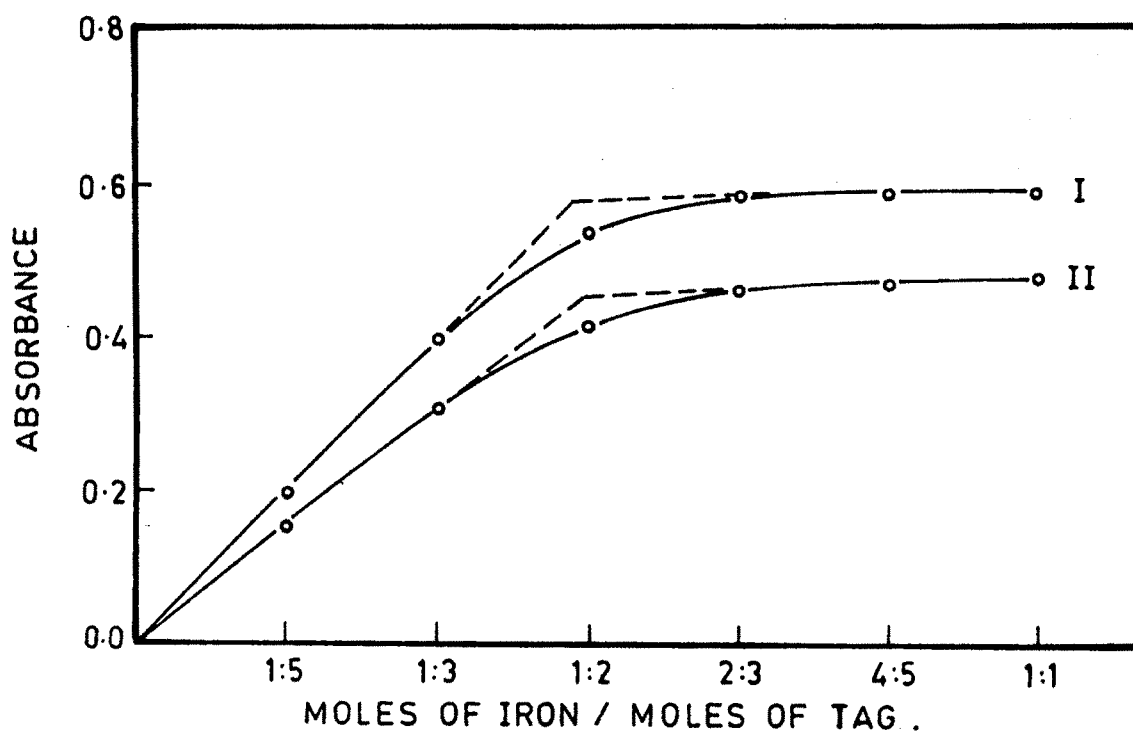


FIG. 3-6 - MOLE RATIO METHOD
I - 360 nm, II - 380 nm

3.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.⁴³ The value of α , degree of dissociation was found to be 0.06897.

The apparent instability constant⁴⁵ was found to be 4.518×10^{-13} for Fe(II) - TAG complex. The change in free energy⁴⁶ of the system is -16.944 K cal/mole.

3.3.9 Precision and accuracy of the method :

In order to test the accuracy and precision of the method, different amounts of iron were determined in six identical samples. The results in table 4.7 show that there is good agreement in the experimental values. The coefficient of variation and standard deviations of methods are also given in table 3.7.

Table 3.7 : Reproducibility of the method

Iron(II) ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation, %
1.5	0.20	0.0020	1.0000
3.0	0.41	0.0038	0.9268
4.5	0.62	0.0062	1.0000
6.0	0.81	0.0080	0.9876

3.3.10 Effect of diverse ions :

Various ions were added to a sample containing a fixed amount of iron (1.0 ppm) and the colour was developed and measured as per recommended procedure. The tolerance limit was assumed to be the amount of foreign ion needed to cause an error less than 2 % in absorbance values. It is found that Co(II), citrate and EDTA^{-4} ions are seriously interfere, while urea is tolerated upto 100.0 ppm. The tolerance limits for the ion are listed in table 3.8.

Table 3.8 : Effect of diverse ions

$$[\text{Fe(II)}] = 1.0 \text{ ppm}; [\text{TAG}] = 1.0 \times 10^{-3} \text{ M}$$

Foreign ions	Added as	Tolerance limit ppm
<u>Cations</u>		
Cr(III)	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	3.0
V(IV)	$\text{VO}\text{SO}_4 \cdot \text{H}_2\text{O}$	3.0
Ba(II)	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	5.0
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	3.0
Ca(II)	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	3.0
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	1.0
Mn(II)	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1.0
Pd(II)	PdCl_2	2.0
Co(II)	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	none
Ni(II)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	1.0
Cd(II)	$\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$	0.8
Cr(VI)	$\text{K}_2\text{Cr}_2\text{O}_7$	0.8
<u>Anions</u>		
Citrate	Citric acid	none
Thiourea	Thiourea	0.1
Oxalate	Potassium oxalate	2.0
EDTA^{-4}	Disodium Salt	none
Urea	Urea	100.0
Acetate	Sodium acetate	10.0
Tartrate	Tartaric acid	4.0

3.4 APPLICATIONSAnalysis of Tonoferon Syrup :

0.05 ml of commercially available Tonoferon syrup was taken in a 50 ml conical flask. To this, 2-3 ml perchloric acid was added and was evaporated almost to dryness. It was then dissolved in distilled water and diluted to 25 ml with distilled water.

1.0 ml (100 ppm) of above diluted solution was taken in a 10 ml volumetric flask. To this 3.0 ml of 1.0×10^{-2} M reagent solution was added and pH was adjusted to 10.0 with buffer solution. It was then diluted upto the mark with distilled ethanol and absorbance was measured at 360 nm against reagent blank. Same procedure was repeated by using 0.8 ml of above diluted solution of Tonoferon syrup, Results are given in table 3.9.

Table 3.9 : Analysis of Tonoferon syrup

Syrup	Amount used	Certified value of Fe	Experimental Value of Fe	Relative standard deviation for five observations
Tonoferon	10 ppm	5.0 %	4.87 %	0.040
	8 ppm	5.0 %	4.93 %	0.044

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