CHAPTER - IV

DETERMINATION OF IRON (III)

4.1 INTRODUCTION

Iron is an important element in industry and plays a prominent role in metallurgy, technology, science, health science and in the development of living forms. Iron has been in use in the samples ranging from food materials, medicinal preparation, blood and other body fluids, ores and minerals, metals and alloys etc.

For the determination of iron, several techniques were applied.Several colorimetric reagents such as 2, 2'-bipyridine[1] and 10 phenanthroline[2] are know. 2-Acetly thiophene guanylhydrazone (ATG) has distinct advantage over the previous methods. The present chapter deals with the application of ATG for estimation of iron and analysis of iron ore.

Numerous analytical reagents were reported for the determination of tracer quantities of iron. Several reagents including salicylic acid[3] sulphosalicylic acid[4], salicylaldoxime[5], pyramidone[6], cupferron[7] and protocatechuric acid[8] are used in the estimation of iron.

In case of α - pyridyl hydrazone[9], glycinecresol red[10], pyridyl-ß-monoxime[11] and 2-benzoylpyridine hydrazone[12], heating is necessary due to slow rate of formation of complex. In case of reagents like o-dianisidine[13], catechol[14], formaldoxime[15], quinisatin oxime[16], 2-pyridyl glyoxime[17] and dimethyl triketone[18], colour formation is very slow and requires longer duration of time. Complexes of p-amino-NN-dimethylaniline[19], 5-sulpho-ß-resorcylic acid[20] and 8-hydroxy-7-nitrosoquinoline-5-sulphonic acid[21] are stable for only 10-20 minutes. Methods involving violuric acid[22], 2-thenoyl trifluoroacetone[23], dinitrosoresorcinol[24], o-hydroxy acetophenone oxime[25] and morin[26] as reagents are not selective, whereas sensitivity of the method is very low in case of chromotrope 2R[27]. Some thiosemicarbazones[28-35] are reported for trace determination of iron. But most of them are affected by some drawbacks.

Recently, iron is determined spectrophotometrically with the reagents such as naphthoxyacetylacetophenone[36], 1-phenyl-3-thiobenzoylthiocarbamide[37], 2-amino-4-phenyl-5--phenylazo thiazole[38], salicylaldehyde thiosemicarbazone[39], with oxime, semicarbazone and thiosemicarbazone of 3--methoxysalicylaldehyde[40],N,N-dimethylformamide[41], 2-hydroxy -1-acetonaphthoneoxime[42], tolmetin[43] and cacotheline[44].

By extractive photometric method, iron is determined with the reagents such as sodium pentamethylene dithiocarbamate[45],cyclohexylthioglycolate[46], 4-(2-pyridylazo) resorcinol[47], bis (4-hydroxypent-2-ylidene) diaminoethane[48] and benzoyl triethyl ammonium chloride[49].

Spectrophoto metric determination of iron is also studied by ferroin perchlorate ion-association complex into mesityl oxide[50] and iron (II) -TPTZ-picrate ion-association complex[51].

4.2 EXPERIMENTAL

4.2.1 Standard Solutions:

Standard iron (III) solution:

Standard iron (III) solution 1mg/ml (1.7910×10^{-2}M) was prepared by dissolving A.R. grade ferric ammonium sulphate in distilled water followed by 2-3 drops of concentrated sulphuric acid and was standardised volumetrically[52] by using literature procedure. Further dilutions were made by diluting the stock solution with distilled water.

Reagent (ATG) solution:

A stock solution of the reagent (ATG) was prepared by dissloving 182 mg of it in 100.0 ml 50% ethanol (1.82 mg/ml ie. 0.01 M).

Buffer solution:

Buffer solution was prepared by dissolving appropriate amounts of sodium hydroxide and borax.

All chemicals used were of analytical grade.

4.2.2 Recommended Procedure:

An aliquot of the solution containing 50.0 µg Fe (III) was taken in a 10 ml volumetric flask. To it was added 1.6 ml of 0.01 m reagent (ATG) and 1.0 drop of formamide. The pH of the solution was adjusted to 2.5 by adding 1.0 ml buffer solution. The solution was diluted upto the mark with distilled water. The absorbances of the complex was measured at 365 nm against reagent blank. The concentration of iron was read out from a calibration curve.

4.3 RESULTS AND DISCUSSION

4.3.1 Spectral Characteristics:

The absorption specturm of Iron (III)-ATG complex of the solution of the concetration 9.011 × 10^{-4}M was recorded at pH 2.5 against reagent blank. The complex shows absorption maximum at 365 nm.The molar extinction coefficient at 365 nm is 0.1197 × 10^4 l $mole^{-1}$ cm^{-1}. The reagent does not absorb in this region. The observations of absorbances and molar extinction coefficients of the complex and the reagent are given in table 4.1 (Figure 4.1).

Table 4.1: Absorbances and molar extinction coefficients of Fe(III)-ATG complex and reagent (ATG)

Wavelength λ, nm	Absorbance		Molar extinction coefficient, ϵ	
	Fe(III)-ATG 9.011×10^{-4} M	ATG, reagent 1.6×10^{-3} M	Fe(III)-ATG complex $\epsilon \times 10^4$ l mole^{-1} cm^{-1}	ATG, reagent $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
345	0.556	0.262	0.0617	0.0163
350	0.815	0.109	0.0904	0.0068
355	0.975	0.035	0.1082	0.0021
360	1.036	-	0.1149	-
365	1.079	-	0.1197	-
370	0.891	-	0.0989	-
380	0.643	-	0.0713	-
390	0.515	-	0.0572	-
400	0.279	-	0.0310	-
420	0.207	-	0.0229	-
440	0.146	-	0.0162	-
460	0.132	-	0.0147	-
480	0.079	-	0.0088	-
500	0.051	-	0.0057	-

4.3.2 Effect of pH:

The pH was varied over the range 1.0 to 8.0 in order to study its effect on the absorbance of Fe(III)-ATG complex at 365 nm by using recommended procedure. The results in table 4.2 show that, over the pH range 1.65 to 3.0 the absorbance remained constant. Above pH 3.0, the

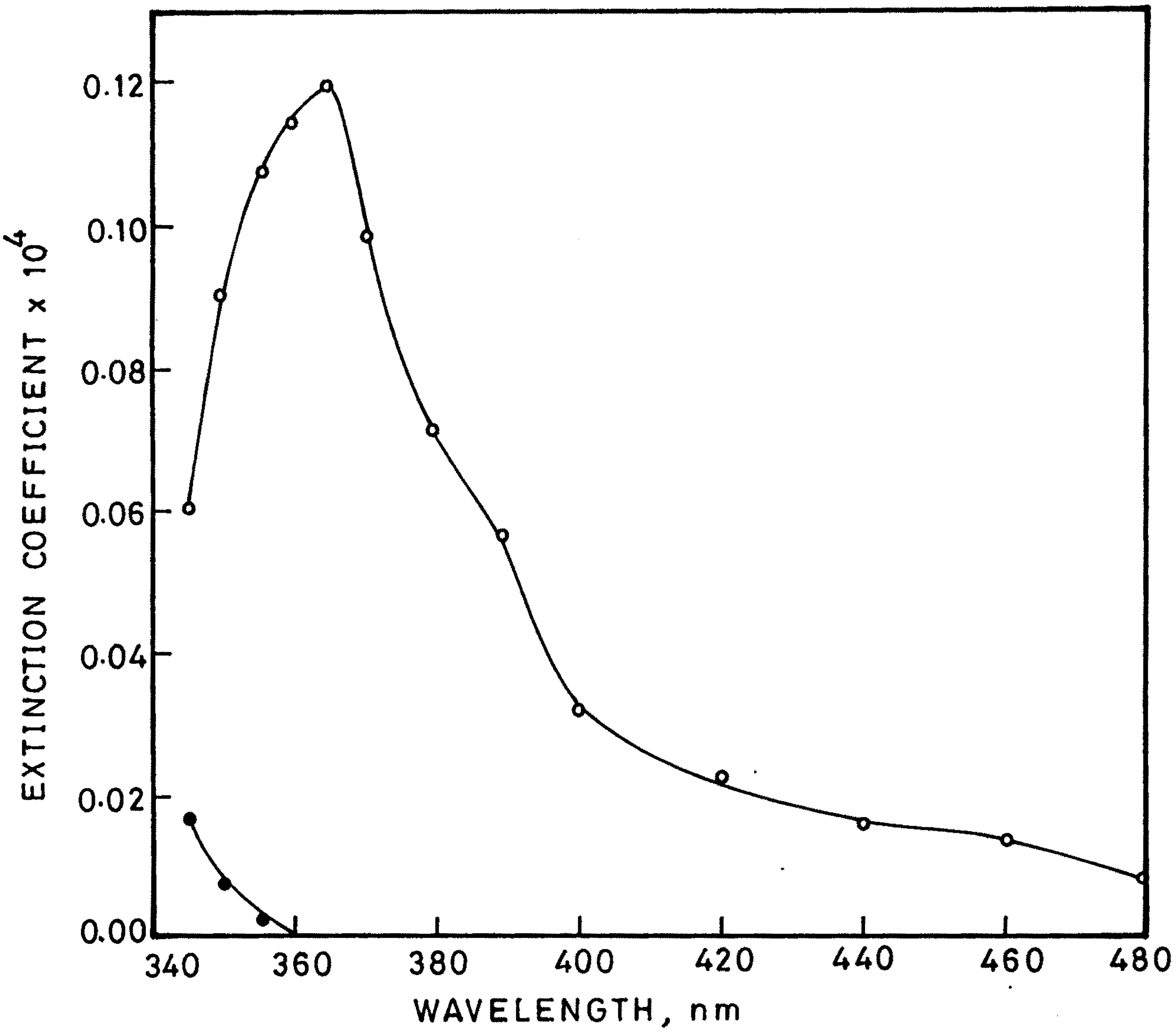


FIG. 4·1 - ○—○ ABSORPTION SPECTRUM OF IRON(III) - ATG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (ATG).

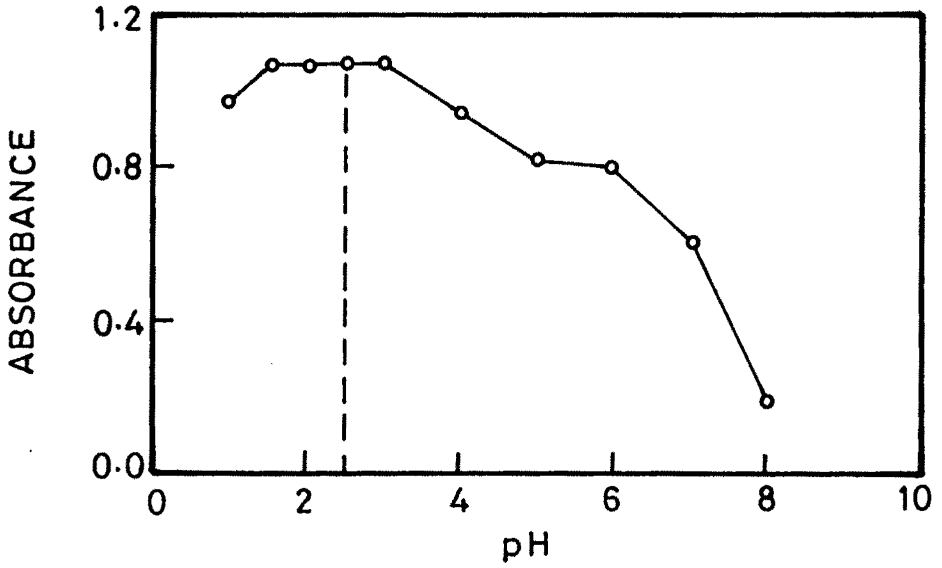


FIG. 4·2 - EFFECT OF pH.

absorbance starts decreasing. Hence, pH 2.5 was selected for further studies (Figure 4.2)

Table 4.2: Effect of pH
[Fe(III)] = 5.0 ppm; [ATG] = 1.5 x 10^{-3} M

pH	Absorbance at 365 nm
1.00	0.993
1.65	1.068
2.00	1.068
2.50	1.068
3.00	1.068
4.00	0.947
5.00	0.839
6.00	0.800
7.00	0.610
8.00	0.203

4.3.3 Effect of Reagent Concentration:

It was found that about a two-fold molar concentration of the reagent relative to the metal ion concentration was satisfactory.

A series of solutions were prepared in which the volume of 1.0x10^{-2} M reagent was varied from 0.5 to 3.0 ml, while the concentration of iron was kept constant at

9.0111×10^{-4} M. The pH value of each solution was adjusted to 2.5 and each solution was made upto the mark in 10 ml volumetric flask. The absorbances were measured at 365 nm wavelength against reagent blank. The results are given in table 4.3.

Table 4.3: Effect of reagent concentration
[Fe(III)] = 5.0 ppm; [ATG] = 1.0×10^{-2} M .

Amount of reagent, ml	Absorbance at 365 nm
0.5	0.786
1.0	0.891
1.2	0.963
1.4	1.026
1.6	1.064
1.8	1.025
2.0	1.009
2.5	1.005
3.0	1.002

4.3.4 Stability and Reaction Rate:

Iron(III)-ATG complex formation is instantaneous and independent upon temperature. The colour of the complex is stable for several hours.

4.3.5 Validity of Beer's Law:

The calibration graph (Figure 4.3) prepared from the results given in table 4.4 indicates that Beer's law is valid upto 17.0 ppm of iron(III). The optimum concentration range at 365 nm as calculated according to Ringbom plot[53] is from 10.0 to 24.0 ppm of Fe(III) (Figure 4.4).

Table 4.4: Validity of Beer's law
[ATG] = 1.0×10^{-2} M

Amount of Iron (III), ppm	Absorbance at 365 nm	Transmittance, %	$-(\Delta c/c)/\Delta p$
4.0	0.104	78.7	5.60
8.0	0.209	61.8	3.26
12.0	0.310	49.0	2.98
16.0	0.408	39.1	2.73
20.0	0.476	33.4	2.72
24.0	0.528	29.6	2.77
28.0	0.572	26.8	2.89
32.0	0.598	25.2	2.89

4.3.6 <u>Composition of the Complex</u>:

Job's method of continuous variation[54], mole ratio method[55] and slope ratio method[56] were used to determine the composition of the complex. For these methods, equimolar solutions of reagent and metal were used. The Job's plot of absorbance against mole fraction of the reagent (Table 4.5; Figure 4.5) indicated the existence of 1:2 (Iron:ATG) complex. This composition was confirmed by mole ratio study (Table 4.6; Figure 4.6) and slope ratio study.

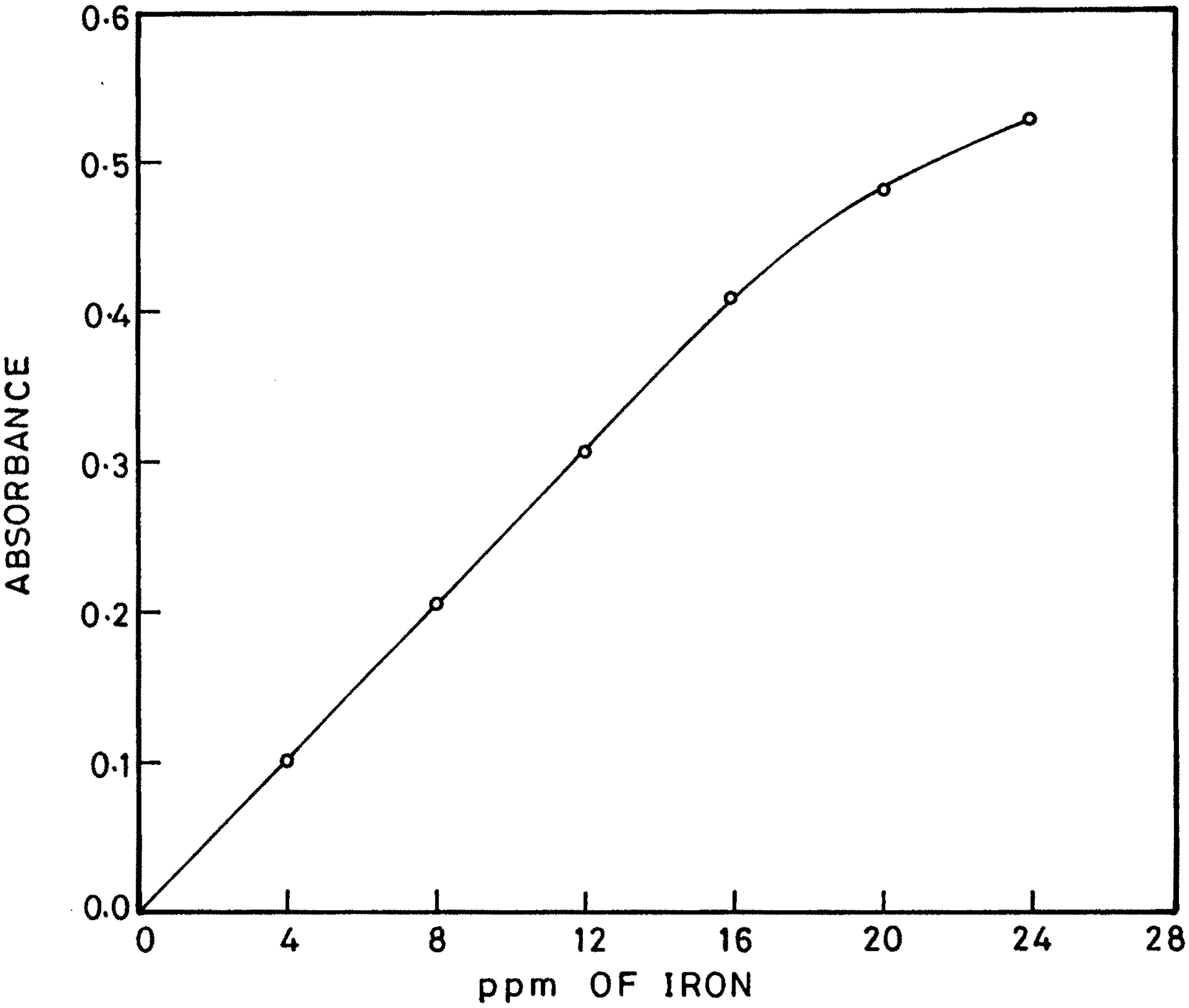


FIG. 4·3– VALIDITY OF BEER'S LAW.

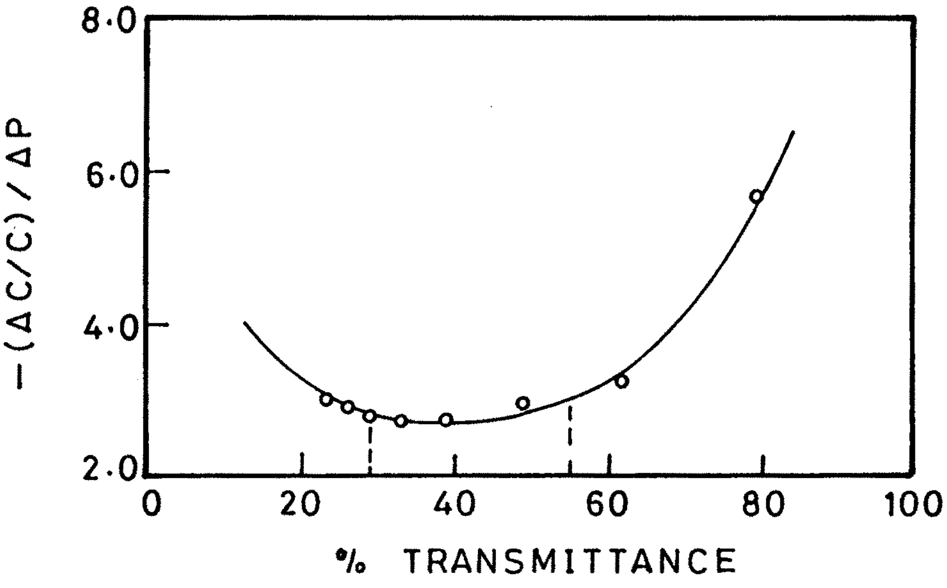


FIG. 4·4 – RINGBOM PLOT.

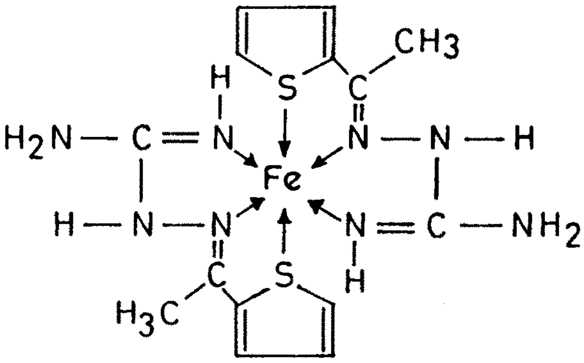
Table 4.5: Job's continuous variation method
$[Fe(III)]=[ATG]=1.8\times10^{-3}$ M

[Fe(III)], ml	[ATG], ml	$\frac{[ATG]}{[Fe(III)]+[ATG]}$	Absorbance at λ	
			365 nm	380 nm
4.0	0.0	-	-	-
3.6	0.4	0.1	0.182	0.108
3.2	0.8	0.2	0.303	0.195
2.8	1.2	0.3	0.396	0.242
2.4	1.6	0.4	0.460	0.320
2.0	2.0	0.5	0.524	0.365
1.6	2.4	0.6	0.558	0.405
1.33	2.66	0.66	0.568	0.426
1.2	2.80	0.7	0.541	0.396
1.0	3.0	0.75	0.506	0.356
0.8	3.2	0.8	0.443	0.303
0.4	3.6	0.9	0.280	0.182
0.0	4.0	1.0	-	-

Table 4.6: Mole ratio method
[Fe(III)] = [ATG] = 1.8×10^{-3} M

[Fe(III)], ml	[ATG], ml	$\frac{[ATG]}{[Fe(III)]}$	Absorbance at λ	
			365 nm	380nm
2.0	0.0	0.0	-	-
2.0	1.0	0.5	0.138	0.091
2.0	2.0	1.0	0.253	0.177
2.0	3.0	1.5	0.346	0.245
2.0	4.0	2.0	0.429	0.302
2.0	5.0	2.5	0.486	0.345
2.0	6.0	3.0	0.507	0.378
2.0	7.0	3.5	0.514	0.392

Hence, the probable structure for Fe(III)-ATG complex may be shown as:



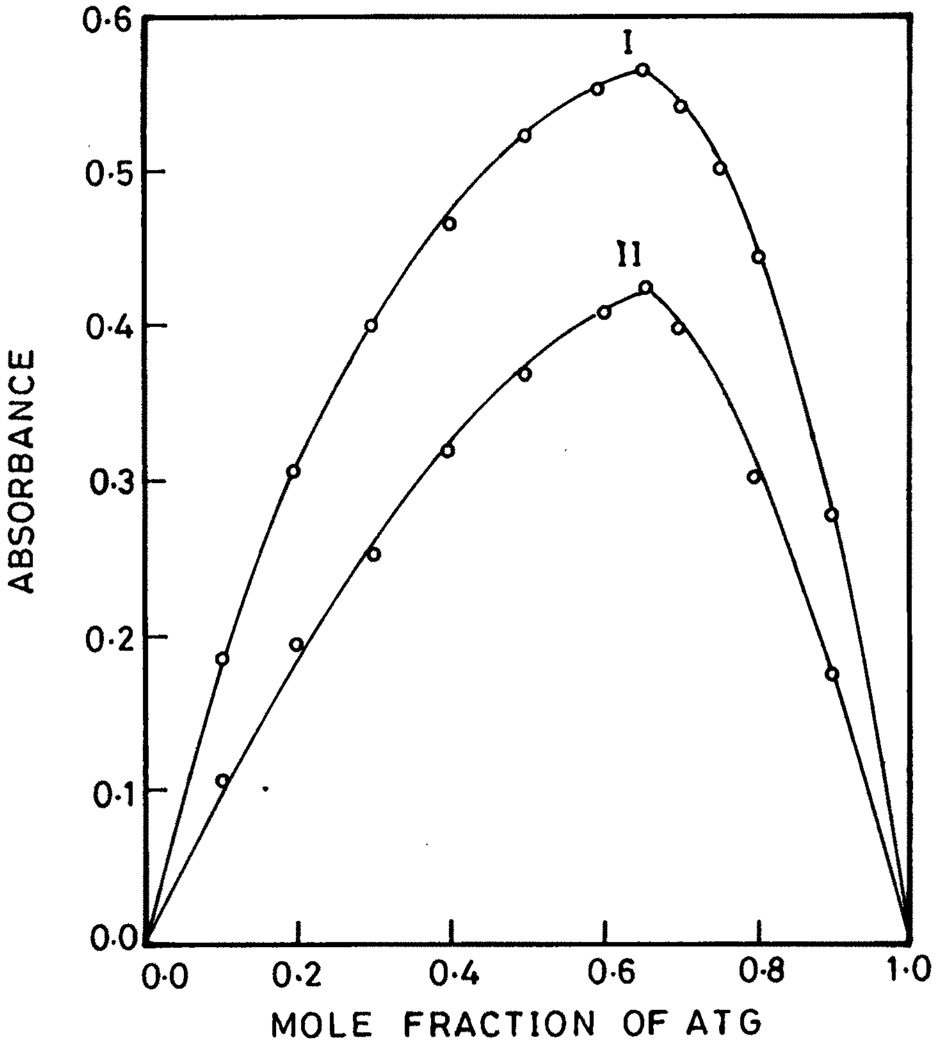


FIG. 4·5 – JOB'S CONTINUOUS VARIATION METHOD.

I — 365 nm ; II — 380 nm

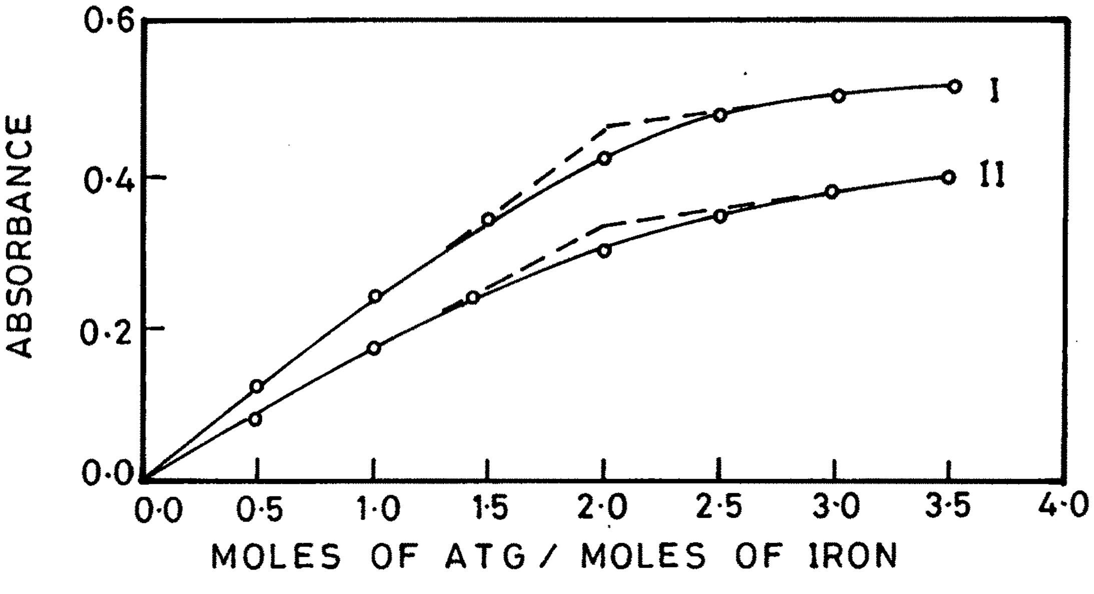


FIG. 4·6 – MOLE RATIO METHOD.

I — 365 nm ; II — 380 nm

4.3.7 Sensitivity of the Method:

The photometric sensitivity was calculated by Sandell's method[57] and was found to be 0.3503 µg/cm^2. There is no effect of light on complex and reagent.

4.3.8 Degree of Dissociation and Instability Constant:

The degree of dissociation, α, was obtained from the mole ratio plot (Figure 4.6) and was found to be 0.0652.

The apparent instability constant[58] was found to be 0.1537×10^{-10} for Fe(III)-ATG complex.

4.3.9 Precision and Accuracy of the Mehtod:

To test the reliability, reproducibility, precision and accuracy of the method, different amounts of iron were determined as per recommended procedure. The results summarized in table 4.7 show that there is an excellent agreement in the experimental values.

Table 4.7: Precison and accuracy of the method.

Iron(III), ppm	Mean absorbance of five observations	Standard deviation	Coefficient of variation, %
2.0	0.052	0.0015	2.88
6.0	0.155	0.0029	1.90
10.0	0.258	0.0018	0.72
14.0	0.363	0.0018	0.51

4.3.10 Effect of Diverse Ions:

A number of foreign ions were carried through the recommended procedure and tested for interferences. The tolerance limit was set at the amount required to cause ± 2.0% deviation in absorbance.

It is evident that Al(III), Au(III), Pd(II), thiosulphate, thiourea, $EDTA^{-4}$, thiocyanate and borate ions interfere seriously. The ions showing interference can be tolerated in presence of appropriate masking agents. Tolerance limits of Mg(II), Y(III), urea and acetate ions are 300.0, 420.0, 800.0 and 980.0 ppm respectively (Table 4.8).

Table 4.8: Effect of diverse ions
[Fe(III)]=5.0 ppm, [ATG] = 1.6×10^{-3} M

Foreign ions	Added as	Tolerance limit, ppm
Cations:		
Al(III)	$AlCl_3.6H_2O$	None
Pb(II)	$Pb(NO_3)_2$	35.0
Cu(II)	$CuSO_4.5H_2O$	18.0
Ba(II)	$BaCl_2.2H_2O$	110.0
Zn(II)	$ZnSO_4.7H_2O$	15.0
Mg(II)	$MgSO_4.7H_2O$	300.0
Cd(II)	$CdSO_4.8/_3 H_2O$	240.0

Foreign ions	Added as	Tolerance limit, ppm
Tl(I)	$Tl(NO_3)$	280.0
Y (III)	$Y(NO_3)_3.6H_2O$	420.0
Be(II)	$BeSO_4.4H_2O$	16.0
Sn(II)	$SnCl_2.2H_2O$	25.0
Bi(III)	$Bi(NO_3)_3.5H_2O$	12.0
Au(III)	$AuCl_3$	None
Mo(VI)	$(NH_4)_2MoO_4$	6.0
Pd(II)	$PdCl_2$	None
Pt(IV)	H_2PtCl_6	45.0
Anions:		
Thiosulphate	Sodium thiosulphate	None
Citrate	Citric Acid	75.0
Thiourea	Thiourea	None
Tartrate	Tartaric acid	100.0
$EDTA^{-4}$	Disodium salt	None
Acetate	Sodium acetate	980.0
Thiocyanate	Potassium thiocyanate	None
Phosphate	Sodium phosphate	25.0
Oxalate	Potassium oxalate	5.0
Urea	Urea	800.0
Bromate	Potassium bromate	96.0
Persulphate	Potassium persulphate	5.0
Borate	Boric acid	None

4.4 APPLICATION

Determination of Iron in Ore:

About 0.4 g of ore sample was weighed accurately and dissolved in a mixture of 15.0 ml concentrated hydrochloric acid and 10.0 ml nitric acid. The solution was heated till all the nitrous fumes were removed. Sulphuric acid(1:1), 20.0 ml was added and the solution was evaporated almost to dryness. Distilled water, 50.0 ml was added and the residue was digested till all the salts were dissolved. It was cooled and filtered through a filter paper. The working solution, 20 µg of iron was prepared by appropriate dilution of this solution. A suitable aliquot, 1.0 ml of this solution was taken and the procedure was followed. The experiments were performed with 5 different portions of solutions and the results were compared with a standard o-phenanthroline method[59].

The percentage of iron was found to be 13.53 which is in good agreement with a standard o-phenanthroline method.

Table 4.9: Determination of iron in ore.

Ore	Certified value of Fe, %	Experimental value of Fe, %	Relative standard deviation for five observations
Iron	13.60	13.53	0.04

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