CHAPTER - IV

DETERMINATION OF IRON

4.1 INTRODUCTION :

Iron is a key element in industrial civilization and plays an important role in science, health science, technology and metallurgy. The analytical chemists are concerned with iron in the samples ranging from food materials, medicinal preparation, blood and other body fluids, ores and minerals, metals and alloys etc. Several techniques were applied for the determination of very low to high percentage of iron. Although several reagents such as ammonium sulphocynide, 2,2'-bipyridine[1] and 1,10-phenanthroline[2] are known as colorimetric reagents, the search for new reagents continues. 2-Benzoyl pyridine guanylhydrazone has distinct advantage over the previous methods. The present section deals with application of BPG for estimation of iron and analysis of fesovit syrup.

For the determination of tracer quantities of iron, numerous colorimetric reagents are reported. Phenolic compounds give purple or violet colour complexes with iron(III). 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], pyridil-β- 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-β-resorcylic acid[20] and 8-hydroxy -7-nitrosoquinoline-5-sulphonic acid[21] are only stable for 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 methods is very low in case of o-hydroxy acetophenone oxime[25] and chromotrope 2R.[27]

Recently for trace determination of iron, some thiosemicarbazones[28-35] are reported. But most of them are affected by some drawbacks. The proposed reagent, BPG, forms complexes instantaneously and the method has the desired sensitivity for colorimetric determination of iron in μg level.

4.2 EXPERIMENTAL :

4.2.1 Standard solutions :

Standard iron (II) solution :

Stock solution of Fe(II) was prepared by dissolving A.R. grade ammonium ferrous sulphate hexahydrate in distilled water followed by 2-3 drops of concentrated sulphuric acid and was standardised volumetrically[36] by using literature procedure.

The reagent forms colour only with Fe(II) ion and not with Fe(III). Therefore this method is useful for the determination of Fe (II).

Reagent solution :

0.6 mg/ml in ethanol (2.511 x 10^{-3}M).

Buffer solution :

1:1 ammonia solution of pH 10.0 was used.

4.2.2 Recommended procedure :

An aliquot of the solution containing about 2.5 µg of iron (II) was taken in a 10 ml volumetric flask. Then 1 ml of 0.6% (2.511 x 10^{-3}M) reagent (BPG) solution was added which provides desired excess quantity to complete the complex formation. By adding 1 ml of 1:1 ammonia solution, the pH was adjusted to 10.0; and the solution was diluted upto the mark with distilled ethanol. The absorbance was measured at 415 nm against corresponding 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 spectrum of Iron (II)- BPG complex of the solution containing 4.476 x 10^{-5}M iron and excess of the reagent (2.570 x 10^{-3}M) was recorded at pH 10.0 against reagent blank. The complex shows absorption maximum at 415 nm. The molar extinction coefficient at 415 nm is 1.1610 x 10^{4} 1 $mole^{-1}cm^{-1}$. The reagent does not absorb in this region. Absorption spectra of the complex and reagent are shown in figure 4.1. The observations for the spectra are given in table 4.1.

4.3.2 Effect of pH :

To study the effect of pH of the solution on the absorbance of the complex, a series of solutions containing 4.476 x 10^{-5}M Fe(II) and 2.510 x 10^{-3}M reagent (BPG) was prepared as per the recommended procedure over a range of pH from 2 to 13. The absorbances were measured against corresponding reagent blank. It was found that the complex has maximum and constant absorabance over the pH range 10 to 13. Therefore pH 10.0 was selected as the optimum pH and further addition of 1:1 ammonia solution was preferred for further study. The plot of observations is shown in figure 4.2.

Table 4.1 : Molar extinction coefficients of the Fe(II)-BPG complex and the reagent (BPG).

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Fe(II)-BPG complex $\epsilon \times 10^4$ l mole^{-1}cm^{-1}	BPG $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
360	0.641	0.2948
370	0.719	0.1115
380	0.821	0.0509
385	0.915	0.0422
390	0.994	0.0387
395	1.083	0.0341
400	1.117	0.0298
405	1.150	0.0199
410	1.158	0.0174
415	1.161	0.0124
420	1.155	0.0049
425	1.117	0.0040
430	1.072	0.0030
440	0.016	0.0010
450	0.916	0.0000
460	0.838	-
470	0.770	-
480	0.648	-
490	0.491	-
500	0.335	-
510	0.245	-
520	0.156	-
530	0.125	-
540	0.103	-

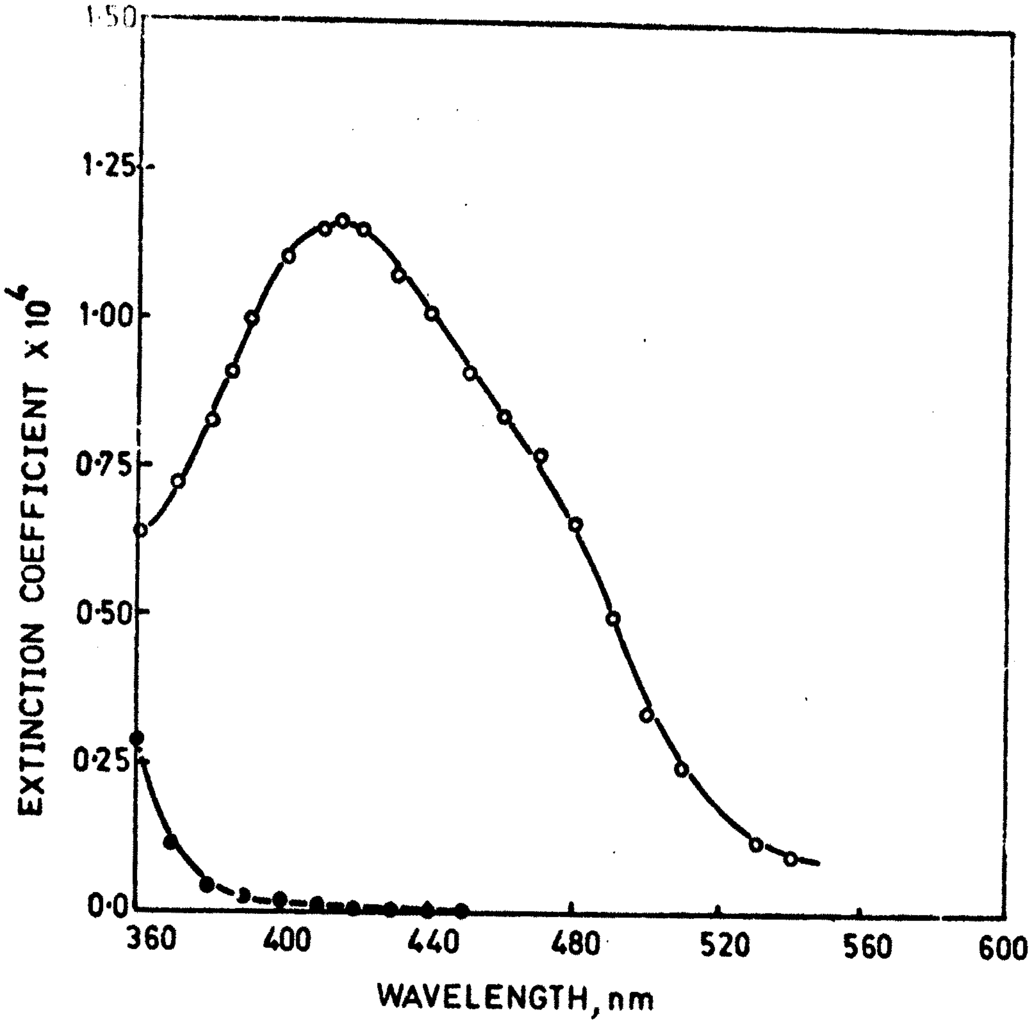

FIG. 4·1 o—o ABSORPTION SPECTRUM OF IRON-BPG COMPLEX
●—● ABSORPTION SPECTRUM OF REAGENT (BPG)

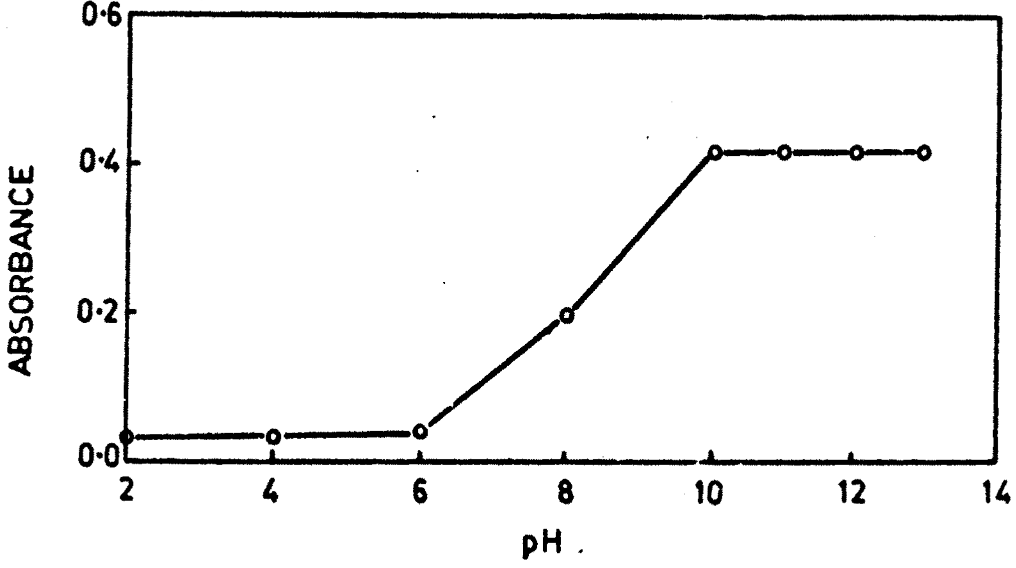

FIG. 4·2 EFFECT OF pH

4.3.3 Effect of reagent concentration :

A series of solutions containing same amount of iron (4.476×10^{-5}M) and different amounts of reagent (5.02×10^{-5}M to 3.514×10^{-4}M) were prepared at pH 10.0. The complex was developed as per the recommended procedure. Results in the table 4.2 show that six-fold molar excess of the reagent is sufficient for full colour development.

Table 4.2 Effect of reagent concentration

$[\text{Fe(II)}] = 2.5$ ppm; $[\text{BPG}] = 2.511 \times 10^{-3}$M

ml, of reagent	Absorbance at 413 nm
0.2	0.25
0.4	0.35
0.6	0.40
0.8	0.46
1.0	0.49
1.2	0.49
1.4	0.49

4.3.4 Reaction rate and stability :

The complex formation is instantaneous and colour of the complex is stable for several hours.

4.3.5 Validity of Beer's law :

For the study of validity of Beer's law, the solutions containing different amounts of iron and same amount of reagent (BPG) 0.6 ml (1.506×10^{-4}M) were taken. The absorbance measurements were recorded at 415 nm against, corresponding reagent blank. It was found that Beer's law is valid upto 12 ppm (Fig.4.3). The Ringbom plot[37] indicated that optimum concentration range is 1.12 to 1.37 ppm of Fe (II) at 415 nm (Fig.4.4).

4.3.6 Composition of the complex :

The composition of the complex Fe(II)- BPG was determined by Job's continuous variation method[38], mole ratio method[39] and slope ratio method[40]. The complexes were developed as per the recommended procedure and absorbances were measured. The plot of absorbances against the mole fraction of the reagent indicated the existence of 1:2 complex with respect to metal and ligand (Fig.4.5). For mole ratio method, solutions containing same final concentration of reagent (4.476×10^{-5}M)

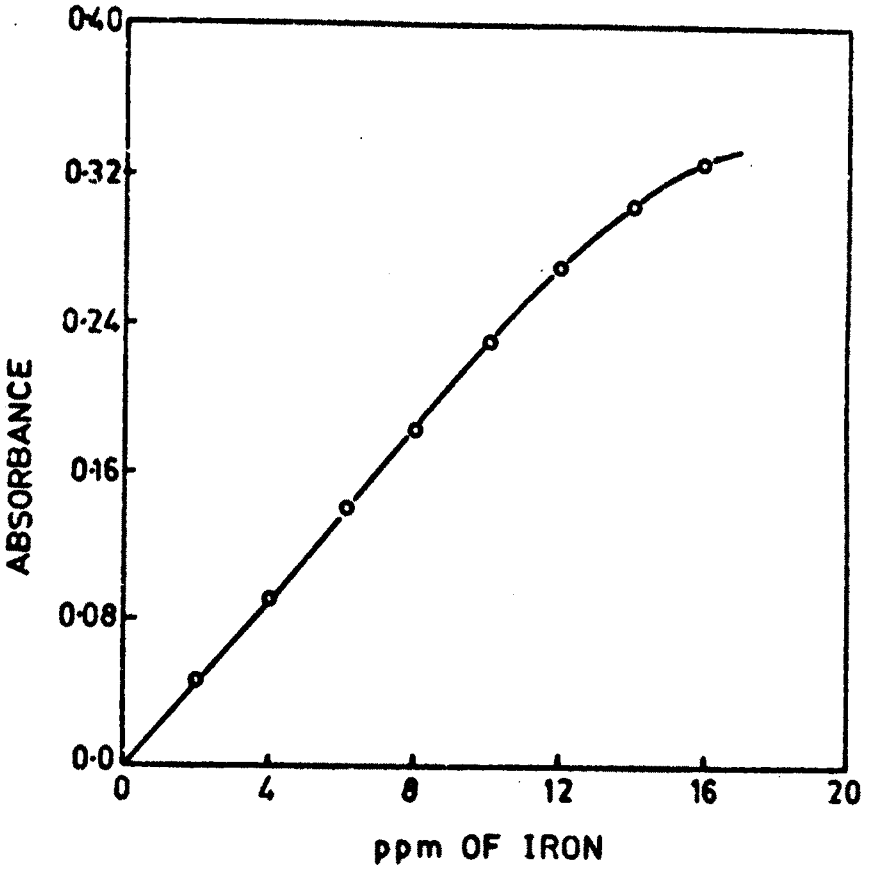

FIG. 4·3 VALIDITY OF BEER'S LAW

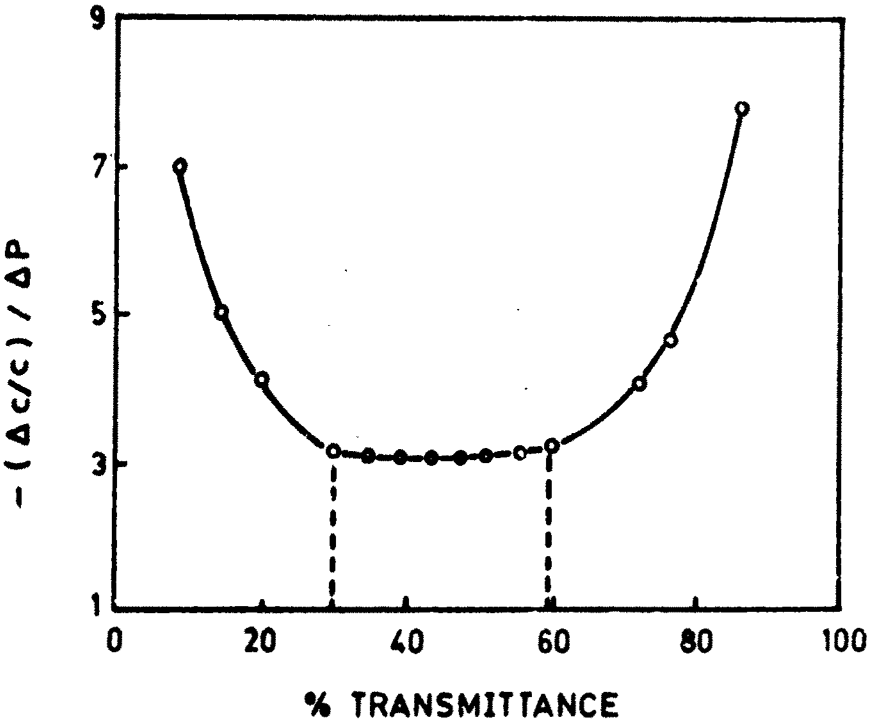

FIG. 4·4 RINGBOM PLOT

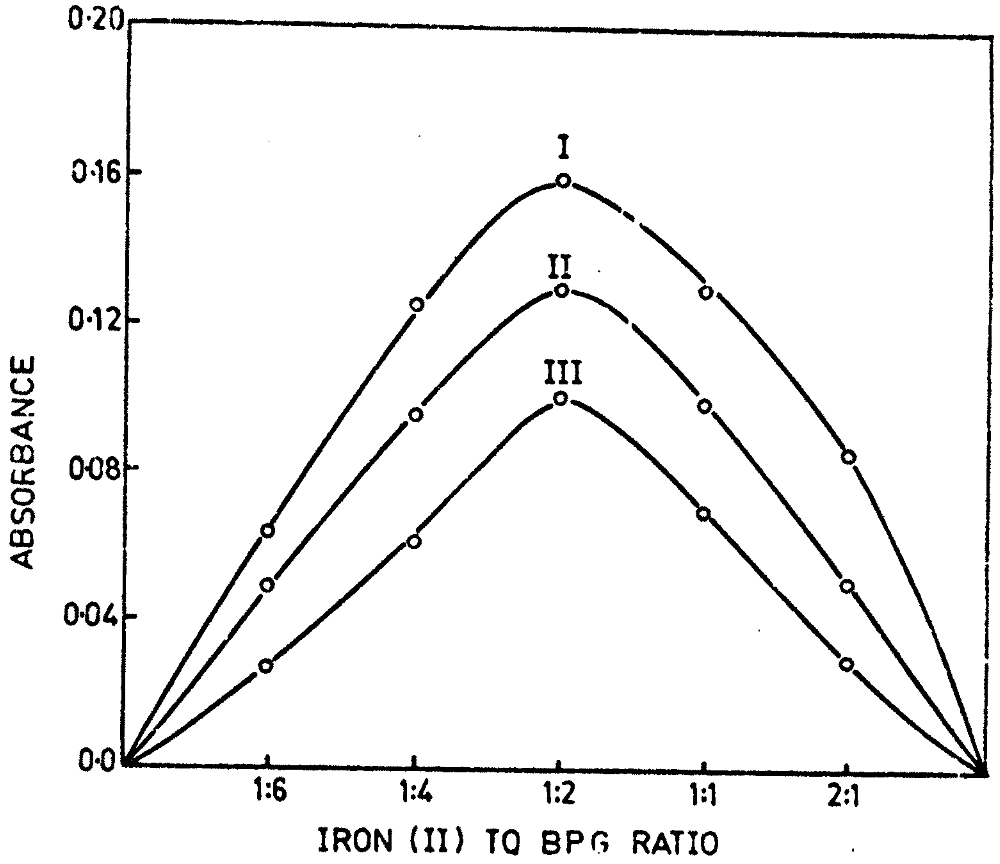

FIG.4·5 JOB'S CONTINUOUS VARIATION METHOD.
I – 413 nm, II – 440 nm, III – 470 nm.

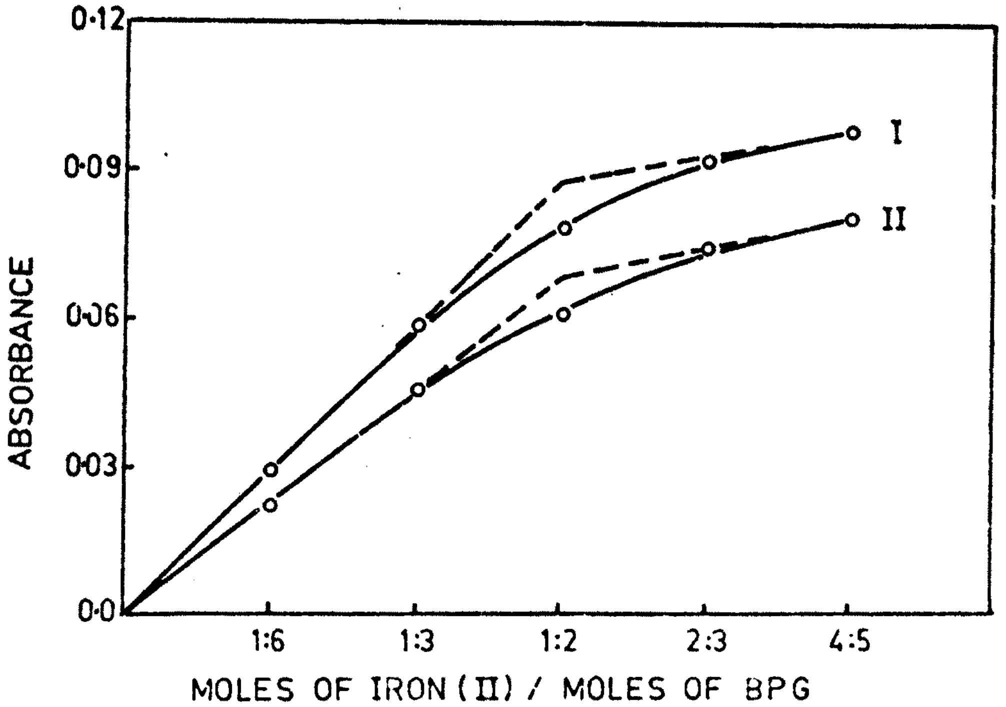

FIG.4·6 MOLE RATIO METHOD.
I – 413 nm, II – 440 nm.

and varying amounts of iron ranging from 0.4476×10^{-5} M to 3.580×10^{-5} M were prepared and absorbances of solutions were measured. The plot of absorbance against metal to reagent ratio shows formation of 1:2 complex which confirms the results of Job's method (Fig.4.5). Slope ratio method also confirms the 1:2 complex of Fe(II)- BPG.

4.3.7 Sensitivity of the method :

The photometric sensitivity of the method was calculated by Sandell's method[41] and was found to be 0.04578 $\mu g/cm^2$ at 415 nm.

4.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.[40] The value of α, degree of dissociation was found to be 0.1017.

The apparent instability constant[42] was found to be 9.376×10^{-12} for Fe(II)-BPG complex. The change in free energy[43] of the system is - 15.13 K cal/mole.

4.3.9 Precision and accuracy of the method :

In order to test the accuracy and precision of the method, different amounts of iron were determined in 10 identical samples. The results in table 4.3 show that there is good agreement in the experimental values. The coefficient of variation and standard deviations of methods are also given in table 4.3.

Table 4.3 : Reproducibility of the method :

Iron(II) ppm	Mean of 10 observations	Standard deviation	Coefficient of variation, %
2	0.044	0.001	2.27
4	0.092	0.002	2.17
6	0.136	0.003	2.20

4.3.10 Effect of diverse ions :

The effect of diverse ions was studied by using 2.5 ppm of iron and 1.0 ml of 2.008×10^{-4}M reagent. The complexes were developed as per the recommended procedure and the absorbances were measured. The results indicate that V(V), Cu(II), Cr(VI) and Fe(III) interfere seriously. While the tolerance limit of Ca(II) is 60 ppm. For various foreign ions, the tolerance limits are given in table 4.4.

Table 4.4 : Effect of diverse ions :

$[\mathrm{Fe(II)}] = 2.5$ ppm

$[\mathrm{BPG}] = 2.008 \times 10^{-4}$ M

Foreign ions	Added as	Tolerance limit, ppm
Cations		
Mn(II)	$MnCl_2 \cdot 4H_2O$	2
Ce(IV)	$Ce(SO_4)_2$	10
U(VI)	$UO_2(NO_3)_2$	10
Pb(II)	$Pb(NO_3)_2$	6
V(V)	V_2O_5	none
Zn(II)	$ZnSO_4 \cdot 7H_2O$	10
Cu(II)	$CuSO_4 \cdot 5H_2O$	none
Hg(II)	$HgCl_2$	2
Cr(VI)	K_2CrO_4	none
Al(III)	$AlCl_3 \cdot 6H_2O$	1
Fe(III)	$FeCl_3$	none
Ba(II)	$BaCl_2 \cdot 2H_2O$	3
Tl(I)	$TlCl$	4
W(VI)	$Na_2WO_4 \cdot 2H_2O$	40
Ni(II)	$NiSO_4 \cdot 6H_2O$	2
Bi(III)	$Bi(NO_3)_3$	10
Ca(II)	$CaCl_2$	60
Co(II)	$CoSO_4 \cdot 7H_2O$	1
Ag(I)	$AgNO_3$	4
Anions :		
Thiourea	Thiourea	30
Fluoride	Ammonium fluoride	2
Citrate	Sodium citrate	10

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Foreign ions	Added as	Tolerance limit, ppm
<u>Anions</u> :		
Oxalate	Potassium Oxalate	10
EDTA^{-4}	Disodium salt	6
Acetate	Sodium acetate	20
Tartrate	Antimony potassium tartrate	10
Phosphate	Potassium hydrogen orthophosphate	1
Thiocyanate	Potassium thiocyanate	20

4.4 APPLICATIONS :

Analysis of Fesovit syrup :

0.1 ml of commercially available fesovit 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.

0.5 ml of above diluted solution was taken in a 10 ml volumetric flask. To this 0.5 ml reagent solution (2.008 x 10^{-4}M) was added and pH was adjusted to 10 with 1:1 ammonia. It was then diluted upto the mark with distilled ethanol, and absorbance was measured at 415 nm against reagent blank.

Results are given in table 4.5.

Table 4.5 : *Analysis of Fesovit syrup* :

Syrup	Certified value of Fe, %	Experimental value of Fe, %	Relative standard deviation for 10 observations.
Fesovit	1.226	1.218	0.07

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