CHAPTER - III

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SPECTROPHOTOMETRIC DETERMINATION OF IRON (III)

WITH 3,5-DICHLORO SAT.

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INTRODUCTION

The element iron is known from ancient times. Due to its abundance in nature, it ranks forth most element in the earth's crust. To a very small extent iron occurs in metallic state which is meteoric in origin. It is malleable, ductile, tough, silvery gray, and magnetic metal. Iron is the important constituent of red haemoglobin of blood. It is perhaps the most useful of all the metals. The iron piller at Kutubminar near Delhi was erected at the beginning of the christian era. Nowa-days iron is used on large scale in the manufacture of structural steel, magnets and dyes (e.g. inks, blue print paper and rough pigments). The variety of iron alloys are known and widely used. Many of the iron alloys have valuable properties and have industrial uses. The iron alloys find applications as magnetic alloy electrical and heat and corrosion resistance alloys and thermal expansion alloys etc.

The element iron is the 6th element of the first transition series. It belongs to VIII group of the periodic table. It occurs in two states as ferrous and ferric iron respectively.

Numerous reagents were reported in the literature for the determination of iron but few of them are well suited for the determination of traces of iron. Some reagents react with ferric iron and other with ferrous iron. Among those reagents which have been reported, the thiocyanate method is the most frequently employed reagent for the spectrophotometric determination of small amounts of iron.

But in this method the intensity of the colour in the iron thiocyanate solution depends upon various factors such as excess of thiocyanate, a kind of acid used and standing time. The spectrophotometric studies of iron with the reagent 1,10 phenanthroline $^{2-3}$, and its derivativies $^{4-7}$, have been also reported. However, the method is less sensitive and metal ions like W, Ni, Co, Cu, etc. show strong interference during the determination of iron.

Among the various reagents that have been proposed for the photometric determination of iron, the most recent are some derivatives of phenols and napthols⁸, azoderivative of antipyrine⁹, 2,6 pyridine diol¹⁰, disodium 3-(2-pyridy1)-1,2,4-triazine-5,6-di(4'-pheny1)sulphonate¹¹), 2,4,,6-tri(2'-pyridy1)-1,3,5 triazine¹², Cacotheline¹³, which is the nitrate derivative of bisdimethyl mono nitrobrucine hydrate. Besides these reagents, some of the promising analytical reagents investigated include 2-furylmethanethiol, 3-(2-fury1)-2-

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mercapto propenoic acid and 3,4,5.6-tetrahydro-2mercaptopyrimidine¹⁴, hydrazinium hydrazine carbodithioate¹⁵ di-2-pyridyl ketone thiosemicarbazone¹⁶, 2-amino-5-nitro sopyrimidine 4,6-diol¹⁷, 4-phenyl-3-TSC of biacetyl monoxime¹⁸.

However these methods suffer from many disadvantages, eg. with 2,6-pyridine diol, heating for 30 min is required and the complex dissociates within 20 min while in case of 2,4,6-tri(2'-pyridyl)-1,3,5triazine, the violet complex of iron is stable only for 1 hour. Besides many metal ions associated with iron interference seriously in the determination of iron.

Many reagents have been reported for photometric determination of iron in the literature. Some of those include Oximes :2-hydroxy-4 ethoxy acetophenone oxime¹⁹, 2-hydroxy-1-napthaldoxime²⁰, and 2,6-diacetyl pyride dioxime²¹ Organic acids : thioglycolic acid²², tannic acid²³, pyrazine-2,3, di-carboxylic acid²⁴. 1-(2-carboxy -5-sulphanatophenyl)-3-hydroxy-3-phenyltriazen [2-(3-hydroxy-3-phenyltriazen)-4-sulphobenzoic acid]²⁵, N-m-sulphophenyl benzo hydroxamic acid²⁶; Ketones : For example thenoyltrifluoroacetone²⁷, 2,2'-dipyridyl-ketone amino ethylimine²⁸, naphthoxyacetyl-acetophenone²⁹; Thiosemicarbazones : di-2-pyridyl ketone thiosemicarbazone³⁰, 4-phenyl-3-thiosemi-carbazone¹⁸, 3-methoxy TSC³¹, picolinaldehyde 4-phenyl 3-thiosemicarbazone³². Coumarines : 6,7-dihydroxy-4-methylcoumarin³³; Substituted pyrimidines : 2-furylmethanethiol, 3-(2-furyl)-2mercaptopropenoic acid and 3,4,5,6-tetrahydro-2mercaptopyrimidine¹⁴, 4-amino-5-nitroso-pyrimidine-2, 6diol³⁴, 1,2,3,4-tetrahydro-6-hydroxy-5-nitroso-pyrimidine -2,5-dione³⁵;

Substituted phenols : 4-(4,5-dimethyl-2-thiazolylazo)-2-methyl-resorcinol³⁶, <math>4-(4-methyl-2-thiazolylazo resorcinol³⁷, Hydrazones : 2,2'-dipyridyl-2-benzo thioazolyl hydrazone³⁸, 2-2'-dipyridyl [di-(2-pyridyl) Ketone]. 2-Pyridylhydrazone³⁹, These methods however, suffer from either low sensitivity or interference of many metal ions associated with iron e.g. in the photometric determination of iron. Cu and Zr(IV) interfere by forming precipitate with the reagent 2-hydroxy-1-naphth-aldoxime or low stability of the complex.

However, the proposed method for determination of iron is free from disadvantages mentioned above. The proposed reagents 3,5-dichloro SAT reacts with iron in alkaline medium, to form green coloured complex which is stable for more than 4 days. The complex is measured at 590nm, against water as a blank. Thus the present method, besides being, highly sensitive, is very simple to carry out as no extraction and no multiplicity of solvents are required. A summary of the some selected reagents used for the spectrophotometric determination of the iron is presented in Table No. 1, describing the optimum conditions for the method, spectral properties of the complex, interferences due to the foreign ions alongwith the remarks.

TABLE NO. 1 :- SUMMARY OF THE REAGENTS REPORTED FOR Fe(III).

Reagent	Conditions	λmax, Beer's range, Molar extinction coefficient	Interferen- ce	Remarks	Ref No.
1	2	3	4	5	6
1,10-Phenanth- roline	HCl + KSCN	λ max=525nm upto 3 ppm $\epsilon = 20500$	Co Ni Cull V W Co EDTA		2
	pH=3.5 to 6	$\lambda \max = 510 \text{ nm}$ upto 3 ppm $\varepsilon = 16750$ S = 3.3ng/cm ²	cu , w		3
4,7-bis(4'-ph- enylazoanilno) 1,10-phenanthr- oline	pH=5.7 - 7	λmax=520nm 0.1 - 1ppm € = 44000		150 fold molar excess R is required	7
5-dimethylamino -2-nitrosophen- ol	рН=7 - 9.5	λmax=750nm	Ni ^{II} , Cu ^{II} EDTA	Determination in microamts in river and city water.	8
2,6-pyridine diol	pH=7 - 10.2	λmax=420nm upto 4.8 € = 10800		1:2 Complex R blank is needed Heating for 30 min.	10
Disodium 3-(2- pyridyl)-1,2,4- triazine-5,6-di (4'-phenylsulp- honate)		upto 1.6	Serious in- terference₀f Cu(II)	Determination in nonferrous metals and alloys. Redu- ctants and masking agent must be used.	11
2,4,6-tri(2'- pyridyl)-1,3,5- triazine	pH=2 - 2.5	λmax=595nm C = 21500		Complex stable for 1 hr.	12

1	2	3	4	5	6
Cacotheline roline	100-500 ug Fe+5ml H ₃ PO + 0.5ml aq. R	λmax=530nm upto 50ppm S = 0.05µg/cm ²			13
Hydrazinium hydrazine carbodithioate	рН= 4 - 6	λmax=570nm upto 300 μg € = 2800		Ten fold molar excess R is required 2:1 Complex	15
Di-2-pyridylke- tone thiosemic- arbazone	pH=2.5-7.5	λmax=620nm upto 4 ppm € = 9300			16
2-amino-5-nitr- osopyrimidine- 4,6-diol	pH = 5.0	λmax=640nm upto 207µg/ml	Oxalate, EDTA, Citr- ate, Cu, V, Fe' BO3 & Co		17
2-hydroxy-4- ethoxy acetophenone oxime		λmax=525mm			19
2-hydroxy-1- naphthaldoxime	pH=2.3-2.7	$\lambda \max = 450 \text{ nm}$ upto 24 $\varepsilon = 200$ S=27.9ng/cm ²	Cu(II) and Zr(IV)	1:1 Complex stable for six hrs. R blank in needed	20
2,6-diacetyl pyride dioxime	pH = 12.5	E = 11600			21
Thioglycolic acid		λmax=530nm € = 3900 S=0.014µg/ml		Fe determined in limestone, silicates portland cement	22

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1	2	3	4	5	6
Tannic acid	pH=4.1-4.4	λmax=550nm		Fe determined in microamts.	23
Pyrazine-2,3-di carboxylic acid	рН= 5.5	λmax=475nm upto 22 ppm	Cu(II), Cd, Co, Cr(III) Al		24
N-m-sulphophen- yl benzo hydro- xamic acid	pH=2.7-4.1	λmax=475nm upto 13ppm	Tartrate Citrate Oxalate V W , V , F and PO		26
Theno yltriflu- oroacetone	рН = 4.0	λmax=480nm upto 13 ppm			27
2-2'-dipyridyl- kethone amino ethylimine	pH=7.1-10.1	λmax=608mm upto 50μg € = 17100	Cr(III), Cu Co, Cyanide & sulphide	1:2 Complex	28
Naphthoxyacetyl _acetophenone	pH = 5.5	λmax=390nm upto 8 μg S = 0.008μg/cm	EDTA	Method satis- factorily used to dete- rmine Fe in drug and ore	29
3-methoxy sali- cylaldehyde thiosemicarbaz- one	pH=5.8-7.0	λmax=590nm € = 5060	Cu, Co, Cr Ag		31
Picolinaldehyde 4-phenyl 3-thio semicarbazone		λmax=390nm upto 8 ppm € = 35600			32

1	2	3	4	5	6
6,7-dihydroxy-4 -methylcoumarin	pH = 3.5 pH = 10	$\lambda max=375nm$ $\lambda max=440nm$ $S = 2-5ng/cm^2$		Green Complex Red Complex	33
Bromopyrogallol red-benzyldime- thyl tetradecy- lammonium chloride	pH=3.0-4.5	λmax=660nm € = 55000		R is Partially sensitive	40

EXPERIMENTAL

Preparation of Standard Iron Solution :-

A standard stock solution of iron(III) (1mg/ml)was prepared by dissolving 1.206 gm of ferric chloride (FeCl₃6H₂O AR) in dilute hydrochloric acid. The solution was diluted to 250ml in volumetric flask with double distilled water. The solution was standardised by the method which is described in Vogel . A 25 ml of the stock solution of iron is pipetted in a 250ml conical flask and is made 5-6N with respect to HCl. The solution is heated to 70 to 91 C. It is then reduced by adding concentrated stannous chloride solution dropwise from a burette, with stirring, until the yellow colour of the solution has disappeared. The solution is then rapidly cooled under the tap water to about 25 C. The slight excess of stannous chloride present is removed by adding 10ml of 5% solution of mercuric chloride with thorough mixing. A slight silky white precipitate of mercurous chloride should be obtained. When too much stannous chloride has been used then a heavy precipitate forms or gray or black precipate is obtained. In this case the solution is discarded. The solution is diluted to 200ml with 2.5% sulphuric acid, then 10ml of 85% phosphoric acid is added. This whole solution is titrated against 0.025 N potassium dichromate using 8 drops of sodium diphenylamine sulfonate indicator. The end point is colourless to purple violet. The determination is

repeated with two other similar quantities of the stock solution. The stock solution was found to contain 0.672mg of iron per ml. The working solutions of lower concentration were prepared by diluting the stock solution with distilled water as required.

Reagent Solution :-

A 0.2% solution of reagent was prepared by dissolving 0.2gm 3,5-dichloro SAT in 100ml of hot ethyl alcohol (double distilled). The reagent solution is colourless. The solution is quite stable towards light, heat and can be kept over a week period.

The solutions of diverse ions used in the study were prepared by dissolving AR grade reagents in distilled water or dilute hydrochloric acid. The chemicals used to prepare buffer solution were also of AR grade.

Buffer Solution :-

A buffer solution of pH 10 was prepared by dissolving 17.5gm ammonium chloride(AR) in 142 ml concentrated ammonia solution (sp.gr. 0.88-0.90). The solution was then diluted to 250ml with deionised water. This solution was prepared daily.

Apparatus :-

For all the absorbance measurements a Carl-Zeiss

(JENA) spectrophotometer (spekol) equipped with 1cm quartz cells was used. ELICO pH meter, Model L1-120 equipped with glass electrode was used for pH measurements.

Recommended Procedure :-

To a solution containing upto 20.1 ppm of Fe(III), 5ml of 0.2% reagent solution in ethanol was added. The solution was mixed and 5ml of pH 10 buffer solution was added. Again the solution was shaken and diluted to 25ml in a volumetric flask with distilled water. The absorption measurements of green complex of Fe(III) with the reagent 3,5-dichloro SAT were made at 590nm against water as a blank.

RESULTS AND DISCUSSION

Spectral Characteristics :-

The absorption spectrum of Fe(III) -3,5-dichloro SAT complex using 10 ppm of iron (III) solution and 0.2% reagent in ethanol is shown in Fig.1. The solution of 3,5-dichloro SAT in ethanol is colourless and does not absorb significantly in the visible region. Therefore for all the absorption measurements water is used as a blank. The absorption measurements were made in the region 400-600nm. The Fe(III) 3,5-dichloro SAT complex exhibits the absorption maxima at 590nm. The molar extinction coefficient as determined from Beer's law



FIG.1 - ABSORBANCE SPECTRUM OF Fe(III) -

-3,5 - DICHLORO SAT COMPLEX .

Fe(III) = 10 ppm.

plot is 2.680 x 10^3 L mole⁻¹cm⁻¹ and the Sandell's sensitivity was 21ng/cm² at 590nm.

Effect of pH :-

The effect of pH on the absorbance spectrum of the iron complex was studied by varying the pH of the solutions from 1 to 12. For this, a series of solutions containing 6.72 ppm of iron and 5ml of 0.2% reagent were prepared. The pH of the each solution was adjusted in the range varying from 1-12 using 0.1N HCl and 0.1N NaOH Then the solution was made to 25ml with distilled water in a volumetric flask. The absorbance of the Fe(III)-3,5-dichloro SAT complex was measured at 590nm using water as a blank. The plot of the absorbance versus pH value shows that the complex exhibits maximum and constant absorbance in the pH range 8 - 10 (Fig.2). If pH > 10 decreases in abrosbance occurs and at pH =/< 7, the turbidity was formed and the absorbance could not be measured. Thus for all subsequent measurements, the pH of the solution was maintained at 10.

Effects of Reagent Concentration :-

In order to obtain the optimum amount of reagent required for the complexation of Fe(III)-3,5-dichloro SAT complex, the solutions containing fixed amount of Fe(III) and different amounts of the reagent (0.2%) varying from 1 to 10 ml were prepared. The colour of the



complex was developed as outlined in the recommended procedure and the absorbance of the each solution was measured at 590nm against water as a blank. The plot of the absorbance versus reagent in ml indicates that for 6.72 ppm of Fe(III), 3ml of 0.2% reagent was required for full colour development. This corresponds to 7 fold, molar excess of the reagent relative to iron. The results are shown in Fig.3. There is no significant effect of higher reagent concentration on the absorption spectrum of the Fe(III)-3,5-dichloro SAT complex and the complex was stable for more than 96 hours. For all subsequent measurements 3ml of the reagent solution was used.

Validity of Beer's Law :-

For the study of the validity of Beer's law, the solutions containing different amounts of iron upto 20.1ppm and the fixed amount of reagent (0.2%) were used. The colour of the complex was developed by following the recommended procedure. The absorption measurement of each solutions was made at 590nm against water as a blank. The absorbance of the green complex of iron was plotted versus ppm of iron taken. (Fig 4). From Fig 4 it was found that the Beer's Law is valid upto 20.1 ppm of iron.

Composition of the Complex :-

The metal to reagent ratio in the Fe(III)-3,5-



dichloro SAT complex was determined by using Job's method of continuous variation and mole ratio method. An equimolar solutions of metal and reagent (1.785 x 10^{-3} M) were used for Job's method and mole ratio method. The solutions containing different ratios of metal and reagent were prepared. To each solution 5ml of buffer solution of pH 10 was added and then the volume was made upto 25ml with distilled water. The absorbance of each solution was measured at 590nm against water as a blank. The results are shown in Fig. 5) which indicates that the iron(III) forms 1:3 complex with the reagent 3,5-dichloro SAT.

The results obtained by using the Job's method were confirmed by the mole ratio method. For mole ratio method a series of solutions containing fixed amount of iron and different amounts of reagent $(1.785 \times 10^{-3} \text{M})$ were prepared. Then 5ml of buffer solution of pH 10 was added and the volume of a each solution was made upto 25ml with distilled water in a volumetric flask. The absorbance of the solutions were measured at 590nm against water as a blank. The plot of the absorbance versus the reagent to metal ratio (Fig. 6) confirms the results obtained by application of Job's method.

Effect of Diverse Ions :-

The effect of diverse ions on the determination of 0.168 mg of Fe(III) with the reagent 3,5-dichloro SAT

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was investigated by following the recommended procedure. Initially foreign ion was added to the iron(III) solution in large excess 100 fold for cations and 500 fold for anions. The tests were repeated with successively smaller amount of foreign ion when the interference of ion was intensive. An error of less than 2% in the absorbance of the complex at 590nm was considered to be tolerable. In Table No. 2 the tolerance limits of various ions has been shown. These results show that relatively large amount of anions except EDTA, nitrite, citrate and tartrate could be tolerated in the determination of 0.168 mg of Fe(III).

Reproducibility, Accuracy and Sensitivity Data :-

In order to study the reproducibility and accuracy the method, absorption measurements of with ten different identical solutions containing 8.4ppm iron were performed following the recommended procedure and concentrations of the solutions were determined using the calibration curve. The results are shown in Table No. 3. It is observed that there is an excellent agreement in the experimental values. The method has high precision and accuracy.

Average of these ten readings are calculated. From the average readings deviations was found out in each case and then standard deviation was calculated. From the standard deviation, the reproducibility of the

TABLE NO. 2 :- EFFECT OF DIVERSE IONS. -----Fe(III) = 0.168 mg, Buffer pH 10 = 5 ml.3,5-dichloro SAT = 0.2% in alcohol, $\lambda \max = 590$ nm. TOLERANCE LIMIT FOREIGN ION in mg 20 Mg(II) 5 Zn(II) 10 Sb(III) Mn(II) Interfere Al(III) Interfere Cr(VI) Interfere Interfere Cu(II) Interfere Co(II) 10 Cd(II) 15 As(III) Au(III) Interfere Interfere Ni(II) Pb(II) Interfere Interfere Bi(II) 8 Re Se 4 Ru Interfere Interfere Hg Interfere Zr Acetate 360 Oxalate 500 250 Ascorbate 500 Succinate Tartrate Interfere EDTA Interfere Citrate Interfere Nitrite Interfere Phosphate 250

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results with 95% confidence limit was calculated. The Sandell's sensitivity of the reagent was 21ng/cm^2 which was calculated from Beer's law plot. The stability constant K of the complex as calculated from mole ratio plot⁴¹ was found to be 3.087 x 10⁻¹⁶.

TABLE NO. 3 :- PRECISION AND ACCURACY OF THE METHOD.

Sr. No.	Absorbance observed	ppm of Fe found;(x)	x - x	$(x - \overline{x})^2$
1	0.406	8.4	0.01	0.0001
2	0.406	8.4	0.01	0.0001
3	0.400	8.3	0.11	0.0121
4	0.410	8.5	0.09	0.0081
5	0.406	8.4	0.01	0.0001
6	0.410	8.5	0.09	0.0081
7	0.406	8.4	0.01	0.0001
8	0.410	8.5	0.09	0.0081
9	0.400	8.3	0.11	0.0121
10	0.406	8.4	0.01	0.0001
TOTAL		84.1		0.0490

Amount of Fe(III) = 8.4 ppm.

Average value
$$(\overline{x}) = \frac{84.1}{10}$$

Standard deviation (δ)

$$\delta = \sqrt{\frac{(x_1 - \overline{x})^2 + (x_2 - \overline{x})^2 \dots (x_n - \overline{x})^2}{(n-1)}}$$
$$= \sqrt{\frac{0.049}{10 - 1}}$$



Reproducibility with 95% confidence limit

$$= \overline{x} \pm 2.26 \ x - \frac{6}{\sqrt{n}}$$

$$= 8.41 \pm 2.26 \ x - \frac{0.07}{\sqrt{10}}$$

$$= 8.41 \pm 0.050$$
Error (E)
$$= 0bserved reading - Actual reading$$

$$= 8.41 - 8.4$$

$$= 0.01$$
Relative error
$$= 0.01 \ x \ 100$$

Relative error 0.01 x 100 = ------Percent(accuracy) 8.4 = 0.12

% coefficient of variation

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c.v. =
$$\frac{\delta \times 100}{\frac{1}{x}}$$

where δ - standard deviation.
=
$$\frac{0.07 \times 100}{8.41}$$

= 0.8

Molar Extinction coefficient

Absorbance --- x 1000 x Atomic Weight e ppm = slope x 1000 x Atomic Weight $= 0.048 \times 1000 \times 55.847$ $= 2680 \text{ L Mole}^{-1} \text{ cm}^{-1}$ = 2.680×10^3 L Mol⁻¹ cm⁻¹. Sandell's Sensitivity (S) = 10^3 x Atomic Weight x Cmin S Dmin where Cmin = -----€хb 0.001 $= 10^3 \times 55.847 \times ------0$ $2.680 \times 10^3 \times 1$ = 0.021 $\mu g/cm^2$ = 21 ng/cm^2 Stability constant K ≪ C (n≺C)³ К = C(1-≺) $0.0625 \times 8.889 \times 10^{-5} (3 \times 0.0625 \times 8.889 \times 10^{-5})^3$ ----P----- $8.889 \times 10^{-5} (1-0.0625)$ $0.0625 \times 8.889 \times 10^{-5} (4.6299 \times 10^{-15})$ $8.889 \times 10^{-5} (0.9375)$ 0.30869×10^{-15} = 3.0869×10^{-16} =

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