

Determination of Trace Amount of Iron (II) in the Presence of Iron (III) using Extraction Formation Method

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Summary: The suitability of 3-(2-Pyridyl)-5,6-(diphenyl)-1,2,4-triazine (PDT) as a reagent for determination of iron (II) in presence of iron (III) is evaluated. The studies were made of the tris (PDT)-iron (II) complex formed in strong acid solution and its extraction in chloroform and also in 1,1,1-trichloroethane. This serves as a useful method for the determination of microgram quantities of iron (II) in presence of iron (III).

Introduction

The precise determination of iron (II) in microgram quantities present in association with relatively large amount of iron (III) has practical importance not only in steel corrosion investigation but also in the treatment of waste-waters from mining and steel industry.

3-(2-pyridyl)-5,6-(diphenyl)-1,2,4 triazine (PDT) has been reported¹ as spectrophotometric reagent for the direct determination of total iron in strong acid solution without the necessity of neutralization and pH adjustment, using extraction formation method. So far no studies were made to determine iron (II) in presence of iron (III) in acidic media.

The present paper deals with finding a well characterized superior but cheap chromogenic reagent than batho² to extract iron (II) from relatively large amount of iron (III) in dilute acidic solution using suitable masking agents. The results of our studies of the extraction formation behaviour and its applications are discussed here.

Experimental

Apparatus and Reagents

All absorption spectra and absorbance measurements were recorded using SP-500 spectrophotometer and matching cells of 1.0 cm optical path.

For all pH measurements a Pye-unioam model 292 pH meter equipped with a glass calomel electrode was

used.

Separating funnels of squibb type made of boro silicate glass 250 ml capacity, preferably 3.0 cm of stem and less than 1.0 cm in outer diameter were used.

All chemicals unless otherwise stated were of Analar grade.

Standard iron (II) solution.

A stock solution containing 100 ug of iron (II) per ml was prepared by dissolving 0.3921 gram of ammonium iron (II) sulphate $\text{FeSO}_4(\text{NH}_4)_2 \cdot \text{SO}_4 \cdot 6\text{H}_2\text{O}$ (BDH) in 100 ml of concentrated sulfuric acid and diluted with water to 500 ml. Subsequently standard solutions containing 0.5 and 2.5 μg of iron (II) per ml were prepared by diluting 2.5 and 12.5 ml respectively of the stock solution to 500 ml with water acidified with 2.0 ml of concentrated sulfuric acid, cover of carbondioxide bubbling in it was maintained as described by Clark².

Sample solution.

Clark's method² was generally followed for the preparation of sample solution of iron containing material such as ores, alloys and chemical reagents.

Ammonium fluoride 2.0 M.

It was prepared by dissolving 18.5 grams of ammo-

nium fluoride in water, making the total volume upto 250 ml.

Ammonium thiocyanate 45%

45 gram of ammonium thiocyanate was dissolved in water and diluted to 100 ml.

PDT solution 0.1% (w/v).

A 0.1% solution of PDT (obtained from G.F. Smith Chemical Co., Columbus, Ohio) was prepared by dissolving weighed amount in 100 ml of chloroform or 1,1,1-trichloroethane.

Results and discussion

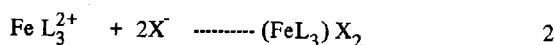
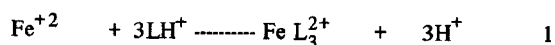
Tests were conducted under ordinary laboratory conditions. Prepared solutions were kept at room temperature. Clark's method² was followed to prevent air oxidation of iron (II).

Iron oxides dissolved more readily in hydrochloric acid than in sulfuric acid or in mixture of hydrochloric or sulfuric acid with phosphoric acid. At room temperature magnetite dissolved rapidly in concentrated hydrochloric acid, some synthetic ferrites and wastite required as long as 3 hours for complete dissolution. To check the effect of acid concentration on the preparation of sample solution, volumes varying from to 10 ml of concentrated hydrochloric acid were used for the preparation of sample solution containing 10 mg of mag-

netite. Highest iron (II) contents were found when the samples were dissolved in 4 or 5 ml of hydrochloric acid and diluted with water to 100 ml. The final solution prepared after dilution was approximately 0.5 to 0.6 N in hydrochloric acid, whereas these substances are partly soluble or soluble at a very slow rate in dilute hydrochloric acid at room temperature. However, their solubility increases on heating the samples in dilute hydrochloric acid but the resultant iron (II) content remains persistently low. The results obtained are consistent with the results reported earlier².

To examine the effect of air exposure, 10 mg of magnetite was dissolved in 4.0 ml of concentrated hydrochloric acid and allowed to stand for varying duration ranging from 5 minutes to 5 hours, before diluting with water. It was found that iron (II) contents decreased on standing in concentrated hydrochloric acid (Table 1).

Preliminary experiments revealed that chelation reactions with iron (II) are exceedingly unfavourable and incomplete in strongly acidic solutions with ferriox type of chromogens (eq-1). However, it has been reported^{1,3} that extraction with an appropriate immiscible solvent (eq-2) can provide the condition necessary for more complete over all formation of the complexes in certain cases. The use of chloroform, PDT and



thiocyanate or 1,1,1-trichloroethane, 3-(2-pyridyl)-5, 6-

Table 1. Iron (II) in Iron oxide materials after preparation in air and under the cover of Carbondioxide.

Iron oxide	Time of preparation (minute).	Content of iron (II), %		
		Prepared in Air 4ml. conc. HCl Room Temperature	Heated	Prepared in Co ₂ 10 ml (1:1 HCl) Heated
Magnetite*	0	11.23		11.85
	10	9.45	10.2	9.9
	60	3.8	5.3	4.6
	180	0.2		0.3

*Chagi area in Baluchistan.

(diphenyl)-1,2,4-triazine (PDT) and thiocyanate as solvent, complexing agent and counter ion respectively has been suggested^{1,3} as the only effective combination. Out of various extraction solvents (S), ligands (L) and counter ions (X) tested, it was found that 1,1,1-trichloroethane in addition to chloroform can be used as immiscible solvent in conjunction with PDT and thiocyanate for the complete extraction formation and determination of iron (II) present in association with iron (III). Other less effective ligands tested includes, 2,4,6-tripyridyl-1,3,5-triazine (TPTZ)^{4,5}, 2,4, bis (5,6-diphenyl-1,2,4-triazine-3yl)-pyridine⁶, 3-(4-phenyl-2-pyridyl) 5,6-diphenyl-1,2,4-triazine (PAT)^{7,8} and 3-(2-pyridyl) 5,6-diphenyl-1,2,4-triazine (unsulfonated ferrozine)⁷. Solvents tested were chloroform, 1,1,1-trichloroethane, isoamyl alcohol, nitro-benzene, methylene chloride, ethylene chloride, methyl isobutyl ketone and various combinations of these each other. None of the common anions [noticeably those which are large and symmetrical such as WO_4^{-2} , WO_4^{-1} , Hg I_4^{-2} , VO_4^{-2} , Mo O_4^{-2} , Pt Cl_4^{-1} , Hg Cl_4^{-2} and Bi Cl_4^{-1}] which takes part in ferrous reactions with 1,10-phenanthroline⁹ and results in the formation of salts which are insoluble or only slightly soluble in aqueous solutions, proved more effective than thiocyanate.

When tris (PDT)-iron (II) complex was removed from a mixture of iron (II) and Iron (III) by extraction formation method without masking iron (III) with fluoride, the colour intensity increased with time which is probably due to photo reduction of iron (III) chelate. But the presence of fluoride in a mixture is seen to stabilize the colour of extract for more than 24 hours under diffused sun light even at 1000 μg of concentration of iron (III) per ml present in the mixture of iron (II) and iron (III). The colour intensity however varies with time when a stale solution of PDT is used. It is, therefore, advisable to prepare fresh solution of PDT reagent weekly.

The wave length of maximum absorbance of resulting complex of PDT with iron (II) in presence of iron (III) in chloroform and 1,1,1-trichloroethane was determined in the usual manner. The spectrophotometric data was analyzed by the method of least square to determine molar absorptivity. The method of Ringbom^{10,11} was used to determine optimum concentration ranges, for the suggested method and to establish the concentration ranges within which the relative analysis error per 1.0%

Table 2. Effect of the Sun Light before the addition of fluoride on the absorbance obtained.

(Volume 10 ml, 2.5 $\mu\text{g Fe}^{+3}$, 1000 $\mu\text{g Fe}^{+3}$)

S.No.	Time	Absorbance for Iron (II) chelate
1	0	0.241
2	5	0.336
3	10	0.401
3	15	0.617

absolute photometric error were 5% and 10%. Method of mole ratio was adopted to develop the stoichiometry of the resulting complex.

The wave length of maximum absorbance, molar absorptivity (shown in Table 3) and stoichiometry (Fig. 1) values of resulting complex of PDT with iron (II) are not significantly different from the reported values obtained in aqueous solution in the total determination of iron⁸.

Effects of variables.

A systematic investigation was carried out on variables like the strength of acid, amount of PDT, amount of ammonium fluoride and prior treatment of the iron (II) sample, regarding their effect on the rate and completeness of formation of iron (II) complex of PDT in presence of iron (III) ion. This was done by preparing a series of solutions in which all but one variable were kept constant. The conditions used for colour development were those recommended in the standard procedure.

For these experiments 10.0 ml of iron (II) solution containing 1.0 μg of iron (II) per ml was mixed with necessary reagents. In all the experiments performed, the overall volume maintained was 100 ml. A 10.0 ml aliquote of PDT solution in chloroform or in 1,1,1-trichloroethane was used for extraction.

The data obtained for several of the variables is summarized in Fig. 2. Each curve merely indicate the completion of the complex formation due to any of the variables, as the procedure was not the same as described in the recommended producer.

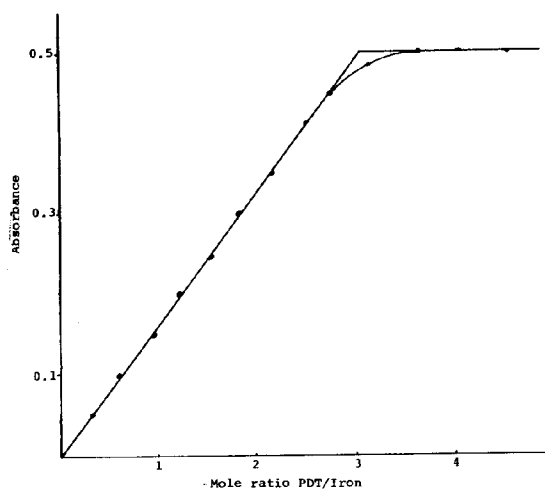


Fig. 1

The amount of sample to be taken for analysis depends upon the type and concentration of acid, as well as on the strength of iron. The final concentration of acid in the treated sample prior to extraction should be at least 0.5M but should in no case exceed 1.0M because above 1.0M acid concentration the ammonium fluoride ceases to be effective as a masking agent for iron (III). However the variation in acid concentration between 0.5 to 1.0M does in no way influence the intensity of the extracted product.

It is apparent from Fig. 2 that the absorbance increases with the amount of PDT reagent added. The curve reaches its maximum at the addition of 1.0 ml of reagent, which provides chromogenic reagent to iron (II)

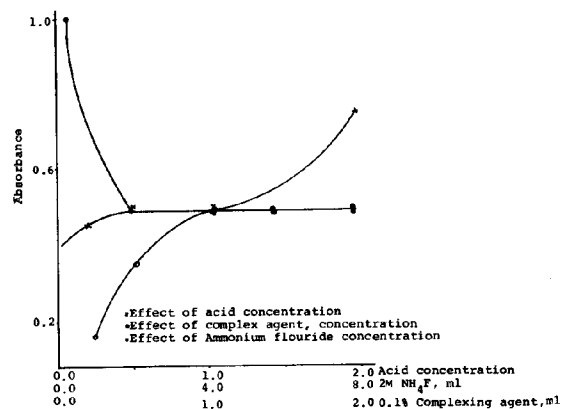


Fig. 2

ratio of about 25 to 1. Beyond which the addition of reagent does not show any change in absorbance. This constant value indicates the completion of the complexation. The recommended 10.0 ml of ferroin reagent used in the standard procedure supplies a ratio of 30 to 1, where sample contains $2.5 \mu\text{g}$ of iron (II) per ml and 150 to 1 for $0.5 \mu\text{g}$ of iron (II) per ml, this quantity is several times higher when iron (III) is not present. It is probably due to the formation of colourless mixed complexes of iron (III) with fluoride and PDT reagent.

Various stabilizing agents including fluorides, tartrates, citrates, phosphates, disodium EDTA and acetate were added. All except fluoride and dihydrogen phosphate were rejected as they either suppressed the colour reaction or gradually increased the colour of the resulting iron (II) complex.

Table 3. Maximum Wave Length, Molar Absorptivity And Result Of Analysis Of Spectrophotometric Data By Ringboms Method For The Complex Of Iron (II).

Solvent	λ max. (nm)	Molar Absorptivity [$\text{Mol}^{-1} \text{cm}^{-1}$]	% Relative Analysis Error 1% Absolute Photometric Error.
Chloroform	555	24,100	2.7 (0.025-1.55 $\mu\text{g}/\text{ml}$ Iron (II))
	(555)	(24,000)	5.0 (0.125-2.5 $\mu\text{g}/\text{ml}$ Iron (II))
			10.0 (0.05-2.5 $\mu\text{g}/\text{ml}$ Iron (II))
1,1,1-trichloroethane	555	24,000	2.9 (0.025-1.55 $\mu\text{g}/\text{ml}$ Iron (II))
	(555)	(24,000)	5.0 (0.125-2.5 $\mu\text{g}/\text{ml}$ Iron (II))
			10.0 (0.05-2.5 $\mu\text{g}/\text{ml}$ Iron (II))

Values obtained in aqueous solutions are given in parenthesis.

The dihydrogen phosphate and fluoride permitted iron (II) to react with PDT in dilute acidic media while iron (III) remained inactivated. The fluoride was preferred over dihydrogen phosphate for its higher solubility and effectiveness in acidic media as a masking agent for iron (III). A large excess of the fluoride has no effect on the colour development of the complex. This indicates that PDT complex of iron (II) is quite stable towards fluoride substitution.

The effects of iron (III) ion on the system was studied by adding a solution of iron (III) to a sample containing 0.5 μg iron (II) per ml and developing according to the standard procedure. It is observed that iron (III) upto 1000 μg per ml has no effect on the determination of iron (II). If the iron (III) concentration is higher than 1000 μg per ml, then larger quantities of fluoride and PDT needs to be added. The calibration curve however is not effected by the presence of iron (III) if the recommended procedure is followed. The tolerance to iron (III) was considered as the maximum concentration which would cause an error not greater than 0.005 in the absorbance reading of the sample.

Recommended procedure.

Suitable aliquot of acid of appropriate strength was mixed with water to make the volume upto 75.0 ml (flask and contents were cooled to room temperature, when necessary). 5.0 ml of thiocyanate, 0.5 ml of ammonium fluoride and an accurately measured sample of iron of appropriate strength (containing 0.5 to 2.5 μg of iron (II) and 1000 μg of iron (III) per ml were added. The contents were finally diluted to the required volume and mixed, and the solution was then transferred to a separating funnel and exactly 10 ml of PDT solution in chloroform or in 1,1,1-trichloroethane was added to it. After shaking for one minute the two layers were allowed to separate and clear out. A portion of the chloroform or 1,1,1-trichloroethane layer was withdrawn into a 10 mm cell and absorption of the solution was measured in the visible region against an identical cell filled with respective solvent. A reagent blank is unnecessary to compensate any traces of iron.

Order of addition of reagents

If fluoride is added before the spectrophotometric

reagent, it helps to stabilize iron (III) against complexing with PDT as well as it helps to keep iron (III) in aqueous phase. However, if the determination is carried out without fluoride a higher value of absorbance is obtained. This is probably due to the photo reduction of iron (III) chelate with PDT to iron (II) chelate. The effect of the time of exposure to direct sun light is shown in table 2. It is therefore advantageous to add the reagents as described in the standard procedure.

Range and precision.

Ringbom plot showed that the complex obeyed Beer's law over the range studied. Under conditions of analysis, similar to those employed in the recommended procedures, the relative analysis error over the optimum range is 0.6% with the reagent studied, when employing spectrophotometer which has a photometric error of 0.2% (table 3).

The precision of the method was checked by studying values from 25 of the samples, all of which had a final concentration, the value of which is at near the centre of the optimum range. A standard deviation of 0.005 absorbance unit was obtained. This study was then an attempt to measure the inherent precision of the method and was performed under ideal and non-variant conditions.

Influence of foreign ions.

The following anions and cations in ratio 1000 to 1 Fe^{+2} do not interfere with the determination: Bi, Ca, Cd, Co, Cr, Cu, Hg, Ir, Mo, Ni, Os, Pd, Pt, Zn, NH_4 , Sb(III), Sn(II), Ti(IV), V(V), W(VI), Ni, acetate, bromide, chloride, nitrate, sulphate, chlorate and phosphate. The cations were present as nitrates and anions as alkali salts. IP Cyanide, oxalate and perchlorate interfere with reaction.

Applications

The spectrophotometric method described in this work was used to determine μg quantities of iron (II) in oxidation products from corrosion of iron and its alloys. Iron (II) was determined in chemical reagents. The procedure has also been applied in the analysis of magnetite and other iron oxides.

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