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Spectrophotometric determination of iron as iron(III) in water samples of certain lakes situated around Tumkur through oxidative nucleophilic coupling reaction between catechol and nitroaniline

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ABSTRACT

A simple, rapid and a sensitive spectrophotometric method is developed here for the determination of iron(III) through iron(III) mediated nucleophilic coupling reaction between catechol and p-nitroaniline, system 1 or catechol and m-nitroaniline, system 2. The method is based on catechol oxidation by iron(III) followed by its nucleophilic coupling with m-nitro aniline or p-nitro aniline in 0.1M hydrochloric acid medium forming a dye with λ_{\max} 540 nm obeying Beer's law in the range, 0.8-20 $\mu\text{g ml}^{-1}$ for both the systems. The molar absorptivity values for system 1 and system 2 were found to be $9.379 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $8.8032 \times 10^2 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively with the corresponding Sandell's sensitivity values, $0.0595 \mu\text{g cm}^{-2}$ and $0.0634 \mu\text{g cm}^{-2}$. The composition of the dye product was determined and found to be 1:2 for both systems. The systems were used for the determination of iron in water samples of certain lakes situated around Tumkur. The results obtained by both the systems were reproducible and comparable with the results of iron determined separately by phenanthroline method.

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KEYWORDS

Iron(III);
Nucleophilic coupling
reactions;
Spectrophotometry;
Lake waters.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust^[1] with biological and environmental significances^[2,3]. Iron is often found in nature in a reasonably high concentration and may enter the hydro-sphere through the weathering of iron salts and minerals. Both iron(II) and iron(III) ions are commonly found dissolved in water either in colloidal form or as inorganic or organic complexes. Irrigation water with iron levels above 0.3 ppm may lead to iron rust stains and

discoloration on foliage plants in overhead irrigation applications. Considering the importance of iron, numerous methods such as spectrophotometry^[4,5], potentiometry^[6], flame^[7] and electrothermal atomic absorption spectrometry^[8], flow injection^[9], photoacoustic^[10], fluorometry^[11] anodic stripping voltammetry^[12], volumetry^[13], and high performance liquid chromatography^[14] are developed for the determination of iron present in environmental samples. Owing to the simplicity, spectrophotometric method involving ammonium thiocyanate or 1, 10-phenanthroline is a com-

Full Paper

monly used method for the determination of iron. However, these methods suffer from low sensitivity or fail to follow the Beer-Lambert's law^[15] or have a narrow analytical range of determination. Hence the method based on catechol oxidation by iron(III) followed by its nucleophilic coupling with m-nitro aniline or p-nitro aniline in 0.1M hydrochloric acid medium forming a dye with λ_{\max} 540 nm and its application to determine iron present in the water samples collected^[16] from certain lakes situated around Tumkur.

EXPERIMENTAL

Apparatus

Elico Spectrophotometer, model SL-27 (Hyderabad, India), Acculab digital balance readable 0.0001g were used.

Reagents

All chemicals used in the experiments were of analytical reagent grade and the water used was distilled water.

Stock solution, 200 $\mu\text{g ml}^{-1}$ iron(III): An accurately weighed amount, 0.8634g of ammonium iron(III) sulphate was transferred to a 50ml beaker. It was dissolved by heating in about 20ml of water and 1.5ml of concentrated hydrochloric acid. The resulting yellow solution was transferred into a 50ml volumetric flask and diluted to the mark with water.

Catechol, 0.005M: An accurately weighed amount, 0.0551 g catechol was transferred to a beaker. It was dissolved in water and transferred the resulting solution into a 100ml volumetric flask and diluted to the mark with water.

m-nitroaniline, 100 μgml^{-1} : An accurately weighed amount, 0.1g m-nitro aniline was transferred to a beaker. It was dissolved in alcohol and transferred the resulting solution into a 100ml volumetric flask and diluted to the mark with water.

p-Nitroaniline, 100 μgml^{-1} : An accurately weighed amount, 0.1g p-nitro aniline was transferred to a beaker. It was dissolved in alcohol and transferred the resulting solution into a 100ml volumetric flask and diluted to the mark with water.

Hydrochloric acid, 0.1M: It was prepared by a suit-

able dilution of concentrated hydrochloric acid (35%, 1.18g cm^{-3}) with water.

RECOMMENDED PROCEDURE

A series of labeled 25 ml volumetric flasks were arranged. To each flask, aliquots of the solution containing 0.8-20 $\mu\text{g ml}^{-1}$ iron(III) (corresponding to 0.1, 0.2, 0.4, 0.5, 0.8, 1.0, 1.5, 2.0, 2.5, ml of 100 $\mu\text{g ml}^{-1}$ iron(III)), 2ml of 0.005M catechol, 0.5ml of 0.1M hydrochloric acid and 2 ml of 0.00072M m-nitro aniline or 2ml of 0.00072M p-nitro aniline were added. Then the solution of each flask was diluted to the mark with water. Absorbance of each solution and the blank (without Iron(III)) were measured at 540 nm against water.

RESULTS AND DISCUSSION

Oxidative coupling reactions are frequently used in analytical determinations^[17,18] involving 3-methyl-2-benzo thiazolinone hydrazone with N, N-dimethyl aniline by hydrogen peroxide^[19], p-amino phenol and p-phenylene diamine^[20]; N-phenyl-p-phenylene-diamine with N, N-dimethyl aniline in the presence of an oxidant^[21], p-anisidine^[22]; 4-amino antipyrine^[23] with N,N-dimethyl aniline as a nucleophile and hydrogen peroxide as an oxidant; the oxidation of N,N-diphenyl amine by hydrogen peroxide, in acidic medium yielding diquinone diimine^[24] and coupling with a nucleophile. The literature on oxidative coupling reactions^[17-24] is the basis for developing this method for the determination of iron(III). Iron(III) oxidises catechol to quinone^[25,26], a quite reactive species that can be attracted by nucleophiles^[25], m-nitro aniline or p-nitro aniline producing a dye product. Thus, under optimized experimental condition and fixed concentrations of nitroamine and catechol, the color intensity of the dye product is proportional to the concentration of iron(III). The stoichiometry between iron(III) and the mixture of catechol and nitro anilines were determined and found to be 2:1 respectively.

Optimization of reaction conditions

The composition of the dye products and the various experimental parameters affecting the development and stability of the dye products are carefully optimized. The studied variables include acids, different volumes

of p-nitro aniline (or m-nitro aniline) and different volumes of hydrochloric acid and color stability with time.

Effects of acids

A series of labeled 25ml volumetric flasks were arranged. To each flask, 0.1-3ml of iron(III) (200 μ g/ml), 2ml of 0.005M catechol, 0.5ml of 0.1M hydrochloric acid/0.5ml of 0.1M sulphuric acid/0.5ml of 0.1M acetic acid and 2ml of 100 μ g ml⁻¹ P-nitro aniline were added. Then the solution of each flask was diluted to the mark with water. Absorbance of each solution and the blank were measured at 540nm against water. The results obtained are tabulated in TABLE 1, indicating almost the same absorbance values. However, 0.1M hydrochloric acid was used throughout the experiment.

TABLE 1 : Effect of acids, 0.5ml each of 0.1M hydrochloric acid/ 0.1M sulphuric acid / 0.1M acetic acid on the determination of iron(III).

Iron(III) (ml)	0.1M HCl	0.1M H ₂ SO ₄	0.1M CH ₃ COOH
	Absorbance	Absorbance	Absorbance
0.1	0.0177	0.0227	0.0232
0.2	0.0301	0.0381	0.0329
0.4	0.0525	0.0521	0.0545
0.5	0.0650	0.0757	0.0788
0.8	0.1007	0.0969	0.0974
1.0	0.1250	0.1356	0.1349
1.5	0.1850	0.1952	0.1771
2.0	0.2425	0.2380	0.2218
2.5	0.3115	0.2823	0.2762

Effect of different volumes of p-nitro aniline and m-nitro aniline

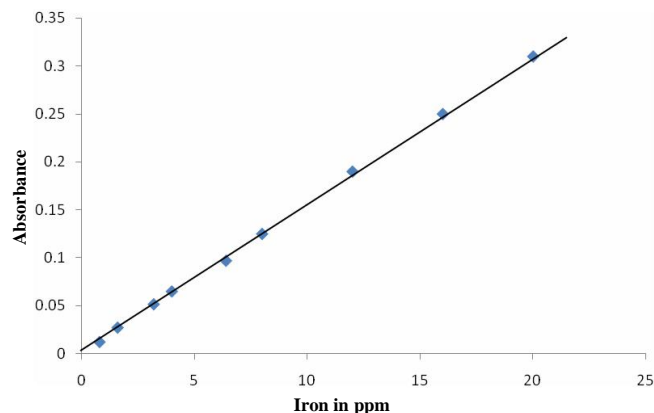
The effect of various volumes (0.5- 4.0 ml) of 100 μ g ml⁻¹ p-nitro aniline (or m-nitro aniline) on absorbance values for the determination of iron(III) was investigated as follows. The experiment was performed using the optimized variables established in the earlier experiments. A series of labeled 25 ml volumetric flasks were arranged. To each flask, 2 ml of 0.005 M catechol, 0.5 ml of 0.1M hydrochloric acid, 2 ml of 100 μ g ml⁻¹ of iron(III) but various volumes (0.5-4.0 ml) of 100 μ g ml⁻¹ p-nitro aniline were added. The solution of each flask was then diluted to the mark with water. Absorbance of each solution and the blank were measured against water at 540 nm. The results obtained are show-

ing increasing absorbance with the volume of p-nitro aniline up to 2.0 ml, afterwards the absorbance values are found to be decreasing with the volume of p-nitro aniline. Therefore, 2 ml of 100 μ g ml⁻¹p- nitro aniline per 25 ml was selected as an optimized volume for the construction of the calibration graph for the determination of iron(III).

Effect of different volumes of 0.1M hydrochloric acid

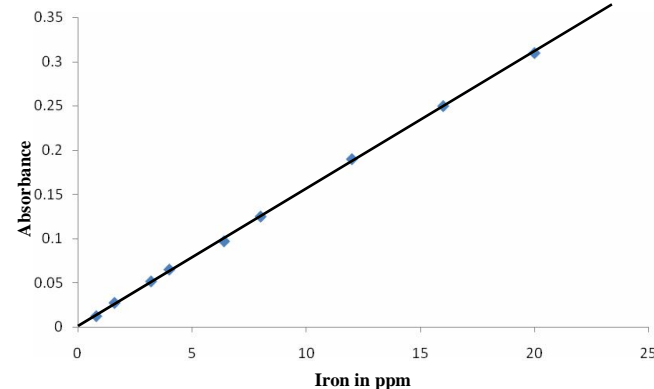
This experiment was carried out similar to the previous one but with various volumes of 0.1M hydrochloric acid. The absorbance values were found to be constant after the addition of 0.5ml. Therefore 0.5ml of 0.1M hydrochloric acid was selected as an optimized volume.

Calibration Graph (system 1)



Graph 1 : Calibration graph for iron(III) with the system 1, catechol + p – nitro aniline.

Calibration Graph (system2)



Graph 2 : Calibration graph for iron(III) with the system 2, catechol + m – nitro aniline.

Effect of foreign ions

For understanding the reaction selectivity, inter-

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TABLE 2 : The analytical parameters for the determination of iron (III).

Parameters	System 1	System 2
Wave length (nm)	540	540
Linear range ($\mu\text{g ml}^{-1}$)	0.8 – 20	0.8 – 20
Molar absorptivity ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)	9.379×10^3	8.803×10^3
Sandel sensitivity per 0.001A ($\mu\text{g cm}^{-2}$)	0.0607	0.0634
Regression equation (y)	$Y = 0.029x$	$Y = 0.0263x$
Slope (b)	0.0151	0.0155
Intercept (a)	0.00446	0.001386
Correlation coefficient(R)	0.9979	0.998

ference of common ions which often accompany iron(III) were investigated in the determination of $4 \mu\text{g ml}^{-1}$ of iron(III) under optimum conditions as given in the recommended procedure. The results obtained are summarized in TABLE 3. It was found that presence of common interfering ions with iron(III) as indicated in TABLE 3 will not interfere in the determination of iron. The maximum concentration of each ion that does not cause more than 4% error in the determination of $4 \mu\text{g ml}^{-1}$ of iron(III) is also shown against the respective ion in TABLE 3. The results obtained would account for good selectivity of the developed methods for the determination of iron as iron(III).

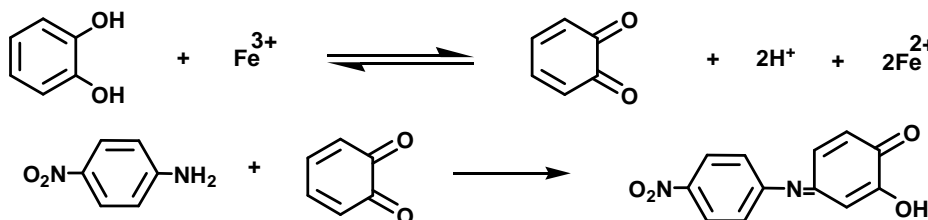
TABLE 3 : Interference of foreign ions in the determination of $4 \mu\text{g ml}^{-1}$ of iron(III)

Ion added	Tolerance limit($\mu\text{g ml}^{-1}$)
Cu^{+2}	320.00
Ni^{+2}	640.00
Cd^{+2}	640.00
Mg^{+2}	640.00
Zn^{+2}	363.84
K^{+}	480.00
SO_4^{-2}	496.00
Cl^{-}	640.00
NO_3^{-}	384.00

These ions concentrations were examined between 640 and 320 $\mu\text{g ml}^{-1}$.

Stoichiometry of the dye product of the system 1 and system 2

The experiment was carried out using a series of solutions of 0.001M iron(III) and the mixture (equal volumes of 0.002M catechol and 0.002M p-nitro aniline / m-nitro aniline) in different proportions totaling to either 10 ml or 5 ml per 25 ml. The results obtained are shown in the TABLES 4, 5, 6 and 7. To each flask 0.5 ml HCl was added and diluted the solutions to 25 ml and the absorbance was measured. The results are accounting for 1:2 stoichiometry between the, 1:1 catechol and nitroaniline mixture and iron(III), Figures 1 and 2.



System 1 : For 10 ml- X axis 1 unit =1ml
For 5 ml- X axis 2 unit = 1 ml

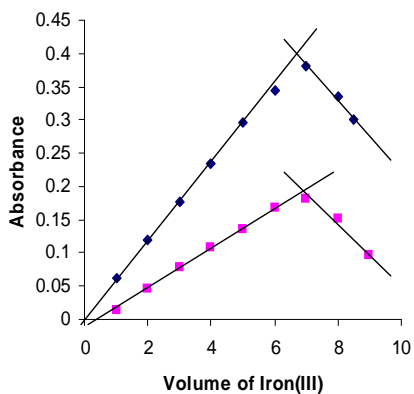


Figure 1 : Composition of Iron(III) and mixture(System 1)

System 2 : For 10 ml- X axis 1 unit =1ml
For 5 ml- X axis 2 unit = 1 ml

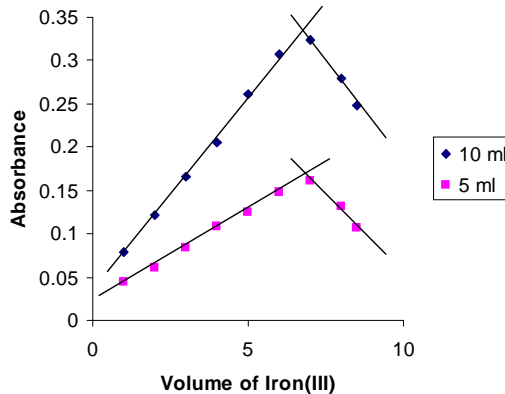


Figure 2 : Composition of Iron(III) and mixture(System 2)

TABLE 4 : For 10 ml (System 1)

Volume of Iron(III) (ml)	Volume of mixture(ml)	Absorbance
9.0	1.0	0.1681
8.5	1.5	0.3012
8.0	2.0	0.3344
7.0	3.0	0.3819
6.0	4.0	0.3439
5.0	5.0	0.2967
4.0	6.0	0.2351
3.0	7.0	0.1765
2.0	8.0	0.1192
1.0	9.0	0.0610

TABLE 5 : For 5 ml (System 1)

Volume of Iron(III) (ml)	Volume of mixture(ml)	Absorbance
4.5	0.5	0.0969
4.25	0.75	0.1362
4.0	1.0	0.1518
3.5	1.5	0.1804
3.0	2.0	0.1675
2.5	2.5	0.1361
2.0	3.0	0.1068
1.5	3.5	0.0773
1.0	4.0	0.0458
0.5	4.5	0.0141

TABLE 6 : For 10 ml (System 2)

Volume of Iron(III) (ml)	Volume of mixture(ml)	Absorbance
9.0	1.0	0.1586
8.5	1.5	0.2478
8.0	2.0	0.2798
7.0	3.0	0.3233
6.0	4.0	0.308
5.0	5.0	0.262
4.0	6.0	0.2048
3.0	7.0	0.1656
2.0	8.0	0.1221
1.0	9.0	0.0794

TABLE 7 : For 5 ml (System 2)

Volume of Iron(III) (ml)	Volume of mixture(ml)	Absorbance
4.5	0.5	0.0726
4.25	0.75	0.1069
4.0	1.0	0.1308
3.5	1.5	0.1612
3.0	2.0	0.1481
2.5	2.5	0.1255
2.0	3.0	0.1079
1.5	3.5	0.0846
1.0	4.0	0.0605
0.5	4.5	0.0443

ANALYTICAL APPLICATIONS

Pre-treatment of water samples

a) For the proposed method: The water samples collected were pretreated with concentrated hydrochloric acid and diluted with deionized water. Iron(II) present in the sample is oxidized to iron(III) by adding very dilute solution of KMnO_4 ^[27]. To each sample, a fixed amount of 5mg/L iron(III) solution was added to bring the value to the range of determination.

b) For phenanthroline method^[27]: The method involved reduction of iron(III) present in the sample to iron(II) with hydroxylamine hydrogensulphate followed by its complexation with 1,10-phenanthroline in a solution buffered at low pH.

To confirm the applicability of the developed method, the total iron present in the water samples of

different lakes situated around Tumkur were determined under optimized experimental conditions. The results obtained in the reference method and new method are shown in TABLE 8.

TABLE 8 : Results of Iron(III) present in water samples obtained from new method and reference method.

Source	Volume of Iron III added (mg/L)	Concentration of total Iron (mg/L)		
		Proposed Methods*		1,10-Phenanthroline method
Lake Water	5	System 1	System 2	
Kallambella	5	9.100	9.000	4.000
Bugudanahalli	5	5.038	5.036	0.040
Maidala	5	5.050	5.054	0.050
Honnudike	5	13.000	13.020	8.100
Kunigal	5	5.040	5.038	0.040
Kadaba	5	7.100	7.140	2.300
Hebbur	5	6.400	6.038	1.370

*Mean Value (n=5)

CONCLUSIONS

The method for determining iron(III) either with

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system 1 or 2 is rapid and sensitive with a wide determination range without requiring stringent reaction conditions and also with reasonable colour stability. The methods are successfully employed for the determination iron(III) in the water samples of seven selected lakes that are situated around Tumkur. The iron(ppm) content of the water samples of the lakes are found to be in the decreasing order: Honnudi(8.00), Kallambella(4.10), Hebbur(1.40), Kadaba(0.21), Maidala(0.05), Kunigal(0.04)~Bugudanahalli(0.04). The iron contents of the lake water samples are also determined by iron(II)- 1,10-Phenanthroline method. The values obtained are agreeing with those obtained by the new method. Therefore, the developed method could be used for the determination of total iron present in water samples.

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