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A Simple and Sensitive Spectrophotometric Method for Iron (III) through a Nucleophilic Coupling of Catechol with 2-Amino-5-methylthiophene-3-Carbonitrile

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Abstract

A simple and sensitive spectrophotometric method is developed for the determination of iron (III) and used for its determination in the laboratory chemicals, lake water samples, green leaves and pharmaceutical samples. The method is based on the catechol oxidation by iron (III) followed by its nucleophilic coupling with 2-amino-5-methylthiophene-3-carbonitrile producing a dye with λ_{max} 490 in 0.1 M hydrochloric acid. The system is obeying the Beer's law in the range 0.4 µg ml^{-1} to 15 µg ml^{-1} of iron (III). The Molar absorptivity, Sandell sensitivity and correlation coefficient of the system were calculated and found to be 1.404 × 103 mol^{-1} cm^{-1}, 0.0398 µg cm^{-2} and 0.9996, respectively. The optimum reaction conditions and other analytical parameters are investigated to enhance the sensitivity of the method. The new method have been applied successfully for the analysis of iron in the laboratory chemicals, lake water samples, green leaves and pharmaceutical samples with good accuracy and precision. The results from the developed method are in good agreement with the official method.

Keywords: ***Nucleophilic coupling reaction; Iron (III); 2-amino-5-methylthiophene-3-carbonitrile; Spectrophotometry***

Introduction

Iron is the second most abundant metal after aluminum and the fourth most abundant element in the earth's crust and forms compounds normally in its divalent and trivalent states [1]. Iron is often found in nature in a reasonably high concentration and may enter the hydrosphere 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

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levels above 0.3 ppm may lead to iron rust stains and discoloration on foliage plants in overhead irrigation applications. Malnutrition arising from a dietary deficiency of critically important mineral micronutrients such as iron (Fe) is a serious problem affecting nearly half of the world's population [2]. Iron deficiency, even in the absence of anemia, can cause fatigue and reduce work performance [3]. A deficiency of iron limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity. On the other hand, excess amounts of iron can result in toxicity and even death. Considering the importance of iron, numerous methods such as spectrophotometry [4,5], potentiometry [6], flame photometry [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, a new spectrophotometric method is developed for the determination of iron (III) in laboratory chemicals, lake water, green leafy vegetables based on catechol oxidation by iron (III) followed by its nucleophiliccouplingwith2-amino-5-methylthiophene-3-carbonitrile in 0.1 M hydrochloric acid medium forming a dye with λ_{max} 490 nm.

Experimental

Elico spectrophotometer model SL27 with 1 cm match quartz cell and, Sartorius digital balance readable 0.0001 g were used.

Reagents and solutions

All the chemicals used in the experiments were of analytical reagent grade and double distilled water was used throughout the experiment to prepare all solutions.

Iron (III) solution 100 µg ml^{-1}: An accurately weighed amount 0.8600 g of ferric ammonium sulfate was transferred to a clean beaker. It was dissolved in a few drops of concentrated hydrochloric acid and was boiled with water for a few minutes to get a clear solution. It was then cooled and transferred to a 100 ml standard flask. It was made up to the mark with water to get 1000 µg ml^{-1}. 5 ml of the stock solution was transferred to a 50 ml standard flask and made up to the mark with water to obtain 100 µg ml^{-1} solutions.

2-amino-5-methylthiophene-3-carbonitrile 1000 µg ml^{-1}: An accurately weighed amount of 0.05 g of the sample was transferred to a beaker. It was dissolved in alcohol and transferred the resulting solution into a 50 ml standard flask and diluted to the mark with alcohol.

Catechol solution 0.005 M: An accurately weighed amount of 0.055 g catechol was transferred to a beaker. It was dissolved in water and transferred the resulting solution into a 100 ml volumetric flask and diluted to the mark with water.

Hydrochloric Acid 0.1 M: It was prepared by suitable dilution of concentrated hydrochloric acid (35%, 1.18 g cm^{-3}) with water.

Recommended procedure: A series of labeled 25 ml of volumetric flasks were arranged. To each flask, standard iron (III) solution (0.1, 0.5, 1.25, 2, 2.5, 3.0, 3.75 ml) and 2.5 ml, 0.005 M catechol, 0.5 ml, 0.1 M hydrochloric acid and 2.5 ml 1000 µg ml^{-1} 2-amino-5-methylthiophene-3-carbonitrile solutions were added to each flask and let aside for about ten minutes. Then the solution of each flask was diluted to the mark with water and absorbance of each solution was measured against water at 490 nm.

Results and Discussion

Oxidative coupling reactions are frequently used in analytical determinations [15-22] involving lamotrigine with 3-Methyl-2-Benzothiazolinone hydrochloride (MBTH) [16], 2′,5-dichlorobenzophenone (MCB) or 2-amino-5-chloro-2'-fluorobenzophenone (MFB) by iron (III) and coupling with phenoxazine (PNZ) [17], 3-methyl-2-benzothiazolinone hydrazone with N-ethyl-N-(2-hydroxy-3-sulfopropyl)-3-methoxyaniline [18], 3-methyl-2-benzothiazolinone hydrazone (MBTH) with N,N-dimethylaniline (DMA) [19]. Hence based on the literature survey about oxidative coupling reactions [15-22] the new method has exploited this type of reactions [15-22] for the determination of iron (III). Iron (III) oxidizes catechol to quinone [20-22], a quite reactive species that can be attracted by a variety of nucleophiles. This reaction prompted to use 2-amino-5-methylthiophene-3-carbonitrile as a nucleophile to attack the quinone formed by the oxidation of catechol by iron (III) in acidic medium producing a dye product having λ_{max} 490. Thus, under experimental conditions and fixed concentrations of nucleophile and catechol, the color intensity of the dye product is proportional to the concentration of iron.

Optimization of reaction conditions

Various experimental parameters have been carefully optimized. The studied variables include different volumes of catechol, different volumes of hydrochloric acid and different volumes of 2-amino-5-methylthiophene-3-carbonitrile in the order of reagents additions.

Effect of different volumes of catechol

By varying the volume of 0.005 M catechol from 0.5 to 3.5 ml and keeping the volumes of other reagents constant, 1ml of 100 µg ml^{-1} iron (III), 0.5 ml of 0.1 M hydrochloric acid, 1.5 ml 1000 µg ml^{-1}, 2-amino-5-methylthiophene-3-carbonitrile were added into a series of labeled 25 ml volumetric flasks. Then the solutions of each flask were diluted to the mark with water. The absorbance of each flask was measured at 490 nm. The results obtained are indicated in **FIG. 1**. Based on the highest absorbance of the solution obtained under the specified experimental conditions, 2.5 ml of 0.005 M catechol was selected as an optimized volume for the construction of the calibration graph for the determination of iron (III).

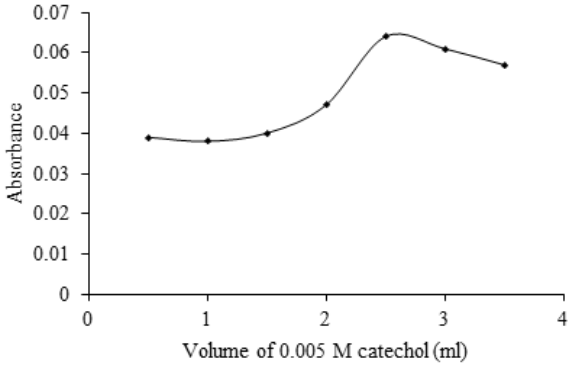

FIG. 1. **Effect of different volumes, 0.5-3.5 ml 5.0 × 10^{-3} M catechol solution +1ml of 100 µg ml^{-1} iron (III) +0.5 ml of 0.1 M hydrochloric acid +1.5 ml 1000 µg ml^{-1} 12-amino-5-methylthiophene-3-carbonitrile, diluted to 25 ml with water.**

Effect of different volumes of 2-amino-5-methylthiophene-3-carbonitrile

To a series of 25 ml volumetric flasks 1 ml of 100 µg ml^{-1} iron (III) 2.5 ml of 0.005 M catechol, 0.5 ml of 0.1 M hydrochloric acid but various volumes of 0.5 ml to 3.5 ml 1000 µg ml^{-1} 2-amino-5-methylthiophene-3-carbonitrilewere added to each flask. The solutions of each flask were diluted to the mark with water. The absorbance of each flask was measured at 490 nm. The results obtained are indicated in **FIG. 2** and showing increasing absorbance with the volume of 2-amino-5-methylthiophene-3-carbonitrile up to 2.5 ml, afterward, the absorbance value is found to be decreasing with the volume of 2-amino-5-methylthiophene-3-carbonitrile. Therefore, 2.5 ml of 1000 µg ml^{-1} 12-amino-5-methylthiophene-3-carbonitrile per 25 ml was selected as an optimized volume for the construction of the calibration graph to be used for the determination of iron (III).

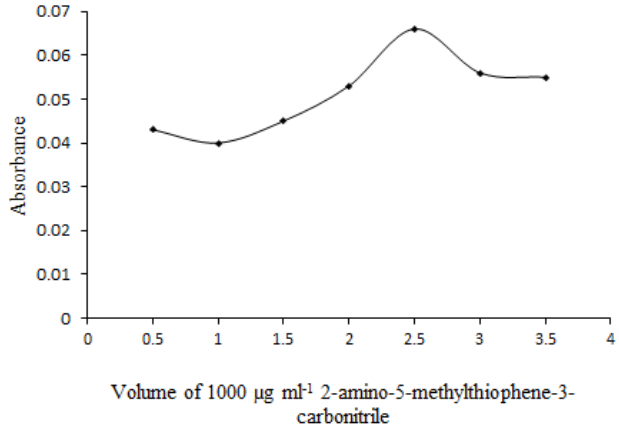

FIG. 2. **Effect of different volumes, 0.5-3.5 ml of 1000 µg ml^{-1} 2-amino-5-methylthiophene-3-carbonitrile +1 ml of 100 µg ml^{-1} iron (III) +2.5 ml of 5.0 × 10^{-3} M catechol +0.5 ml of 0.1 M hydrochloric acid diluted to 25 ml with water.**

Effect of different volumes of 0.1 M hydrochloric acid

The experiment was carried out the same as the previous one but with various volumes (0.25-2.5) of 0.1 M hydrochloric acid. The absorbance values as shown in **FIG. 3** were found to be constant with the increasing volume of 0.1 M hydrochloric acid. Therefore, 0.5 ml of 0.1 M hydrochloric acid was chosen as an optimized volume.

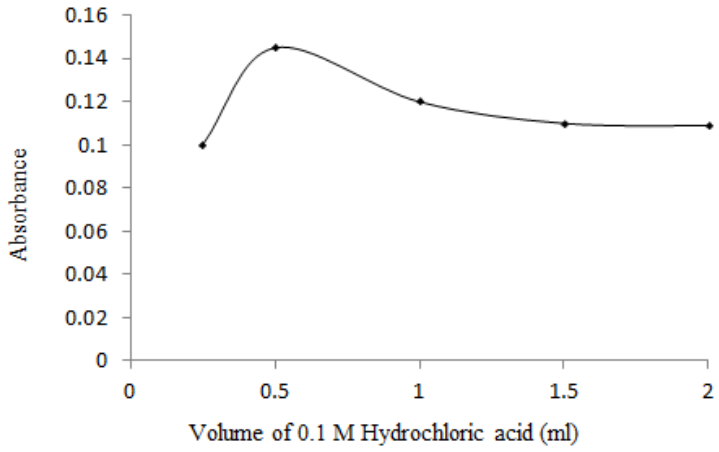

FIG. 3. **Effect of different volumes, 0.25-2.0 ml of of 0.1 M hydrochloric acid +2.5 ml of 5.0 × 10^{-3} M catechol +2.5 ml 0f 1000 µg ml^{-1} 2-amino-5-methylthiophene-3-carbonitrile +1 ml of 100 µg ml^{-1} irons (III) and diluted to 25 ml with water.**

Order of reagents addition

Owing to the importance of the order of addition, various orders of the addition of the reagents were tried and the corresponding absorbance values of the solutions were recorded at 490 nm and were shown in **TABLE 1**, which indicate that the order of the addition of the reagents appeared to be insignificant. For maintaining the uniformity of addition, however, the order of addition shown in serial no. 1 of **TABLE 1** was followed throughout the work.

TABLE 1. **Corresponding absorbance values of the solutions.**

Sl. No	Order of addition	Absorbance
1	A+B +C+D	0.11
2	B+C+D+A	0.105
3	C+D+A+B	0.109
4	D+A+B+C	0.107
A=1 ml of 100 µg ml^{-1} iron (III); B=2.5 ml of 0.005 M catechol; C=0.5 ml of 0.1 M hydrochloric acid; D=2 .5 ml 1000 µg ml^{-1} 2-amino-5-methylthiophene-3-carbonitrile		

Calibration graph

The summary of the analytical parameters established for the optimized method of iron (III) is given in **TABLE 2** and the calibration graph is plotted in **FIG. 4**.

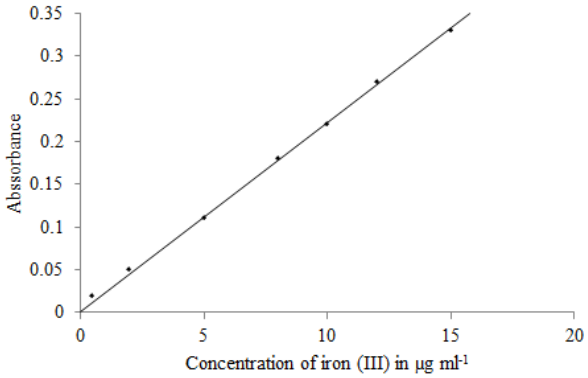

FIG. 4. **Calibration graph for the determination of iron (III) under the experimental conditions.**

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

Analytical parameters	
Wavelength (nm)	490
Linear range (µg ml^{-1})	0.4-15
Molar absorptivity (L mol^{-1} cm^{-1})	1.404×10^3
Sandell sensitivity (µg cm^{-2})	0.0398
Slope	0.0216
Intercept	0.0066
Correlation coefficient	0.9996

Precision and accuracy

The precision and accuracy of the developed method were calculated by performing five replicate determinations of iron (III) at three different concentrations (1 µg ml^{-1}, 5 µg ml^{-1}, 10 µg ml^{-1}) following the recommended procedure. The precision of the method as expressed by relative standard deviation was less than 1.2% whereas accuracy expressed by the calculated relative error was less than 2.6%.

Effect of foreign ions

For understanding the reaction selectivity, interference of common ions which often accompany iron (III) were investigated in the determination of 5 µg 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 the presence of common interfering ions with iron (III) as indicated in **TABLE 3** will not interfere in the determination of iron (III). The maximum concentration of each ion does not cause more than 4% error in the determination of 5 µg ml^{-1} of iron (III). 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 5 µg ml^{-1} of iron (III).**

Ions added	Tolerance limit (µg ml^{-1})
Cd^{2+}	320
Cu^{2+}	640
Mg^{2+}	640
Zn^{2+}	164
K^{+}	600
Ni^{2+}	640
SO_4^{2-}	400
Cl^{-}	400
NO_3^{-}	400

Analytical applications

Determination of iron (III) in chemicals: Accurately weighed amount of 0.144 g of ferric chloride and 0.361 g of ferric nitrate was transferred to a clean beaker and dissolved in 5 drops of concentrated hydrochloric acid and diluted to 50 ml in a standard flask with water. 2.5 ml of the above solution was diluted to 25 ml in a standard flask with water. Known aliquots of the solution were analyzed for the iron (III) determination through the recommended procedures. The results obtained are shown in **TABLE 4.**

Determination of iron (III) in lakes water samples: Water samples from four lakes located in and around Mysore namely, Devikere, Karanji, Maidnahalli, and Kurghalli were collected and iron was estimated by the recommended procedure. The results obtained are tabulated in **TABLE 4.**

Determination of iron (III) in green leaves [16]: Sesame, Amaranthus, drumstick leaves, pumpkin and curry leaves were collected washed thoroughly with water to remove any solid and clay impurities. It was then dried under the shade for 2 to 3 days. 5g of the completely dried samples was incinerated in a silica crucible [16]. The ash was dissolved in concentrated hydrochloric acid and diluted to 50 ml in a standard flask with water. Known volumes of the solution were used for the iron determination through the recommended procedure. The results obtained are tabulated in **TABLE 4**.

Determination of iron (III) in some drugs: Drugs rich in iron like Fesovit, Autrin, and Ferrium XT were powdered and incinerated in a silica crucible for 2 hours. The resulting ash was dissolved in concentrated hydrochloric acid and the solution

was made up to 100 ml in a volumetric flask. Known volumes of the solution were used for the iron determination through the recommended procedure [23]. The results obtained are tabulated in **TABLE 4**.

TABLE 4. **Determination of iron in laboratory chemicals, lake water samples, green leaves, and pharmaceutical samples.**

Sl.No	Sample	Values found by the roposed method in µg ml^{-1}	Official method [23]
1	Ferric chloride	0.806 ± 0.005	0.802 ± 0.010
2	Ferric nitrate	0.794 ± 0.005	0. 800 ± 0.011
3	Karanji lake water	0.550 ± 0.010	0.545 ± 0.030
4	Devikere lake water	0.500 ± 0.010	0.510 ± 0.010
5	Maidnahalli lake water	0.670 ± 0.010	0.690 ± 0.005
6	Kurghalli lake water	0.500 ± 0.012	0.500 ± 0.050
7	Sesame	1.102 ± 0.013	1.000 ± 0.001
8	Amaranthus	12.94 ± 0.005	12.26 ± 0.005
9	Curry leaves	11.0 ± 0.022	11.50 ± 0.002
10	Drumstick leaves	18.46 ± 0.023	19.00 ± 0.089
11	Pumpkin	05.92 ± 0.016	05.00 ± 0.005
12	FerriumXTa	0.920 ± 0.044	0.918 ± 0.070
13	Autrinb	0.960 ± 0.054	0.957 ± 0.010
14	Fesovitc	0.748 ± 0.044	0.751 ± 0.081
Mean values of five replicates, aEmcure pharmaceuticals Ltd, Jammu, India, bWyeth Limited, Mumbai, cGlaxo Smithkline Pharmaceuticals Limited, Bangalore			

Conclusion

The method for determining iron (III) is rapid and sensitive with a wide determination range without requiring stringent reaction conditions and also with reasonable color stability. The method is successfully employed for the determination of iron (III) in the laboratory chemicals, lake water samples, green leaves, and pharmaceutical samples. The iron contents in the laboratory chemicals, lake water samples, green leaves, and pharmaceutical samples were also determined separately by iron (II)-1,10-Phenanthroline method. The results in **TABLE 3**, of the proposed method, compared well with the official method.

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