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Spectrophotometric Determination of Iron(II) with 5-Nitro-6-amino-1,10-phenanthroline

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A new spectrophotometric method is developed for the determination of Fe(II) with 5-nitro-6-amino-1,10-phenanthroline (NAF). In this work, the effect of factors such as pH, amount of reagent (NAF), reaction time and temperature were investigated. The method is based on the formation of a colored product between Fe(II) and NAF. The reaction proceed quantitatively at 20 °C for 210 min in acidic medium. The absorption maximum was at 520 nm. A linear relationship existed between absorbance and Fe(II) concentration over the range 0.1 μg/mL and 0.4 μg/mL. The molar ratio of Fe(II) to the reagent was determined as 1:3. The limiting concentration for interference by Co(II), Ni(II), Cu(II), Zn(II), Mn(II), Al(III), Ca(II) and Mg(II) cations are reported.

Key Words: 5-Nitro-6-amino-1,10-phenanthroline, Visible spectrophotometry, Determination of iron(II).

Introduction

Gravimetric, titrimetric, polarographic, optical and radiochemical methods have been reported for the determination of iron(II) and (III). Numerous reagents have also been reported for the spectrophotometric determination of Fe(II); for example, thiocyanate, dipyridine, tripyridine and 1,10-phenanthroline. The 1,10-phenanthroline family has been extended to the use of dihydroxy, dimethyl, nitro and diphenyl derivatives. The spectrophotometric determination method of a red-orange complex that forms between iron(II) and 1,10-phenanthroline is practical and sensitive. An excess of reducing reagent, such as hydroxylamine or hydroquinone, is needed for iron(III)[1−7].

In the transition series elements zinc(II), copper(I) and copper(II) would be expected to form labile outer orbital complexes with 1,10-phenanthroline since all their 3d are already occupied. Quantitative observations confirm that their rates of reaction with 1,10-phenanthroline are faster than iron(II) (ferroin forms). Nickel(II), however, despite the presence of eight electrons in the 3d orbitals, reacts slowly with 1,10-phenanthroline and mon-, bis and tris-1,10-phenanthroline complexes of nickel(II) have been reported. The manganese complex is much weaker than the iron(II) complex[8].

This paper describes a simple and accurate visible spectrophotometric method and optimum conditions for the direct determination of iron(II). The method is based on a complex formation between iron(II) and

NAF to give an orange-red product showing maximum absorbance at 520 nm. A Fe(II) ion (Lewis acid) reacts with a NAF molecule $C_{12}H_8N_4O_2$ (Lewis base) to form the $[Fe(NAF)_3]^{2+}$ ion.

Experimental

Apparatus: Absorbance measurements were made on a Philips PU 8700 UV-visible single-beam spectrophotometer with a 1 cm glass cell. A circulation thermostat water bath was used for temperature control. All pH measurements were made using a calibrated Metrohm E-510 pH meter with a 6.0204.000 combined glass electrode.

Chemicals: All the chemicals used were analytical reagents or of pure grade; distilled water and 95-100% redistilled ethyl alcohol were also used.

5-Nitro-6-amino-1,10-phenanthroline (NAF) was synthesized in our laboratory as described in the literature[9,10].

Solutions: A stock standard solution of iron(II) (1000 μg/mL) was prepared by dissolving 7.01g $Fe(NH_4)_2(SO_4)_2.6H_2O$ and 1 to 2 mL of concentrated H_2SO_4, which was then diluted to 1 l with water ($K_2Cr_2O_7$ is an oxidimetric primary standard).

Working standard Fe(II) (25 μg/mL) was prepared daily from stock solution by appropriate dilution with water. The working standard contained 0.5% $H_2NOH.HCl$.

Standard metal solutions 587 μg/mL Ni (II) (0.01 M), 589 μg/mL Co(II) (0.01 M) 635 μg/mL Cu (II) (0.01 M), 400 μg/mL Ca (II) (0.01 M), 549 μg/mL Mn(II) (0.01 M), 267 μg/mL Al (III) (0.01 M), 243 μg/mL Mg(II) (0.01 M), and 635 μg/mL Zn(II) (0.01 M) were prepared following appropriate dilution from 0.1 M metal solutions in ethanol.

A sample of 107 μg/mL reagent (NAF) (saturated solutions at 20 °C) was prepared in absolute ethanol.

Buffer solutions were prepared by **x** mL 2 M NaOAc added to (10-x) mL 2 M acetic acid and then diluted to 100 mL with water.

Determination of Fe(II) in optimum conditions: Solutions of 0.4-1.4 mL (0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 mL respectively) standard Fe(II) (25 μg/mL) were transfered into a 10 mL volumetric flask 2 mL of pH 4 buffer and 5 mL of 107 μg/mL NAF. The solutions were diluted with water to 10 mL. The concentrations of Fe(II) used were 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 μg/mL in a 10 mL volumetric flask. After shaking manually, the mixture was allowed to stand for 210 min at 20 °C. The absorbances were measured 520 nm against blank solutions and a calibration curve was prepared. Unknown test solutions were determined directly using the graph.

Results and Discussion

The complex formation between Fe(II) and NAF was performed in ethyl alcohol medium because NAF dissolves very weakly in other solvents such as chloroform, aceton, ethyl acetate, ether, methanol and dichloro methane. Solubility in dimethyl sulfoxide is better the others, though the working conditions are not practical. The absorbtion spectrum of the product showed maximum at 520 nm. The optimum conditions of the method were investigated as follows.

Effect of Reagent Amount

The effect of reagent amounts 107 μg/mL for determination of 2.5 μg/mL iron(II) were examined at 20 °C. The optimum amount of standard 107 μg/mL NAF solution was found to be 5 mL at 0.628 absorbance value. Precipitate was shown when added below 1 mL reagent. The average values of three determination results are given in Table 1.

Table 1. Effect of reagents (iron(II) present in the solution: 2.5 μg/mL).

NAF soln. in et.ol (mL)	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Absorbance	0.458	0.589	0.598	0.601	0.610	0.612	0.625	0.628	0.628

Effect of Temperature

The effect of temperature on the reaction was observed for eight different temperatures under optimum conditions. The highest absorbance was determined at 20 °C as shown in Figure 1.

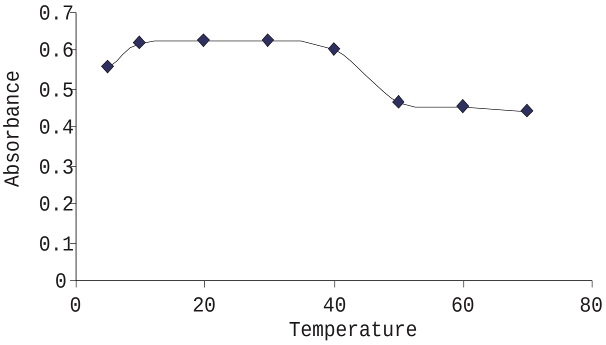

Figure 1. Effect of temperature on the reaction for 2.5 μg/mL iron(II) conc.

Effect of Time

The effect of time on the reaction was observed from 15 min to 300 min under optimum conditions. Optimum results were obtained at 20 °C and 210 min. The absorbance was found to be stable for at least 1.5 h as shown in Figure 2.

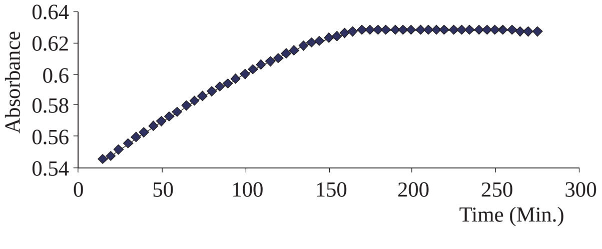

Figure 2. Determination of suitable time for Fe(II)-NAF reaction for iron(II): 25 μg/mL. (Average value of six determinations).

Effect of pH

The procedure was repeated at different pH values between 2.0 and 5.9 with the same amounts of iron(II) (2.5 μg/mL). Absorbance was measured at 20 °C under optimum conditions. Color development (absorbance) was slow below 3.4 and above pH 5. The optimum pH therefore lies between 3.4 and 4.5, and a reading can be taken after 210 min standing. Suitable result were obtained at pH 4 and 210 min. Absorbance and pH values versus time are shown in Figure 3.

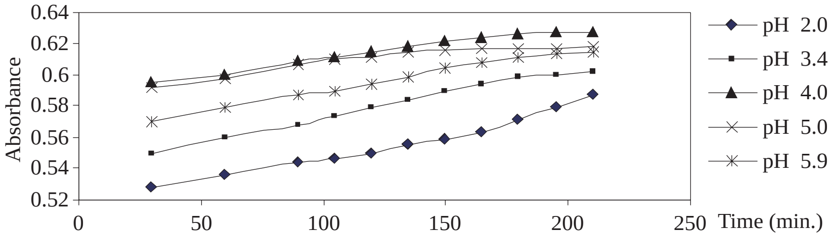

Figure 3. Effect of pH depend on time to absorbance of NAF-iron(II) complex (iron(II) present in the solution: 2.5 μg/mL and average absorbance value of four determination).

Calibration Curve

Under the experimental conditions a linear correlation was obtained between absorbance and Fe(II) concentration over the range of 0.1-4 μg/mL; the regression equation for the straight line was A = 0.249C + 0.0014, where A is the absorbance at 520 nm and C is the concentration of iron(II) (μg/mL) (r = 0.9999). The detection limit is 0.1 μg/mL. The standard and relative standard deviation of the slope and intercept are 0.001-0.016 and 0.57%-2% respectively (n: 7) (Figure 4).

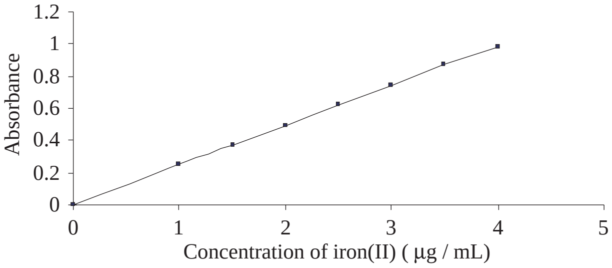

Figure 4. Calibration curve for the determination of iron(II) at optimum conditions (Average value of six determinations).

Mole Ratio Method

A Job's contunious variation method[11] plot of spectrophotometric data from varying the NAF and Fe(II) concentration at pH 4, showed the existence of a 1 to 3 complex, which is assumed to be a tris(5-nitro-6-amino-1,10-phenanthroline)iron(II) complex (Figures 5 and 6).

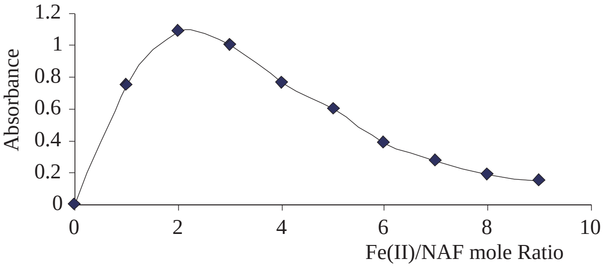

Figure 5. Determination of mole ratio.

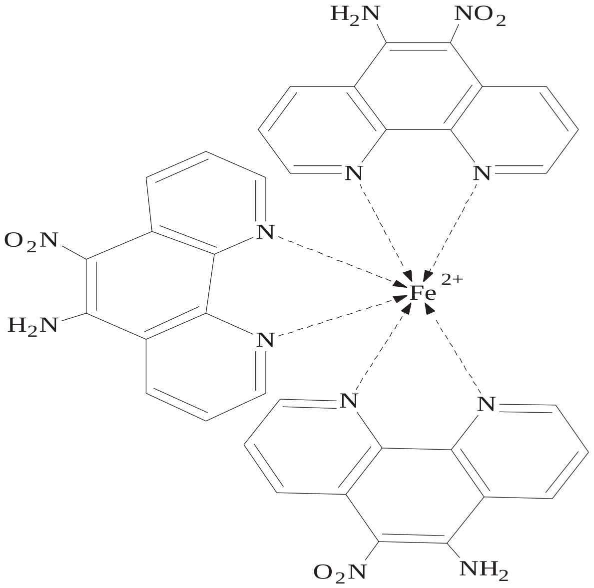

Figure 6. Tris(5-nitro-6-amino-1,10-phenanthroline)iron(II).

Interference study

A number of transition, earth alkaline and earth metal ions were studied for their possible interference in the determination of Fe(II). Co(II), Ni(II) and Cu(II) were found to interfere rather severely, while Zn(II), Mn(II), Al(III) and Ca(II) interfere weakly and Mg(II) does not interfere by this method. Interferences can be obviated by using secondary masking agents. Tolerance limits for the determination results of 2.5 μg/mL iron(II) in Ni(II), Co(II), Cu(II), Zn(II), Mn(II), Al(III), Ca(II) and Mg(II) are given in Table 2. A calibration curve was used for the determination of iron(II) (Figure 4).

Iron(II) can be determined in concentrations below 2.90 μg/mL Ni(II), 5.70 μg/mL Co(II), 4.40 μg/mL Cu(II), 3.10 μg/mL Zn(II), 4.50 μg/mL Mn(II), 0.40 μg/mL Al (III) and 2.43 μg/mL Mg(II). Ca(II) can't be determined, examined concentration because of precipitation by this method.

The effect of interference can be minimized by adjusting the pH within a narrow range. The interference of various catios can be studied and the method applied for the analysis of iron(II) in its alloy and biological materials.

In this work, 1,10-phenanthroline and thiocyanate have been studied for the determination of the same concentration of iron(II). These results were compared with 5-nitro-6-amino-1,10-phenanthroline (NAF). The comparative spectroscopic results are shown in Table 3. In conclusion, NAF has greater sensitivity than other examined reagents because the -NO_2 and -NH_2 are chromofore and oxochrome groups respectively[12,13] for the determination of Fe(II). The compound NAF has a molar absorbancy index of 13,900 for iron. This reagent makes it possible to measure small amounts of iron than can be measured with thiocyanate and 1,10- phenanthroline reagents.

Table 2. Spectrophotometric determination of Fe(II) in presence of diverse metal ions.

Diverse ions with 2,5 μg/mL Fe(II)	Quantity added metal (μg/mL)	Fe(II) found with spectrophotometric method* (μg/mL)
Ni(II)	2.90 5.87 11.74 17.61	2.500 2.055 1.369 1.163
Co(II)	5.70 5.89 11,78 17.67	2.500 2.459 1.237 0.705
Cu(II)	4.40 6.35 12.70 19.05	2.500 2.114 0.657 0.404
Zn(II)	3.10 6.53 13.06 19.59	2.500 2.398 2.041 0.914
Mn(II)	4.50 5.49 10.98 16.47	2.500 2.492 2.492 2.019
Al(III)	0.40 2.67 5.38 8.01	2.500 2.184 2.015 1.821
Ca(II)	2.00 4.00 6.00	Specptrophotometric determination was not possible due to precipitation
Mg(II)	2.43 4.86 7.29	2.496 2.474 2.411

*Average value of three determinations.

Table 3. Spectrophotometric determination of Fe(II) using thiocyanate, 1,10-phenanthroline and NAF reagents.

	λmax (mμ)	Applicable (μg/mL)	Molar Abs. Index
Thiocyanate [a]	470	1-10	6,900
1,10-Phenanthroline [a]	510	0.5-8	11,100
NAF	520	0.1-4	13,900

[a] Spectroscopic result are suitable with the literatures (2,5,14).

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