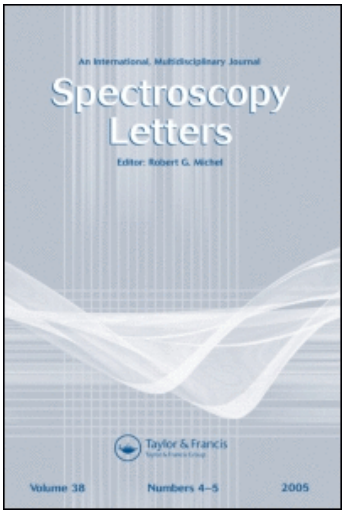

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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF IRON(II) AND IRON(III) IN MIXTURES USING DI-2-PYRIDYL KETONE BENZOYLHYDRAZONE

KEY WORDS: Iron(II), Iron(III), Di-2-Pyridyl Ketone Benzoylhydrazone, Spectrophotometric Determination.

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ABSTRACT

A method for simultaneous spectrophotometric determination of total iron, iron(II) and iron(III) in mixtures containing other metal ions has been described. The method is based on

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the complexation of iron with di-2-pyridyl ketone benzoylhydrazone (DPKBH) in 50% (v/v) ethanolic solution. Iron(II) complex with DPKBH exhibits two absorption maxima at 360 and 650 nm, meanwhile iron(III) complex with DPKBH exhibits only one maximum at 360nm. Iron(II) and iron(III) complexes with DPKBH have similar behaviour at 360nm. Iron forms 1:2 complexes with the reagent. Beer's laws are obeyed over the ranges 0.1-2 $\mu g ml^{-1}$ and 0.4-5 $\mu g ml^{-1}$ for iron(II) complexes at 360 and 650nm respectively. Iron(III) showed results similar to those obtained for iron(II) at 360nm. The effect of pH, effect of excess reagent, the stability of complexes, and the tolerance limit of many metal ions have been reported. The method is applied to the determination of total iron, iron(II), and iron(III) in synthetic solutions.

INTRODUCTION

Nitrogen - containing heterocyclic hydrazones have been widely used as analytical reagents since they can be readily synthesized and give sensitive reactions with most of metal ions (1).

Recently, several nitrogen-containing heterocyclic hydrazones have been suggested for the spectrophotometric determination of Fe(II), among which are 2,2'-dipyridyl-2-quinolylhydrazone(2),2,2'-dipyridyl-2-furancarbothiohydrazone (3), 2-(3-sulfobenzoyl)pyridine benzoylhydrazone(4), di-2-pyridyl ketone benzoylhydrazone(5).

In the present work, a new sensitive and selective method has been described for simultaneous spectrophotometric

determination of Fe(II) and Fe(III) in aqueous solution using di-2-pyridyl ketone benzoylhydrazone without extraction.

EXPERIMENTAL

REAGENTS:

All reagents and solvents were of analytical-reagent grade

Di-2-pyridyl ketone benzoylhydrazone(DPKBH).The ligand was prepared by interaction of di-2-pyridyl ketone and benzoylhydrazone in stoichiometric amounts and was recrystallized from ethanol to a constant melting point (130-132 ^{o}C) (1). The purity of the prepared compound was checked by elemental analysis and the structural form was also confirmed by the infrared spectrum of the ligand measured using potassium bromide disk.

Standard iron(II) solution 10^{-2} M. Ammonium iron(II) sulfate was dissolved in water, acidified with sulfuric acid and standardized titrimetrically(6).

Standard iron(III) solution 10^{-2} M. Iron chloride was dissolved in water and the solution was standardized titrimetrically (7).

Buffer solutions.The buffer solutions used,were perchloric acid for pH values below 3.5, acetic acid-sodium acetate mixtures for pH in the range 3.5 to 6.0, boric acid - borax mixtures for pH in the range 6.5-9.2, and sodium hydroxide - borax mixtures for pH above 9.2.

Apparatus

A Pye-Unicam SP8-100 spectrophotometer was used with a quartz cell(1x1cm). The pH of the solutions were checked

using a Corning model 12 pH meter. All measurements were performed at 22°C.

Procedures:

Three procedures are presented depending on whether iron(II), iron(III) or total iron need to be determined.

A procedure for Iron(II):

A portion of solution containing an amount of iron(II) in the range 2-140 μg is transferred into a 25-ml volumetric flask, then 1 ml of 10^{-3} M DPKBH is added followed by 7.5 ml ethanol, and the volume is completed with the buffer solution (pH 5). The absorbance is measured after 2 min. at 360 nm against a reagent blank as a reference. If the absorbance is higher than 1, then it can be remeasured at 650nm against a reagent blank as a reference. The amount of iron(II) present can be calculated from a previously prepared calibration curves (Fig.1 A and B).

A procedure for Iron(III):

A portion of solution containing an amount of iron(III) in the range 2-50 μg is transferred into a 25-ml volumetric flask, then 1ml of 10^{-3}M DPKBH is added followed by 7.5ml ethanol, and the volume is completed with the buffer solution (pH 5). The absorbance is measured after 2 min. at 360nm against a reagent blank as a reference. The amount of iron (III) present can be calculated from a previously prepared calibration curve (Fig. 1 A).

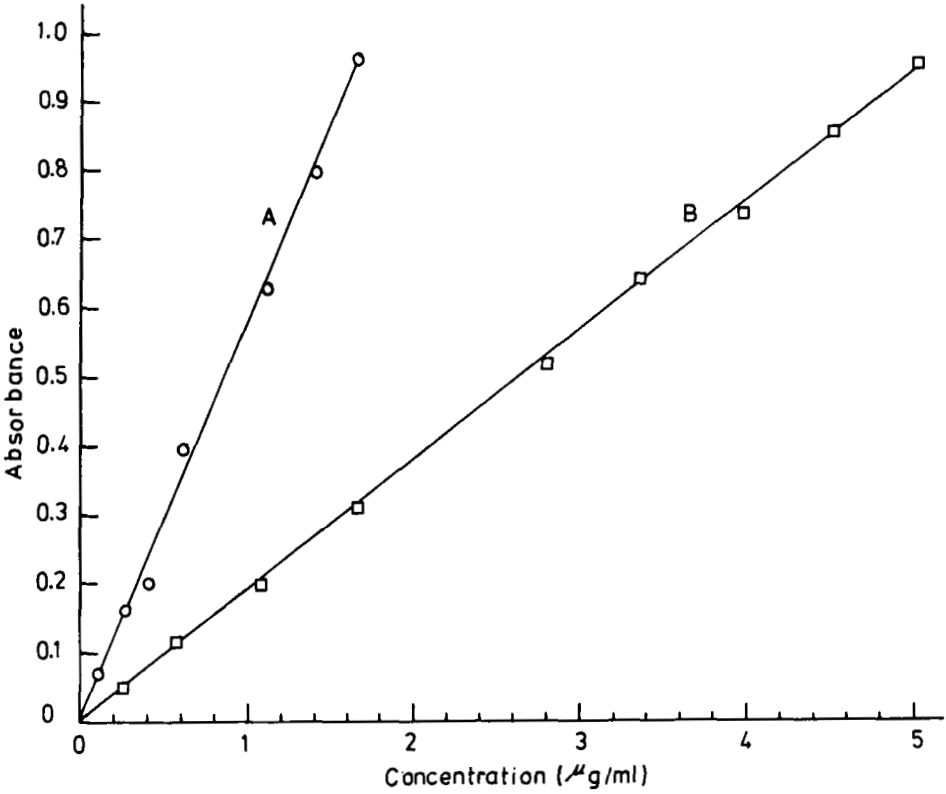

Fig. 1: Calibration curves for :

(A) absorbance as a function of total iron concentration at 360nm.

(B) absorbance as a function of iron(II) concentration at 650 nm.

A procedure for a mixture of Iron(II) and Iron(III):

A portion of solution containing a total amount of iron in the range 2-50 μg is transferred into a 25-ml volumetric flask, then 1ml of 10^{-3}M DPKBH is added followed by 7.5 ml ethanol, and the volume is completed with the buffer solution

(pH 5). The absorbances are measured at 360nm and 650nm against a reagent blank as a reference. The total amount of iron can be calculated from calibration curve A Fig.1, while the amount of iron(II) can be calculated from calibration curve B Fig.1 Subtracting the amount obtained from curve B from the amount obtained from curve A, gives the amount of iron(III) present in the mixture.

RESULTS AND DISCUSSION

Absorption Spectra:

The absorptions of DPKBH and its complexes with iron(II) and iron(III), prepared according to the recommended procedures, were studied at pH 5 in 50% (v/v) aqueous ethanolic solution over the wavelength range 300-700nm.It was found that iron(II) complex exhibits two absorption maxima at 360nm and at 650nm as shown in Fig.2. Meanwhile, iron(III) complex exhibits only one maximum at 360nm. Spectral interference of the reagent can be eliminated by measurements against a reagent blank solution.

Effect of pH:

The effect of pH on the absorbance of iron(II) and iron (III) complexes with DPKBH was studied in the pH range 2-11.6, using solutions prepared as described in the general procedures. The results obtained showed that iron(II) complex has maximum absorbances at 360 nm and 650 nm in the pH range 4-7.4, while iron(III) complex has a maximum absorbance at 360 nm in the same pH range. So all the measurements take place at pH 5.0.

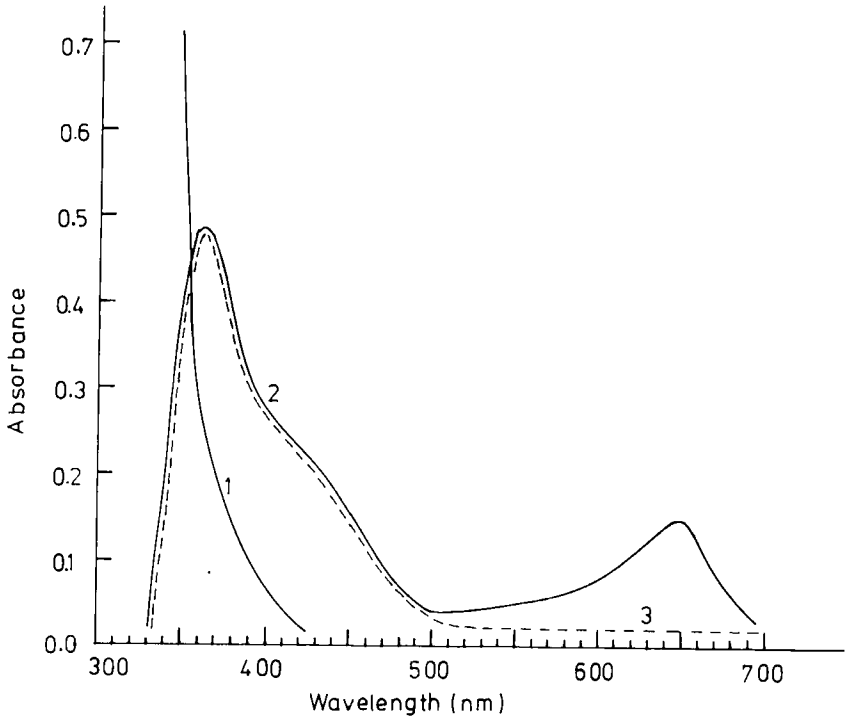

Fig. 2: Absorption spectra for:

(1) 4 x 10^{-5} M DPKBH.

(2) Iron(II) - DPKBH complex at iron(II) conc. of 0.8 μg ml^{-1} with reagent blank as a reference.

(3) Iron(III) - DPKBH complex at iron(III) concentration of 0.8 μg/ml with reagent blank as a reference.

Composition of the complexes:

The compositions of iron(II) and iron(III) complexes with DPKBH were established by continuous variation and mole ratio methods.Plots of both methods suggested that iron(II) : DPKBH ratio of 1:2 at 360nm and at 650nm, while iron(III) showed a 1:2 ratio at 360nm, which confirm that iron(II) and iron(III) form identical complexes with DPKBH in aqueous solutions.

Effect of Excess Reagent:

The absorbances of iron(II) and iron(III) complexes with DPKBH exhibit dependence on reagent concentration. In the course of the present work the effect of excess reagent was studied at both 360nm and 650nm at pH 5.0 and in the presence of 50% ethanol. It was found that keeping the iron concentration fixed and increasing the reagent concentration, affected an increase in the absorbances up to an iron: reagent mole ratio of 1:3 beyond which any further increase did not affect the absorbance.

Stability of the complexes:

The color of iron(II) and iron(III) complexes with DPKBH are attained within 1 min. after the addition of iron(II) and /or iron(III) ions and the color intensity remains constant for at least 12 hrs. The value of the apparent stability constant ($\log \beta$) and the free energy change of the formation of the complexes ($-\Delta \overset{\bullet}{G}$) were presented in Table 1.

Beer's Laws and Sensitivities:

Following the recommended procedures, calibration curves for iron(II) at 360nm and 650nm, and for iron(III) at 360nm were established. The results obtained are shown in Fig.1. A rectilinear relationship is obtained between the absorbance and the concentration of iron(II) within the range 0.1-2 $\mu g ml^{-1}$ at 360nm (Fig.1A) and within the range 0.4-5 $\mu g\ ml^{-1}$ at 650nm (Fig.1B). Iron(III) showed similar results to those obtained from iron(II) at 360 nm.

Precision and accuracy:

The precision of the methods was estimated for 27 μg of

Table 1

The Apparent Stability Constant of iron(II) and iron(III) complexes with DPKBH at pH 5.0 in presence of 50% aqueous Ethanol.

Type of Complex	λmax (nm)	Molar absorptivity $l.mol^{-1}.cm^{-1}(x10^{4})$	Stability constant (log β)	$-\Delta G^{\circ}$ $KCal.mol^{-1}$	Relative Standard Deviation*
Fe(II) :DPKBH	360	3.0	8.98	10.85	5.6 %
Fe(II) :DPKBH	650	1.1	7.95	10.80	4.3 %
Fe(III):DPKBH	360	2.9	7.97	10.83	5.5 %

* 6 determinations for each

iron. The relative standard deviations are presented in Table 1.

Effect of foreign ions:

The effect of foreign ions was studied for the determination of 27 μg of iron. The results obtained are presented in Table 2. The cations were added in the form of chlorides, nitrates, or sulfates. All the interferred ions showed a positive interference except platinum(II) and phosphate which showed negative interferences.

Table 2

Effect of Foreign Ions on Determination of 27 μg of Iron.

Ion	Tolerance Limit(μg) In The Determination of Iron(II) and Total Iron	
	(at 650 nm) Iron(II)	(at 360 nm) Total Iron
Pd(II)	10,000	25
U(V1)	10,000	300
Pt(II)	100	50
Cu(II)	10,000	25
Co(II)	25	10
Hg(II)	10,000	25
Ni(II)	25	10
PO_4^{3-}	90	50
Li(I),Na(I),Ag(I),Be(II), Mg(II),Mn(II),Ca(II),Ba(II), Pb(II),Al(III),La(III),Cr(III) Th(IV),Cd(II),and Ce(III).	10,000	10,000
Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-}, CH_3COO^- , and Borax.	10,000	10,000

Table 3

Application to the Determination of Total iron, Iron(II), and Iron(III) in Synthetic Samples Containing Different Amounts of Other Metal Ions.

No.	Composition of Synthetic Mixture (μg/25ml)	Iron Found (at 650nm) Iron(II)	Iron Found (at 360nm) Total Iron
1.	Fe(II) 27	27	25
2.	Fe(III) 14	--	14
3.	Fe(II) 27, Fe(III) 14	28	40
4.	Fe(II) 18, Fe(III) 7	19	25
5.	Fe(II) 18, Fe(III) 7, Pt(II) 50, U(VI) 100.	19	27
6.	Fe(II) 27, Fe(III) 14, Cu(II) 10, Ni(II) 10.	29	42
7.	Fe(II) 18, Fe(III) 7, Pt(II) 50.	16	25

Applications:

The method was applied to the determination of total iron, iron(II), and iron(III) in synthetic samples containing different amounts of other metal ions. The results obtained are presented in Table 3. By subtracting the amounts obtained at 650nm [iron(II)] from those obtained at 360nm [total iron]

the amount of iron(III) that is present in the samples can be obtained.

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