

Derivative Spectrophotometric Determination of Iron(II) Using Diacetylmonoxime Benzoyl Hydrazone

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Diacetylmonoxime benzoyl hydrazone is a chromogenic reagent for the determination of Fe(II) and gives a yellow coloured water-soluble complex with Fe(II) in acidic buffer medium (pH 6.25). The molar absorptivity and Sandell's sensitivity of the complex at λ_{\max} 360 nm is found to be $1.25 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0045 \mu\text{g/cm}^2$ of Fe(II) respectively. Beer's law validity range is from 0.11–2.24 $\mu\text{g/mL}$. Iron(II) gives 1 : 1 (M : L) complex with diacetylmonoxime benzoyl hydrozone and stability constant of the complex is 1.1×10^4 . The developed direct and first order derivative spectrophotometric method was employed for the determination of iron in alloy samples and effect of various diverse ions is also studied.

Key Words: Iron(II), Alloys, Derivative spectrophotometric method, Diacetyl monoxime benzoyl hydrazone.

INTRODUCTION

The analytical applications of hydrazone derivatives have been reviewed by Singh *et al.*¹ In continuation of ongoing work on the analytical applications of oxime-hydrazones^{2–4}, the derivative spectrophotometric determination of Fe(II) using diacetylmonoxime benzoyl hydrazone (DMBH) has been reported. The derivative technique⁵ is a very useful technique because it is the key for the potential enhancement of resolution of overlapping bands, facilitates the detection of poorly resolved absorption peaks arising from admixtures or impurities in solution or for structural reasons and it enables the exact determination of λ_{\max} of the particular analyte species and increases the sensitivity of spectrophotometric procedures. In addition, it is an excellent background elimination technique and it decreases the interference of foreign ions, and may be advantageously used for the determination of metal ions. Recently, many authors^{6–8} reported derivative spectrophotometric determination of various metal ions.

EXPERIMENTAL

The ligand, diacetylmonoxime benzoyl hydrazone (DMBH) is synthesized as described earlier³. The reagent solution (0.01 M) was prepared by dissolving 200 mg of the compound in 100 mL of dimethyl formamide. Hydrochloric acid (1 M)-sodium acetate (1 M) (pH 0.5–3.5), acetic acid (0.2 M)-sodium acetate (0.2 M) (pH 4.0–6.0) and ammonium hydroxide (2.0 M) ammonium chloride (2.0 M) (8.0–11.0) are used in the determination of pKa values of reagents. The standard Fe(II) solution (1×10^{-2} M) was prepared using analytical reagent grade ferrous ammonium sulphate (AR Merck). Solutions of diverse ions of suitable concen-

trations are prepared using AR grade chemicals. Shimadzu 160 A UV-Visible spectrophotometer equipped with 1.0 cm quartz cells and an Elico model L1-120 digital pH-meter were used in the present investigation.

Direct spectrophotometry: An aliquot of the solution containing 0.11–2.24 $\mu\text{g/mL}$ of Fe(II), 10 mL of buffer solution ($\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$) (pH 6.25) and 1 mL of 0.01 M DMBH reagent were taken in a 25 mL volumetric flask and the solution was diluted to the mark with distilled water. The absorbance of the solution was recorded at 360 nm (Fig. 1) against the corresponding reagent blank. The measured absorbance was used to compute the amount of Fe(II) from predetermined calibration plot.

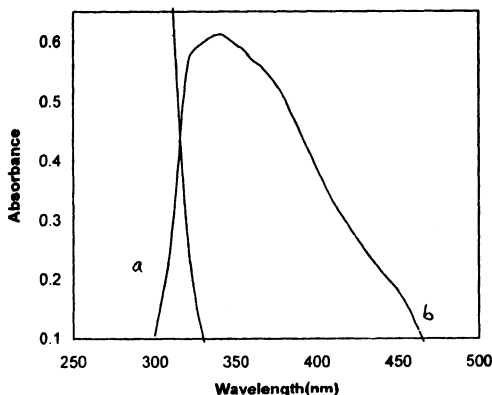


Fig. 1. Absorption spectra of (a) DMBH vs. water blank, (b) Fe(II)-DMBH vs. reagent blank, Fe(II) = 4×10^{-5} M, [DMBH] = 4×10^{-4} M, pH = 6.25

First derivative spectrophotometry: For the above solution, first order derivative spectra (Fig. 2) were recorded with a scan speed fast having a degree of freedom 9, in the wavelength range 300–600 nm. The derivative peak height was measured by peak zero method at 400 nm.

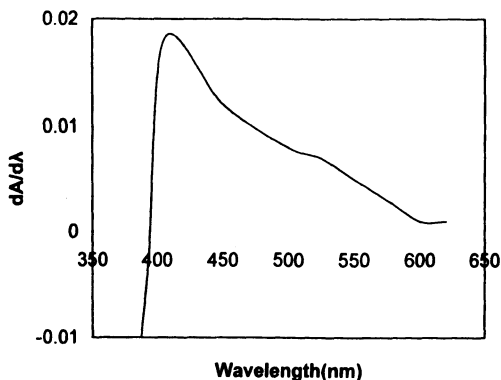


Fig. 2. First derivative spectrum of DMBH vs. reagent blank, Fe(II) = 2.234 $\mu\text{g/mL}$, [DMBH] = 4×10^{-4} M, pH = 6.25

The peak height was plotted against the amount of Fe(II) to obtain the calibration curve (Fig. 3).

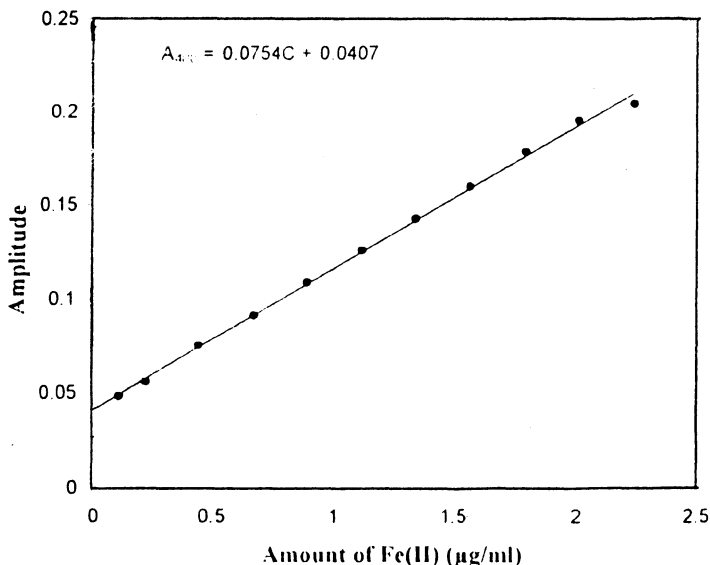
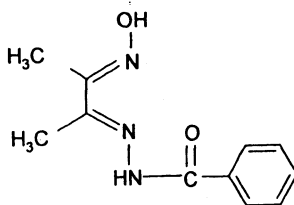


Fig. 3. First derivative amplitude vs. amount of Fe(II) ($\mu\text{g/mL}$); $\text{pH} = 6.25$, $[\text{DMBH}] = 4 \times 10^{-4} \text{ M}$, wavelength = 400 nm

Analysis of alloys: A solution of the alloy (50–100 mg) was prepared in aqua regia. An aliquot was taken, treated with 10% hydroxylamine hydrochloride (4 mL) and stock solution was prepared.

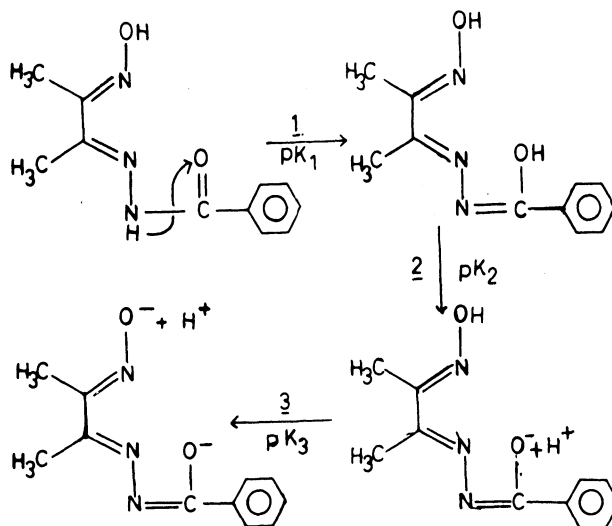
RESULTS AND DISCUSSION

The reagent diacetylmonoxime benzoylhydrazide (DMBH) (I) is prepared by simple condensation of one mole of diacetylmonoxime with benzhydrazide.



DMBH (I)

The pK_a values are determined by recording the UV-Visible spectra of micro molar (10^{-6} M) solution of the reagent at various pH values. The values of the deprotonation of DMBH reagent are found to be 3 (pK_1), 7 (pK_2) and 9 (pK_3). The pK_1 and pK_2 may be assigned to the deprotonation of imine ($-\text{NH}$) through enolization and deprotonation of enol, while pK_3 is assigned to the deprotonation of oxime hydrazone ($=\text{N}-\text{OH}$). The possible species which may be formed at different pH values shown in Scheme-1.



Scheme-1

Diacetylmonoxime benzoylhydrazone (DMBH) reagent is a blend of two functional groups, viz., oxime and hydrazone. The reagent solution is found to be stable for 60 min. The complex formation reactions between Fe(II) and DMBH have been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. The various physicochemical and analytical properties of Fe(II)-DMBH complex are presented in Table-1.

TABLE-1
PHYSICOCHEMICAL AND ANALYTICAL CHARACTERISTICS OF
IRON(II)-DMBH COMPLEX

Characteristics	Results
λ_{\max} (nm)	360
pH range (optimum)	6.0–6.5
Mole of reagent required per mole of metal ion for full colour development	10
Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	1.25×10^4
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.00446
Beer's law validity range ($\mu\text{g}/\text{mL}$)	0.11–2.24
Optimum concentration range ($\mu\text{g}/\text{mL}$)	0.45–2.02
Composition of complex (M : L) obtained in Job's and mole ratio method	1 : 1
Stability constant of the complex	1.1×10^4
Standard deviation in the determination of 1.12 $\mu\text{g}/\text{mL}$ of Fe(II) for ten determinations	0.0024
Relative standard deviation	0.22%

Interference

The effect of various diverse ions in the determination of Fe(II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance or amplitude. The results are given in Table-2. The data

obtained in the first derivative method is also incorporated. The data suggested that several associated anions and cations do not interfere when they are present in large excess. The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as Fe(III), Cu(II) and Al(III) is decreased with fluoride, thiourea and triethanolamine.

TABLE-2
TOLERANCE LIMIT OF FOREIGN IONS IN THE DETERMINATION OF
(1.12 µg/mL) IRON(II)

Ion added	Zero order (µg/mL)	First derivative (µg/mL)	Ion added	Zero order (µg/mL)	First derivative (µg/mL)
Iodide	1015	1025	Bi(III)	42	49
Thiourea	913	924	Al(III)*	32	38
Bromide	768	769	Mg(II)	19	24
Thiocyanate	580	584	Zr(II)	18	25
Urea	480	480	Mn(II)	11	15
Phosphate	460	462	Cu(II)†	8	12
Nitrate	446	460	W(V)	7	10
Acetate	424	437	Al(III)	6	09
Hypo	408	420	Pb(II)	5	08
Chloride	341	356	Cd(II)	3.5	07
Triethanolamine	176	186	Ag(I)	3.0	06
Tartarate	147	149	Mo(II)	3.0	7.5
Fluoride	114	119	Zn(II)	4.0	5.5
Citrate	45	52	Fe(III)‡	5.0	6.5
Oxalate	30	38	V (V)	3.5	5.5

*Masked by triethanolamine (220 µg/mL)
by fluoride (100 µg/mL).

†Masked by thiourea (300 µg/mL)

‡Masked

TABLE-3
ESTIMATION OF IRON IN ALLOY SAMPLES

Name of the sample	Iron (%)		
	Certified value	Amount found*	Error (%)
(a) BAS-85a	1.150	1.18	+2.60
(b) Ferrovandium (BCS-205/3)	47.217	46.60	-1.30
(c) Lincolnrshire iron ore (BSC-301/1)	23.800	24.20	+1.68

Average of five determinations

Al(III) is masked by triethanolamine.

a = Cu 0.90%; Ni 0.91%; Mn 0.02%; Si 2.04%; Mg 0.18%; Zn 0.01%; rest Al.

b = Ni 0.053%; Al 0.414%; Cu 0.054%; V 50.16%

c = SiO₂ 7.40%; Al₂O₃ 4.26%; TiO₂ 0.16%; CaO 22.6%; MgO 1.73%; Na₂O 0.07%; K₂O 0.32%; S 0.040%; P 0.35%; Mn 0.970%.

Applications

The developed method was applied to the determination of Fe(II) in various alloy samples (Table-3) and also compared with recently reported spectrophotometric methods (Table-4). The method using DMBH is found to be more sensitive and selective for the spectrophotometric determination of iron(II) in aqueous medium.

TABLE-4
COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR THE
DETERMINATION OF IRON(II)

Reagent	λ_{\max} (nm)	pH	Molar absorptivity (ϵ) ($L \text{ mol}^{-1} \text{ cm}^{-1}$)	Extraction	Beer's law range	Ref.
Di-(2-pyridyl) ketoxime	534	10.5–13.5	1.5×10^4	Chloroform	Upto 4 ppm	9
Di-pyridyl ketone thiosemicarbazone	620	2.5–7.5	0.93×10^4	—	1–4 ppm	10
2-acetyl pyridine-4- phenyl thiosemi- carbazone	650	4.9–11.0	0.68×10^4	Benzene	2–9 ppm	11
2,2'-dipyridyl ketone 2-pyrimidyl hydrazone	540	1.5–2.5	1.15×10^4	—	Upto 5 ppm	12
2,2'-dipyridyl-2,4-dioxy benzoic acid	523	2.0–8.0	7.2×10^3	—	1.4–56 $\mu\text{g/mL}$	13
Diacetyl monoxime benzoyl hydrazone	360	6.25	1.25	Aqueous	0.11–2.24 $(\mu\text{g/mL})$	Present method

REFERENCES

1. R.B. Singh, P. Jain and R.P. Singh, *Talanta*, **29**, 77 (1982).
2. M. Ramesh, K.B. Chandra Sekhar and K.H. Reddy, *Indian J. Chem.*, **39A**, 1337 (2000).
3. K.B. Chandra Sekhar and K.H. Reddy, *J. Indian Chem. Soc.*, **78**, 340 (2001).
4. ———, *J. Indian Coun. Chem.*, **18**, 1 (2001).
5. L. Sommer, *Analytical Absorption Spectrophotometry in the Visible and Ultra-violet*, Elsevier, Amsterdam, p. 186 (1989).
6. O. Babaiah, C.K. Rao, T.S. Reddy and V.K. Reddy, *Talanta*, **43**, 551 (1996).
7. N. Devanna, K.B. Chandra Sekhar and K.N. Jayaveera, *Asian J. Chem.*, **16**, 1889 (2004).
8. K.B. Chandra Sekhar and K.H. Reddy, *Res. J. Chem. Environ.*, **8**, 12 (2004).
9. J.L.A. Alduan, J.R.C. Suaruz and J.F.C. Palomer, *Rev. Acad. Liencie, Exactus, Fisquim. Nat. Zaragoza*, **31**, 91 (1976).
10. M.P. Martinez, M. Valcarcel and F. Pino, *Anal. Chim. Acta*, **81**, 157 (1976).
11. M.T. Martinez Aguilar, J.M. Canopavon and F. Pino, *Anal. Chim. Acta*, **90**, 335 (1977).
12. R.B. Singh, B.S. Garg and R.P. Singh, *Indian J. Chem.*, **17A** (1979).
13. Liu-Gureau, Dumitru, Zait, Gheorghe, Mereanu, Vasile, Rusu, Valentine, Plaugue and Victor, *Bull. Acad. Stiinite Repas. Mold. Stiinite Biol. Chim.*, **6** (1995).