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Synthesis, characterisation and spectrophotometric determination of Fe(II) complex of 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone{(E)-N'-(2,4-dihydroxybenzylidene)isonicotinohydrazide, it's application & biological activity

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ABSTRACT

Synthesis of 2,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone. Melting point,Elemental analysis,Effect of diverse ion and Antimicrobial activity are studied. A simple,Sensitive and specific spectrophotometric method for the determination of Fe (II) is developed based on the colour reaction between iron (II) and 2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone[2,4-DHBINH]. The optimum condition for complete colour development have been established by studying parameters like Effect of medium,Reagent concentration,Time period. Stability constant, Dissociation constant and Change in the free energy of the complex are determined. Composition of the metal and ligand has been determined by Job's variation and mole ratio method. Application of this 2,4-DHBINH for antimicrobial activity and determination of iron in the potable water have been performed.

Keywords: Iron(II)*,2,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone*, Spectrophotometry, *Antimicrobial Samples*, Water Samples.

INTRODUCTION

Iron is a key element in industries and play a vital role in Science technology, Health, Science and Metallurgy. Biologically iron is involved in different processes. As an oxygen carrier in blood of mammals ,birds and fish (haemoglobin),electron carrier in plants,animals and bacteria (cytochrome), oxygen storage in muscle tissue (myoglobin),storage of Fe in animals (Ferretin & transferring) & number of other enzymes like aldehyde oxidase (oxidation of aldehyde) ,catalase & peroxidase (decomposition of H_2O_2),succinnic dehydrogenase (the aerobic oxidation of carbohydrates.

Iron has been determined by flame atomic absorption spectrophotometer after preconcentration by Escherichia Coli immobilized on Sepiolite.[1] Iron (III) forms complexes with new quadridentate N,O donar ligand has been reported by Swamy et.[2] Thermogram for Fe (II) complexes show second stage mass loss curve at 420^0 to 560^o with corresponding exothermic peak at DSC at 820^o in Fe(III) complex that the water molecules are coordinated [3] Iron (III) have been determined by using pyridoxal-4-phenyl-3-thiosemicarbazone by sensitive & extractive spectrophotometric method .[4] The spectrophotometric methods for iron (III) determination exhibit moderate sensitivity .[5-14] Iron (II) & iron (III) in pharmaceutical products have been determined in asynchronous merging zones system spectrophotometrically.[15]

The stability constants of iron, cobalt & nickel complexes with O-methoxybenzoic acid 7 nitrilotriacetic acid are found to decrease in the order Ni > Co > Fe > Mn which is in accordance with the values reported earlier [16] and Irving-Williams order.[17] Ligand of iron having quinazoline 4 (3H) one, shows a variety of biological activities [18] Iron(II,III) as their 4,7-diphenyl 1,10 phenanthroline chelates was studied by ion paired chromatography .[19-22] 1,10-phenanthroline has been shown to be a reliable colorimetric reagent for Fe(II) .[23-25] Albert and Fallab [26-30] investigated the hydrazides have been made as complexing agents for iron.Mixed ligand complexes of iron with 2-amino 3- hydroxy pyridine and some nitrogen donars have been described by Prakash et .[31] 2-amino-3-hydroxypyridine (AHP) was used as a potential complexation reagent for the spectrophotometric, polarographic and titrimetric determination for different metal ions .[32] It was also used in the synthesis as analgesics .[33]

MATERIALS AND METHODS

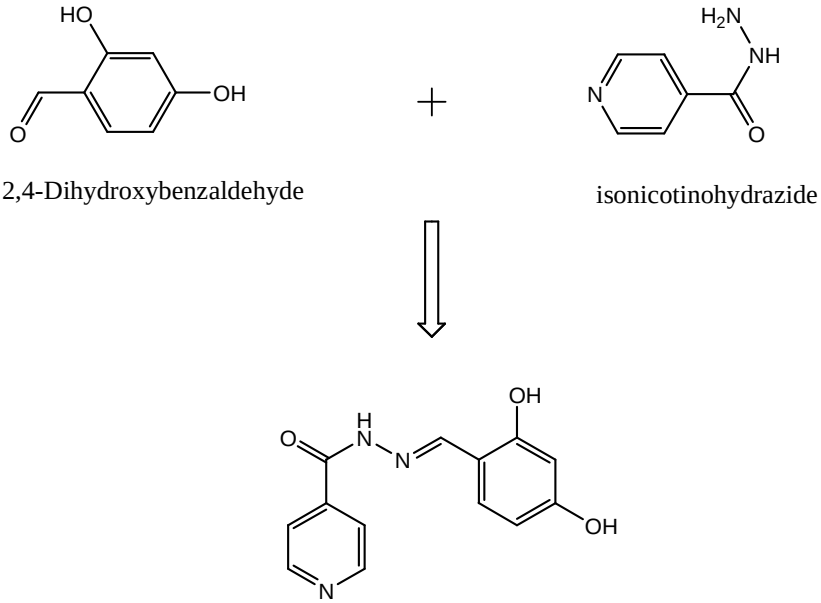
All chemicals were of AR grade and were used as supplied without further purification.An Elico Uv-Visible spectrophotometer model UV-SL 164 equipped with 1 cm quartz cell is used for spectrophotometric measurements. An Elico pH meter LI-610 is used for pH measurements. Elemental analysis and antimicrobial activity was done in laboratory approved by central government for AGMARK. Four water samples from Panchaganga river (Kolhapur),Pravara river (Sangamner), Ganga river (Nashik) and Godaveri river (Kopargaon) were taken for analysis.

Synthesis and Characterisation of 2,4-DHBINH

Synthesis of 2,4-DHBINH

2,4-Dihydroxybenzaldehyde isonicotnoyl hydrazone (2,4-DHBINH) was prepared by conducting 2,4- dihydroxybenzaldehyde and isonicotinohydrazide in methanol medium for ten hours.

The crude product is crystallized in methanol is greenish black in colour. The recrystallized product has melting point is 298^0 C and molecular weight by formula is 257.



2,4-Dihydroxybenzaldehyde isonicotinohydrazide

(*E*)-*N*'-(2,4-dihydroxybenzylidene)isonicotinohydrazide

RESULTS AND DISCUSSION

Characterisation of 2,4-DHBINH

Elemental analysis of 2,4-DHBINH

The elemental analysis of 2,4-DHBINH was done in laboratory approved by central government for AGMARK.It shows the result of elemental analysis in Table 1.

Absorption Spectra of 2,4-DHBINH

The absorption spectra of 2,4-DHBINH was recorded against blank solution containing buffer (pH=7) and is shown in fig 1. Absorption spectra was recorded in the wavelength range 350-700 nm. The complex shown as absorption maximum at 395 nm. At 395 nm wavelength the molar absorptivity of 2,4-DHBINH is 2.9844×10^{3} L.mol $^{-1}$.cm $^{-1}$.

Antimicrobial Activity of 2,4-DHBINH

Antimicrobial Activity of 2,4-DHBINH has done in laboratory approved by Central Government for AGMARK.It shows the result are noted in Table 2.

Physico-chemical and Analytical Characteristic of Fe (II)- 2,4-DHBINH

Physico-chemical & Analytical characteristic of Fe (II)- 2,4-DHBINH was studied and given in Table 3.

Preparation of Sample solution

The water samples are collected from four rivers namely Panchaganga river (Kolhapur), Pravara river (Sangamner), Ganga river (Nashik) and Godaveri river (Kopargaon). The water samples are directly analysed.

Procedure --To a 10 ml volumetric flask containing 5 ml of buffer (pH=7.0) sol^{n} 2.5 ml of DMF and 0.4 ml of 5.0×10^{-3} reagent sol^{n} a known aliquat of sample sol^{n}is added and made upto the

mark with distilled water. The absorbance is measured at 395 nm against the reagent blank. The amount of iron present is determined from a predetermined calibration plot and the result are presented in Table 4.

Composition of Complex

The composition of the Fe (II)- 2,4-DHBINH complex is found to be 1:1. It was determined by studying Job'S method. The ratio of metal ion to ligand molecule in the coloured complex was found to be 1:1.is shown in Fig 2.

NMR H-1 Prediction

NMR H-1 Prediction of 2,4-DHBINH is an shown in Table 5.and Fig No.3.

Table No. 1. Elemental analysis of 2,4-DHBINH

Sr.No.	Chemical Analysis	Percentage found	Percentage Expected
1)	Carbon	59.29	60.70
2)	Hydrogen	03.80	04.28
3)	Oxygen	17.90	18.77
4)	Nitrogen	14.44	16.34

Table No. 2. Antimicrobial Activity of 2,4-DHBINH

Sr.No.	Antimicrobial	Activity
1)	Klebsiella Pneumoniae	Nil
2)	Vibriae Cholerease	Nil
3)	Bacillus Megaterium	Nil
4)	Salmonalla typhi	Nil
5)	Shigella Flexneri	Nil

Table No. 3 . Physico-chemical and Analytical Characteristic of Fe (II)- 2,4-DHBINH

Sr.No.	Characteristics	Result
1)	Absorption Spectra	395 nm
2)	Molar absorptivity	3.55×10^4 Lit.mol^{-1}.cm^{-1}
3)	pH range (optimum)	7.0
4)	Reagent required for maximum complexation	4.0 ml
5)	pKa	7.240×10^8
6)	Beer's law validity range (ppm)	0.10 to 1.50 µg / ml
7)	Composition of complex (M : L)	1:1
8)	Stability Constant	6.30×10^4
9)	Dissociation Constant	3.703×10^{-5}
10)	Change in free energy	27.38 KJ / mole
11)	Sandell's Sensitivity (µg /cm^2)	0.016 µg /cm^2

Table No. 4. Determination of Iron in Potable Water

Sr. No.	pH of Collected Water	Iron Found (ppm)
1)	7.10	0.860 ppm
2)	7.07	0.837 ppm
3)	7.41	0.832 ppm
4)	7.25	0.800 ppm
5)	7.06	0.802 ppm

Table No. 5. Tolerance limit of diverse ions in the Determination of Fe (II)

Sr. No.	Metal ion	Salt	Interference
1)	Mg (II)	$MgSo_4$	240
2)	Cu (II)	$CuSo_4$	88
3)	Cd (II)	$CdCl_2$	40
4)	Mn (II)	$MnCl_2$	30
5)	Co (II)	$CoSo_4$	Interferes
6)	Ce (IV)	Ce $(So_4)_2$	14
7)	Ba (II)	$BaCl_2$	14
8)	Cr (III)	$K_2Cr_2O_7$	05
9)	Hg (II)	$HgCl_2$	02
10)	Ti (V)	K-titanyl oxalate	05
11)	Ni (II)	$NiCl_2$	04
12)	Sn (II)	$SnCl_2$	03
13)	Pb (II)	$PbSo_4$	75
14)	V (v)	V_2O_5	Interferes
15)	Zn (II)	$ZnSo_4$	43
16)	Al (III)	$AlCl_3$	Interferes
17)	Pd (II)	$PdCl_2$	Interferes
18)	Ni (II)	$NiCl_2$	04

Fig 1. Absorption Spectra of 2,4-DHBINH

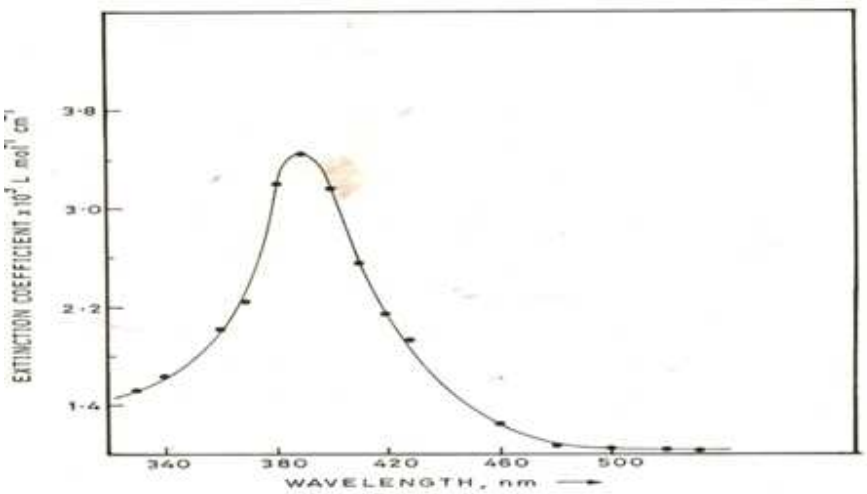


Table No 6. NMR H-1 Prediction

Sr.No.	Types of Proton	Node	Chemical Shift (PPM)
1)	Benzylidenimin	CH	8.12
2)	Benzylidenimin 1-O from 1-benzene	CH	6.19
3)	Aromatic C-OH	OH	5.05
4)	Sec. Amide	NH	8.11
5)	4-pyridine 1-C=O	CH	7.87
6)	4-pyridine 1-C=O	CH	9.16

Fig. -2 Determination of formula of the complex by Mole Ratio Method

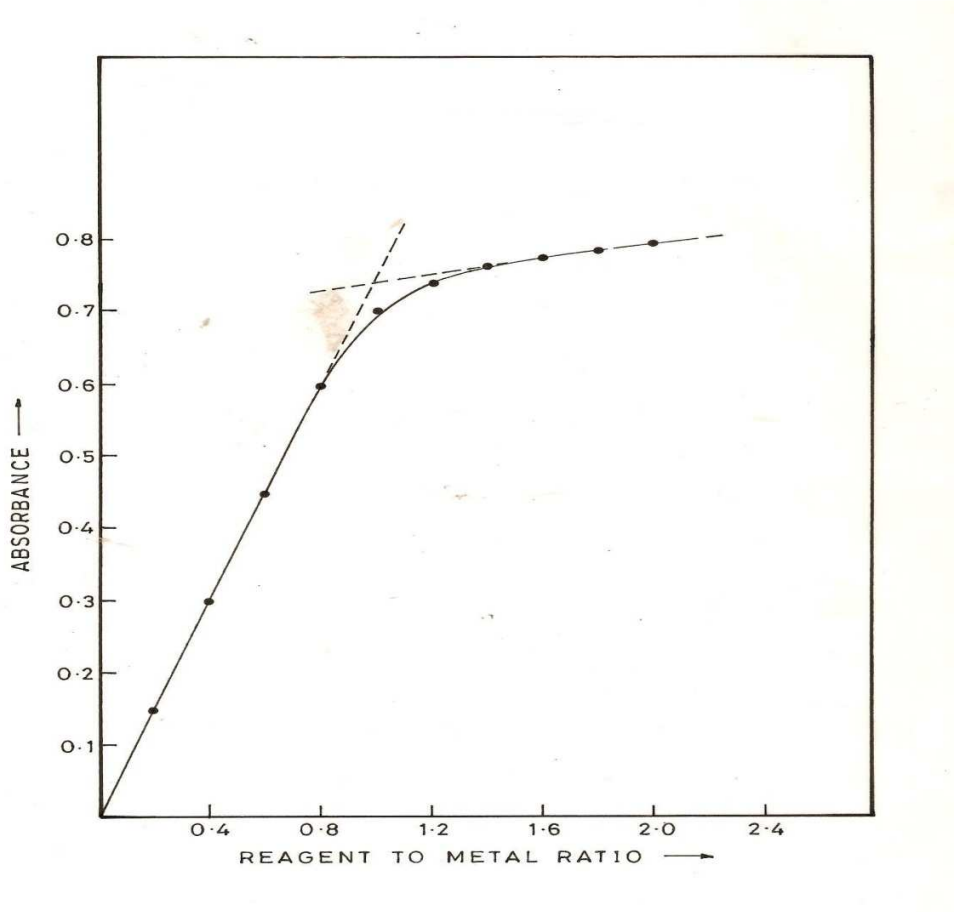
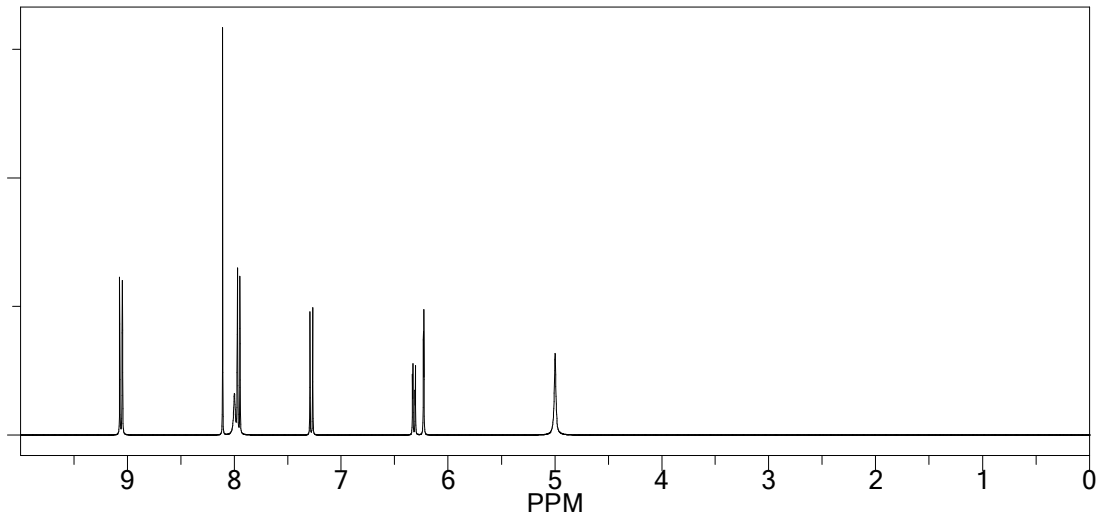


Fig. -3 NMR H-1 Prediction



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