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DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL (II) USING 3,5-DIMETHOXY-4-HYDROXY BENZALDEHYDE ISONICOTINOYL HYDRAZONE(DMHBIH)

K.Aruna Bai, G.V.S.Vallinath*, K.B.Chandrasekhar and N.Devanna
[1]Department of Chemistry, Jawaharlal Nehru Technological University,
Anantapur, Anantapur - 515002, (A.P) India.
*E-mail: vallinath999@gmail.com

ABSTRACT

Derivative spectrophotometric determination of Nickel (II) with 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) reagent has been proposed. Direct and derivative method has been developed for the spectrophotometric determination of micro amounts of Nickel (II) in basic buffer solution(pH9.0). The reagent DMHBIH gives bright yellow coloured water soluble complex [(Ni(II)- DMHBIH] in basic buffer solution. The maximum absorbance was observed in the pH range 8.5-9.5. The molar absorptivity and sandell's sensitivity of Nickel (II) complex with DMHBIH at λ_{max} 386 nm was found to be 1.22 x 10^4 $L.mol^{-1}cm^{-1}$ and 0.00826 $\mu g/cm^2$. Beer's law validity range varies from 0.234 to 2.94 µg /ml. Nickel (II) forms 1:1 complex with DMHBIH and stability constant of Nickel (II) complex was $9.4X10^6$. The first order derivative amplitude was measured by the peak height method at λ_{max} 440 nm. The second order derivative amplitude was measured by the peak height method at λ_{max} 470 nm. The developed spectrophotometric method was applied for the determination of Nickel (II) in alloy samples.

Keywords: Nickel (II), derivative spectrophotometry, 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH).

INTRODUCTION

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al.[1]. Hydrazones are important class of known analytical reagents[2-8]. These reagents are formed by the condensation of hydrazides and a carbonyl compound. Hydrazones are also found to have biological activity. These compounds contain an azomethine nitrogen atom and this is responsible for their reactivity with number of transition metal ions which form coloured complexes. In continuation of our ongoing work on the analytical applications of hydrazones, we report herein spectrophotometric determination of Nickel (II) using 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH). Spectrophotometric methods for the determination of metal ions with 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) are not exploited much.

Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. It has been widely used in pharmaceutical analysis, amino acid and protein analysis, clinical and environmental chemistry etc[9]. but less often in inorganic analysis.[10,11].

In this paper a first-order derivative spectrophotometric method is described for the determination of nickel (II) in alloys.

EXPERIMENTAL

Spectrophotometric measurements were made in a Schimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1cm quartz cells, an ELICO LI-120 digital pH meter for pH adjustments and Sartorius electronic balance was used for weighing.

All reagents used were of AR grade unless otherwise stated. All solutions were prepared with doubly distilled water. The standard Nickel (II) solution(0.1M) was prepared using analytical reagent grade ammonical nickel sulphate.

The reagent 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) was prepared by simple condensation of 1 mole of 3,5-Dimethoxy-4-hydroxybenzaldehyde with 1 mole of isonicotinoylhydrazone (Fig.1)

The reagent solution(0.01M) was prepared by dissolving 0.3022 g of DMHBIH in 100 ml of dimethyl formamide. The reagent solution is stable for 48 hrs. Buffer solutions were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate.

Reaction with metal ions

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer(pH 1.0-11), 0.5 ml of metal ion($1x10^{-3}$M) and 0.5 ml of $1x10^{-2}$M DMHBIH solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 200-800 nm range against reagent blank. The results are summarized in Table-1.

Recommended procedure

Direct spectrophotometry : An aliquot of the solution containing 0.294 to 2.94 μg/mL of nickel (II), 3 ml of buffer solution (pH 9.0) and 0.5 ml of $1x10^{-2}$M DMHBIH reagent were taken in a 10ml standard volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 386 nm in a 1.0 cm cell against corresponding reagent blank prepared in the same way but without nickel (II) metal solution. The measured absorbance was used to compute the amount of nickel (II) from the calibration plot. Wavelength values are plotted against absorbance and presented in fig-2.

First derivative spectrophotometry

For the above solution, first-order derivative spectrum was recorded with a scan speed having a degree of freedom 9, in the wavelength range from 350-800 nm. The derivative peak height was measured by peak-zero method at 440 nm.

The peak height was plotted against the amount of Nickel (II) to obtain the calibration curve. Wavelength values are plotted against absorbance and presented in Fig-3.

RESULTS AND DISCUSSION

3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) reagent is a blend of a carbonyl compound and a hydrazine. The reagent solution is stable for 48 hrs. in alkaline medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

Determination of Nickel (II) using DMHBIH

Nickel (II) reacts with HDBIH in alkaline medium to give bright yellow coloured water-soluble complex. The colour reaction between Nickel (II) and DMHBIH are instantaneous even at room temperature in the pH range 8.5-9.5. The absorbance of the bright yellow coloured species remains constant for more than 2hrs. The maximum colour intensity is observed at pH 9.0.

A 10-fold molar excess of reagent is adequate for full colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between Nickel (II) and DMHBIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of nickel (II) and DMHBIH are summarized in Table-2.

Effect of Diverse ions

The effect of various diverse ions in the determination of Nickel (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 ±2 % in the absorbance or amplitude. The results are given in table-3. The data suggests that several associated anions and cations do not interfere when they are

present in large excess such as phosphate, bromide, sulphate, iodide, urea, U(VI), Ba(II), Mn(II), Ca(II). The interference of associated metal ion Fe(III) is decreased with masking agent Fluoride.

Applications

The proposed method was applied for determination of Nickel (II) in alloy samples whose composition corresponds to certified samples. The results are given in table-4.

CONCLUSION

From the above discussion, it can be concluded that DMHBIH is a potential reagent for the derivative spectrophotometric determination of Ni (II). It is very easy to synthesize DMHBIH, a novel class of reagent. The present derivative method is simple and rapid without the need for heating or extraction compared to other reagents that were used for the spectrophotometric determination of Nickel (II)[12-14]. The comparision is presented in Table-5.

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REFERENCES

1. R.B.Singh, P. Jain and R.P. Singh, *Talanta*, **29**,77 (1982).
2. K.B. Chandrasekhar and K. Hussain Reddy, *Indian Journal of Chemistry*, **41**, 1643 (2002).
3. K. Hussain Reddy and K.B.Chandrasekhar, *Indian Journal of Chemistry*, **40**, 727 (2001).
4. M. Ramesh, K.B.Chandrasekhar and K.Hussain Reddy, *Indian Journal of Chemistry*, **39**, 1337 (2000).
5. M. Rameswara rao, K. Hari, N.Devanna and K.B.Chandrasekhar, *Asian Journal of Chemistry*, **2**, 1402 (2008).
6. G. Narender Reddy, K.B.Chandrasekhar, N. Devanna and K.N. Jayaveera *Asian Journal of Chemistry*, **3**, 2257 (2008).
7. V. Kiran Kumar, M. Rameswara rao, K.B.Chandrasekhar and N. Devanna, *Asian Journal of Chemistry*, **3**, 2197 (2008).
8. G.V.S.Vallinath, K.Aruna Bai, N. Devanna and K.B.Chandrasekhar, *Research journal of Chemistry and Environment*, **4**,115 (2009).
9. F. Snachez Rojas, C. Bosch-ojeda and J.M. Cano Pavon, *Talanta*, **35**, 753(1988)
10. A. Bermejo, B.P. Bermoji and F. Bermejo Martinez, *Analyst*, **110**, 1313 (1985).
11. R. Kurodoa, M. Kurosaki and Hayashibe., *Talanta*, **77**, 619 (1990).
12. A.B. Patil, V.N. Patil, M.A. Anuse and P.N. Bhosle, Proceedings of 19th Indian Council of Chemists annual Conference held at Kvempu University Shimoga, Karnataka, 21 (2000).
13. Parchi S. Karnik, Swati A., Maynak and Dave O.P. Proc. 20th Indian Council of Chemists conf. Mysore University, 232 (2001).
14. Nawar N., Khattab M.A, Hosny N.M, *Synth. React. Inorg. Met. Org. Chem..,* **29(8)**, 1365(1999).

Table -1: Analytical Characteristics of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone

Metal ion	p^H	λ_{max} (nm)	Molar absorptivity (ε) ($Lmol^{-1}cm^{-1}$) x 10^4
Ru(III)	4.25	390	1.7
Fe(III)	4.0	386	1.875
Ni(II)	9.0	386	1.22*

*Present work

Table-2: Physico-Chemical and Analytical Characteristics of [Nickel (II)- DMHBIH] Complex

Characteristics	Results
Colour	Bright yellow
λ_{max}(nm)	386
p^H range (optimum)	8.5-9.5
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol $^{-1}$cm^{-1}) (ε)	1.22x10^4
Sandell's sensitivity(μg/cm^2)	0.0082
Beer's law validity range(μg/ml)	0.294-2.94
Optimum concentration range(μg/ml)	0.47-2.35
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	9.4 x10^6
Standard deviation in the determination of μg/ml of Cu(II) for ten determinations	0.000015
Relative standard deviation(%)	0.004

Table-3: Tolerance of Foreign ions in the determination of 0.2175 μg/ml Nickel (II)

Ion added	Tolerance limit (μg/ml)		Ion added	Tolerance limit (μg/ml)	
	Zero	D1		Zero	D1
Bromide	2935	3596	U^{6+}	119	238
Iodide	2348	3173	Bi^{3+}	105	209
Urea	1200	1500	Co^{2+}	88	118
Chloride	1143	1243	Mn^{2+}	82	110
Tetraborate	920	970	Ca^{2+}	80	100
Phosphate	850	950	Sn^{2+}	59	59
Sulphate	840	1410	Cd^{2+}	56	112
Oxalate	780	1760	Zr^{4+}	46	91
Thiocyanide	770	872	Zn^{2+}	65	98
Nitrate	280	620	Cu^{2+}	29	59
Acetate	265	295	Sb^{3+}	12	18
Thiourea	191	230	Ag^{1+}	11	16
Fluoride	170	190	Mo^{6+}	10	14
Tartarate	148	148	As^{3+}	7.5	11
Ascorbic acid	88	176	Pd^{2+}	5.3	11
Hg^{2+}	301	301	V^{5+}	5.1	5.1
Ba^{2+}	275	343	Ru^{3+}	5.05	10
Pb^{2+}	207	207	Fe^{3+}	2.8, 3.8*	2.8,3.8†
W^{6+}	184	276	Al^{3+}	2.7	4.0
Sr^{2+}	131	131	Cr^{3+}	2.6	5.2

*Masked with 160 μg/ml Fluoride.; † Masked with 160 μg/ml Fluoride.

Table-4: Determination of Nickel (II) (μg/ml) in alloy samples (*Average of the best three determinations among five determinations.)

Sample	Nickel (II) %			Error %
	Certified	Found*		
		Zero	D1	
BCS-CRM 38T[a]	41.90	41.85	41.88	-0.11, -0.05
Monel 400[b]	63.01	63.15	63.2	+0.22, +0.30
Ookay[c]	60.00	59.80	59.95	-0.33, -0.08

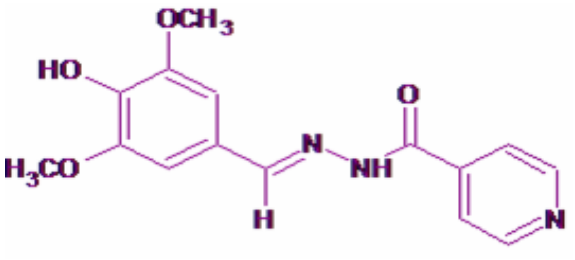

Fig.-1: Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone(DMHBIH)

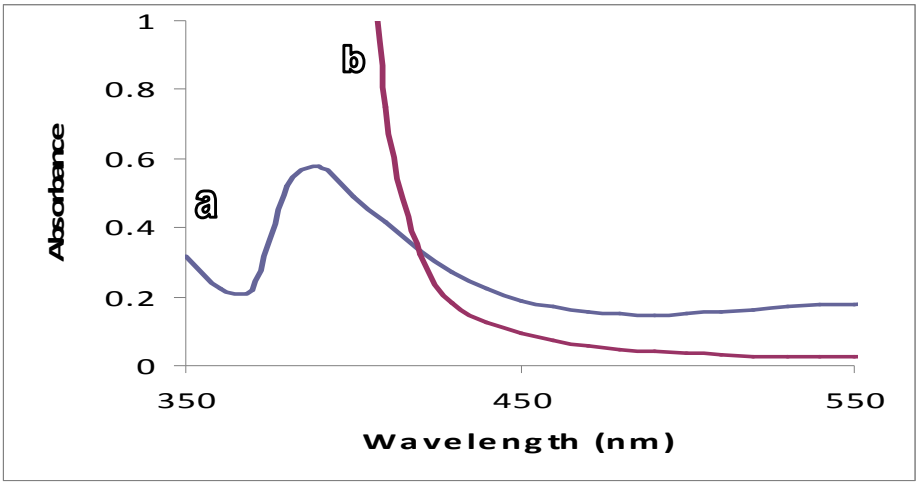

Fig.2. Zero order Absorption spectra
(a) Reagent DMHBIH Vs DMF blank; (b) Ni (II)-DMHBIH complex Vs Reagent blank

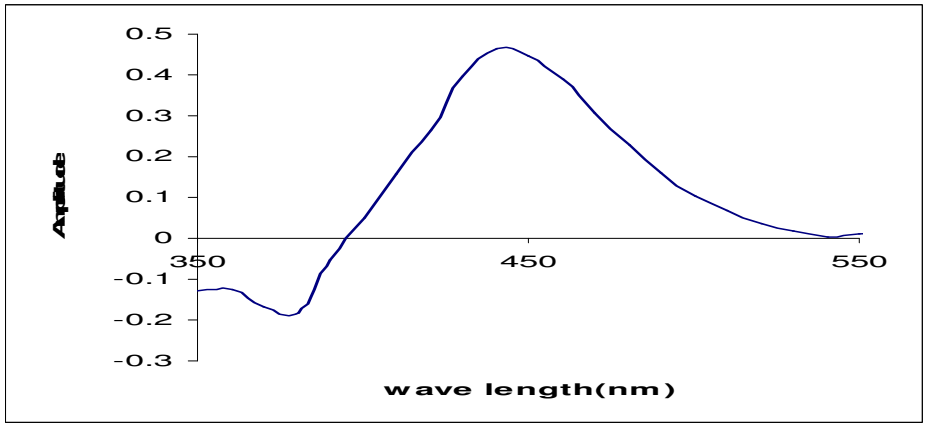

Fig-3: First order spectrum of [Nickel (II)- DMHBIH] System

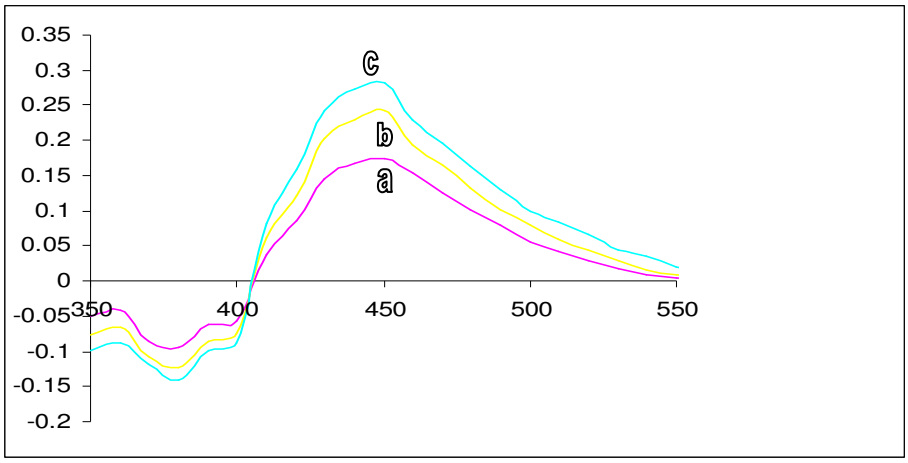

Fig.-4: First order Beer's law derivative spectra of [Ni(II)-DMHBIH] complex
a: 1.174 µg/ml of Ni(II); b: 1.7511 µg/ml of Ni(II); c: 2.348 µg/ml of Ni(II)

Table -5: Comparision of Spectrophotometric methods for the Determination of Nickel (II) using various reagents.

S.No	Reagent	pH	λ_{max} (nm)	Molar absorptivity	Reference
1	9,10-phenanthroquinoneguanylhydrazone	9.4	500	1.029×10^4	12
2	isonitrosoacetylacetonebenzoylhydrazone	10.0	390-400	1.1309×10^4	13
3	O-Aminoacetophenonebenzoylhydrazone	--	--	--	14
6	3,5-dimethoxy-4-hydroxy-benzaldehyde isonicotinoyl hydrazone (DMHBIH)	9.0	386	$1.22 \times 10^{4*}$	Present work

*present work

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