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RESEARCH ARTICLE

Determination of Ni (II) in water and alloy samples with 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate using spectrophotometric method

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Ni (II), 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate, Spectrophotometry, Water and alloy samples.

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Abstract

A simple, sensitive and selective extractive spectrophotometric method was developed for the determination of Ni (II) in various water and alloy samples using newly synthesized reagent 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate Ni(II) forms a blue coloured complex with 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate in phosphate buffer medium (pH 7.5). Under optimum conditions the maximum absorption of the ethanol extracts were measured at 445 nm. Beer's law was obeyed in the range of 0.5 to 1.0 µg mL^{-1} of Nickel. The molar absorptivity and Sandell's sensitivity of the complex were as 6.0×10^{4} l mol^{-1} cm^{-1} and 1.02 µg cm^{-2} respectively. . The detailed study of various interfering ions made the method more sensitive. The method was successfully applied for the determination of Ni (II) in water and alloy samples

Introduction

Nickel can be released into the atmosphere from several industrial processes, including oil and coal burning power plants, trash incinerators, and the metallurgy industry. Moreover, nickel can enter into aquatic bodies through the dissolution of oxide and sulfide rocks containing nickel combined with other elements. Thus, the exposure to nickel may take place by air, food samples, and drinking water, though mainly by skin contact with contaminated soils and alloys containing nickel.

Although nickel is considered as an essential element, which acts as an activator of several enzymes to enhance insulin activity, excessive nickel in the organism is very toxic, which can be manifested by affecting the activity of natural killer cells.[2] Nickel in nature is mainly available in the form of ores like Gernirite, Magnesium nickel silicate of variable composition. The important oxidation state of nickel is Ni(II). In olden days nickel is used as a coinage metal. Now days nickel becomes an important element, not only for industry, but also for biological systems. In rapidly expanding analytical fields, such as environmental, biological and material monitoring for trace metals. Nickel is used in ceramic industry, and also used in batteries which are in convincing to the environment. A dietary deficiency of nickel, leading to various pathological manifestations. Nickel is relatively non toxic element. The high concentration of the nickel does show serious health hazards. The high incident of respiratory track moplacia and dermatitis has been observed when exposed by nickel refineries. In views of this separation and determination of nickel from associated elements is indispensable. Therefore, it is very important to develop sensitive, rapid and economical method for quantitative determination of it's trace amount in various samples of environmental importance. Several analytical techniques have been monitored for the determination of trace level nickel(II), it includes atomic absorption spectrometry (1-4), Inductive coupled plasma emission spectrometry (5-7), and X-Fluorescense spectrometry(8,9), were reviewed. A few reagents are available for the spectrophotometric (10-18) determination of nickel(II) in water, alloy samples and biological samples.The above reported reagents suffer from several disadvantages such as, poor sensitivity, selectivity, required special conditions for the formation of complexes with the reagents is less stable and few are commercial.

2. Material and Methods

2.1 Equipment:

Shimadzu AUY 220 digital electronic balance was used for weighing the substances. The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode. A Perkin- Elmer Lambda 35 UV-Visible spectrophotometer with quartz cells were used for all absorbance measurements.

3.EXPERIMENTAL

All chemicals and solvents used were of analytical grade (AnalaR or BDH) while salicylic acid, formaldehyde were obtained from Sigma-Aldrich and were used without further purification. Molar conductance measurements were carried out using Jenway 4010 conductivity meter. IR spectral analysis was recorded using a Fourier transformed IR Genesis series model in KBr in the range 4000 – 400cm^{-1}. The melting point of the ligands and the decomposition temperature of their complexes were determined using Gallen kemp melting point apparatus.

3.1 Preparation of the Ligand

The ligand was prepared by adding of 0.02 mol L^{-1} 4-nitrobenzaldehyde, 9.4g of 30% isopropyl 3-oxobutanoate with acetic acid and piperidine refluxed in the presence of Isopropyl alcohol the product is formed is yellow coloured crystalline substance. The absorption spectra is showed in Figure .1 . The synthesized ligand showed in Scheme. 1 . This mixture was stirred with 1-benzhydrylazetidin-3-yl 2-amidinoacetate in the presence of sodium methoxide and isopropyl alcohol and refluxed for 8 hours. The precipitate obtained was cooled, filtered and washed several times with cold water as well as hot water / ethanol solution to remove unreacted 4-nitrobenzaldehyde. The isolated white product was recrystallized from acetone and finally dried in air for 24 hours. H^{1}NMR and IR studies of the ligand showned in Table 1,2 and Figures are 4,5.

Table 1 NMR studies of the ligand

Position	^{1}H	δ(ppm)	J(Hz)^1	^{13}C	DEPT
1,5	2H	8.18	d(8.7)	129.00	CH
2,4	2H	7.45	d(8.7)	123.09	CH
3	-	-	-	145.44	-
6	-	-	-	157.22	-
7	1H	4.75-4.83	m	38.67	CH
8	-	-	-	102.59	-
9	-	-	-	145.23	-
10	-	-	-	151.87	-
11	-	-	-	75.99	-
12	-	-	-	165.92	-
13	1H	4.75-4.83	m	61.68	CH
14Ha	1H	2.91	t(6.6)	59.32	CH$_2$
14Hb	1H	3.43	t(7.1)		
14'Ha	1H	2.40	br	59.88	CH$_2$
14'Hb	1H	3.26-3.33	m		
15	1H	4.27	s	76.93	CH
16,16'	-	-	-	142.20,142.30	-
17,21,17',21'	4H	7.14-7.40	m	128.40	CH
18,20,18',20'	4H	7.14-7.40	m	127.01	CH
19,19'	2H	7.14-7.40	m	126.96	CH
22	3H	2.26	s	18.66	CH$_3$
23	-	-	-	167.23	-
24	1H	4.75-4.83	m	66.41	CH
25,25'	6H	1.03 & 1.18	d(6.3)&d(6.3)	21.53,21.82	CH$_3$
NH$_2$	2H	6.78	br	-	-
NH	1H	8.86	s	-	-

s-singlet, d-doublet, t-triplet, m-multiplet, broad.

^{1}.^{1}H-^{1}H Coupling constants.

Table 2 IR studies of the ligand

Wave number (cm^{-1})	Assignment	Mode of Vibration
3437	N-H	Stretching
3027	Aromatic C-H	Stretching
2978,2927,2850	Aliphatic C-H	Stretching
1677,1646	C=O	Stretching
1516	Aromatic $(N=O)_2$	Asymmetric Stretching
1490	Aromatic C=C	Stretching
1452,1385,1373	Aliphatic C-H	Bending
1345	Aromatic $(N=O)_2$	Symmetric Stretching
1287	C-N	Stretching
1215,1106,1067	C-(C=O)-O	Stretching
828,746,705	Aromatic C-H	Bending

Figure 4 NMR spectra of the 3 BPANPC ligand

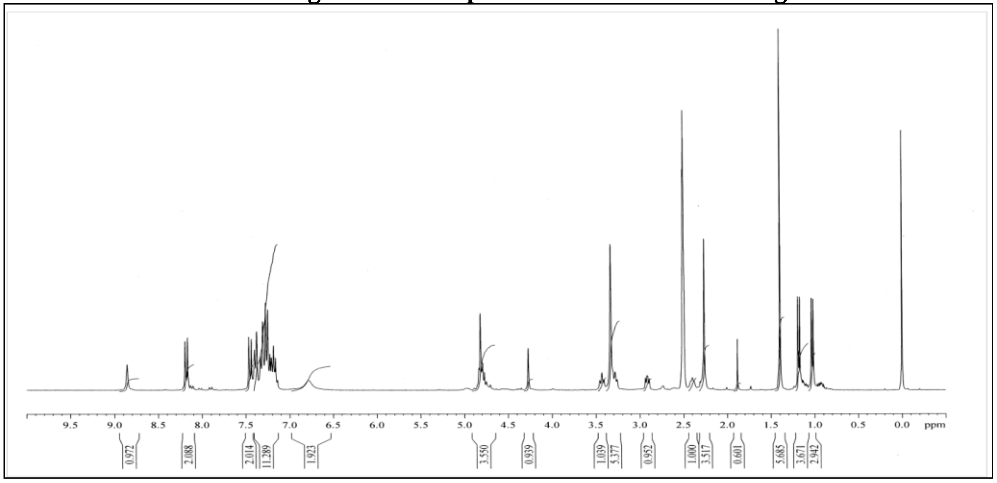
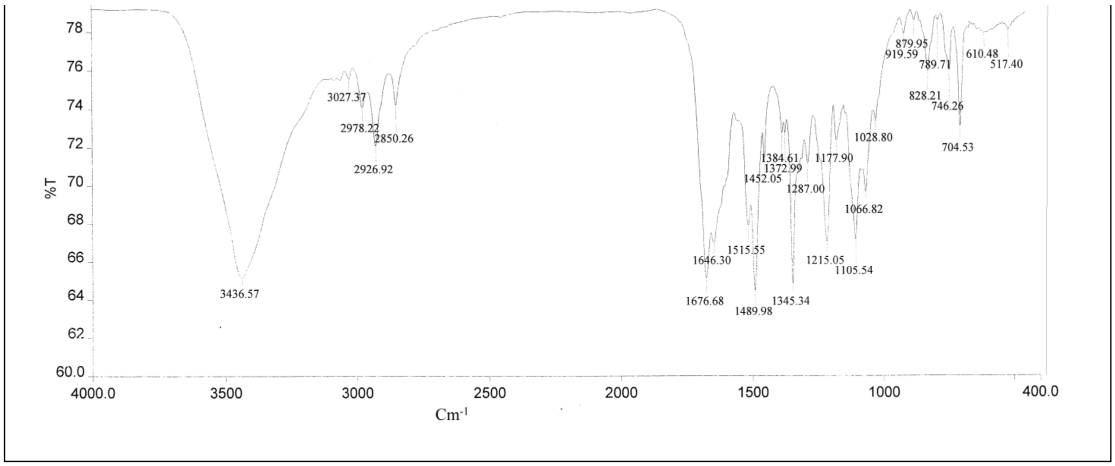


Figure 5 . IR spectra of the 3 BPANPC ligand



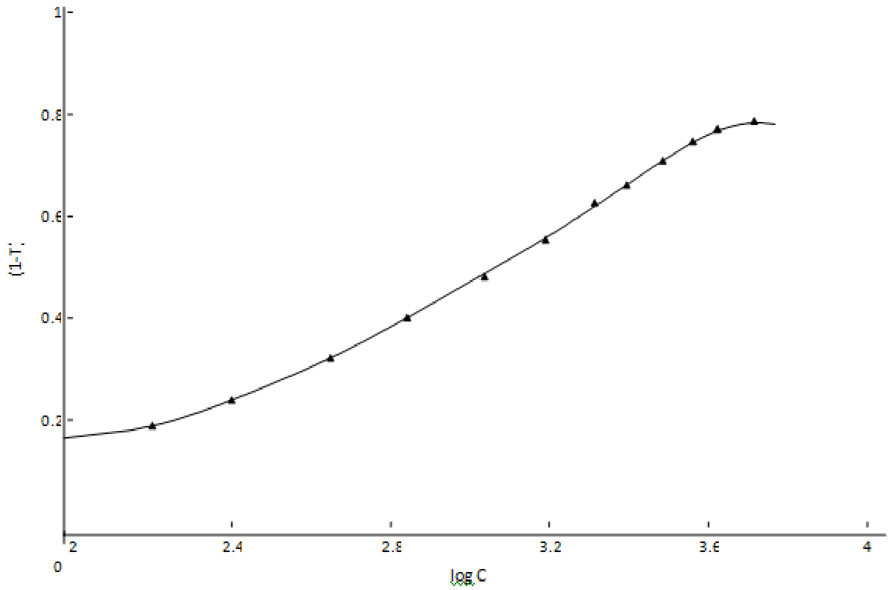
3.1.1 Physicochemical properties of 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate

The 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate being a yellow colour solid, easily soluble in methanol. The spectra of 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate in different pH are shown in Figure 2. At pH 7.5 (KH_2PO_4/NaOH buffer) phosphate buffer, blue, instability and maximum absorption at 320 nm, corresponding to the protonation appears and disappears. According to the absorbance of the reagent at 445 nm, the dissociation constant of 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate was measured to be 1.01×10^{-12} by potentiometric titration.

3.1.2. Ring bom plot for 3-(1-benzhydrylazetidin-3-yl) 5-isopropyl 2-amino-1,4-dihydro-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate Complex

Ringbom's plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log C of Ni(II) and (1-T) (where T is the transmittance). The plot has a sigmoid shape with a linear segment at intermediate absorbance values (0.3-0.8). The slope of the Ringbom plot from Figure.3 is 0.720.

Figure 3. Ringbom plot of Ni(II)- 3 BPANPC complex complex



3.2 Effect of salting out agent

Various salting out agents such as lithium nitrate, thorium sulphate, magnesium sulphate, lithium chloride, ammonium chloride and ammonium sulphate were used for the enhancement of the metal complex extraction into the organic phase in a single step. It is observed that the presence of 1.0 mL of 0.1 M magnesium sulphate solution ensured the complete extraction . It is established that 1.0 mL of 0.1 M magnesium sulphate as salting out agent and a ten-fold molar excess of the reagent quantitatively extracts Ni(II) in to organic phase. Effect of Several anions and cations were studied in detail. **Table 3** summarizes the tolerance limits of interfering ions in the determination of 50 µg l^{-1} Ni (II).

3.3 Digestion of the alloys

1 g of alloy sample was dissolved in a 10 mL of aqua regia, and evaporated to minimum volume, extracted with 10 mL of 2 M HNO_3 and then diluted with double distilled water to a suitable volume (10 mL) it serves as stock solution. The experimental solution was prepared by pipetting out 10 mL of the stock solution in to the 100 mL standard flask and the solution was made up to the mark with distilled water. A known volume of this solution was placed in a 10 mL standard flask and made up to the mark and analysed as per general procedure mentioned earlier. The results were shown in Table 4

Table 3 Tolerance limits of foreign ions on the determination of 50 µg L^{-1} Ni (II) ion

Tolerance limit (µg L^{-1})	Foreign ions [Ni (II) with 3 BPANPC)]
50	NO_3^{-}, K^{+}, borate, Mg^{2+}
5	Li^{+}, $Al^{3+,}$ $PO_4^{3-,}$ NO^{2-}, $SO_4^{2-,}$ ClO_4
2	$Ca^{2+,}$ $Sr^{2+,}$ $IO^{3-,}$ $BrO^{3-,}$ B (III), ClO3
1	$Mn^{2+,}$ Ce (IV) , $Fe^{3+,}$ Mo (VI), Br
0.3	Ti (IV), Bi (III), V (V), Cr (VI), Cr (VI), Ba2+ W (WI) 0.3
0.1	Cd^{2+}, Pd^{2+}, Cr^{3+}, $La^{3+,}$ Cl^{-}, $Zn^{2+,}$ $Cu^{2+,}$ Zr (IV)
0.05	Bi (III), Pb2+, Hg $^{2+,}$ Th (IV), Ag^{+}, Sn (IV)
0.03	Se (IV), Te (IV), Au^{3+}
0.02	Co^{2+}

Table 4 Determination of Ni (II) in standard alloy samples

Samples	Proposed method
Steel(GBW01329)*a*	0.173 ± 0.009
Steel(GBW08532)*b*	0.423 ± 0.006

a C(0.188), Si(0.305), Mn(1.44), P(0.013), S(0.046), Cr(0.389), Ni(0.166),Cu(0.277), V(0.158), Ti(0.285), Al(0.112), B(0.023).

*b*C(0.506), Si(1.96),Mn(0.755), P(0.034), S(0.012), Cr(0.102), Ni(0.314), Cu(0.126), V(0.241),Ti(--), Al(0.201), B(0.019).

*c*Mean ± Standard deviation (n = 10)

3.4 Procedure for the determination of Ni(II) in natural water samples.

Different water samples were collected from various places in and around Tirupati, A.P., India. The samples (150 mL) were stored at 0-5 °C in metal free polyethylene bottles. Water samples were filtered through Whatman Filter paper no. 41 and clean solution was collected into 250 mL beaker. The contents were diluted up to the mark with double distilled water. 15 mL of this solution was further diluted to get working solution for determination of Ni(II) . The results were summarized in Table 6.

Table 6 Determination of Ni (II) in water samples

Sample	Proposed method		
	Nickel added µg mL^{-1}	Found[a] µg mL^{-1}	Recovery (%)[a]
Lake water[b]	-	0.59	-
	1.0	1.59	97.0±0.23
	1.40	1.99	99.2±0.07
River water[b]	-	0.19	-
	0.60	0.79	97.3±0.07
	1.0	1.19	98.0±0.27
Spring water[b]	-	0.38	-
	0.60	0.98	96.3±0.09
	0.80	1.18	98.6±0.06
Polluted water[b]	-	0.58	-
	0.90	1.48	98.8± 0.16
	1.20	1.78	98.3±0.07

[a] n=5, [b] Collected around Tirupati area

Figure 1 (A) Absorption spectra of Ni(II)- 3 BPANPC complex vs Reagent blank (B) Reagent blank

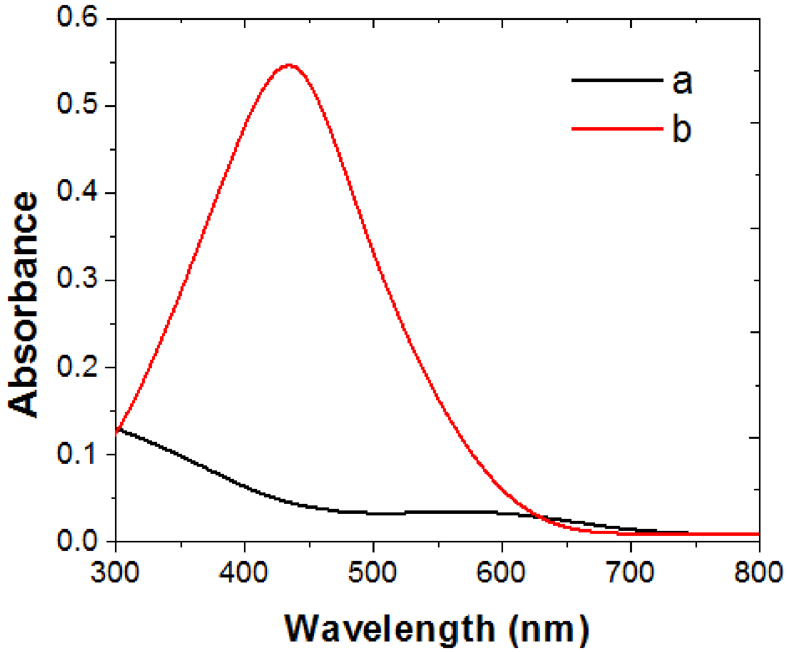


Figure 2 Effect of pHon the absorbance of Ni(II)- 3 BPANPC complex

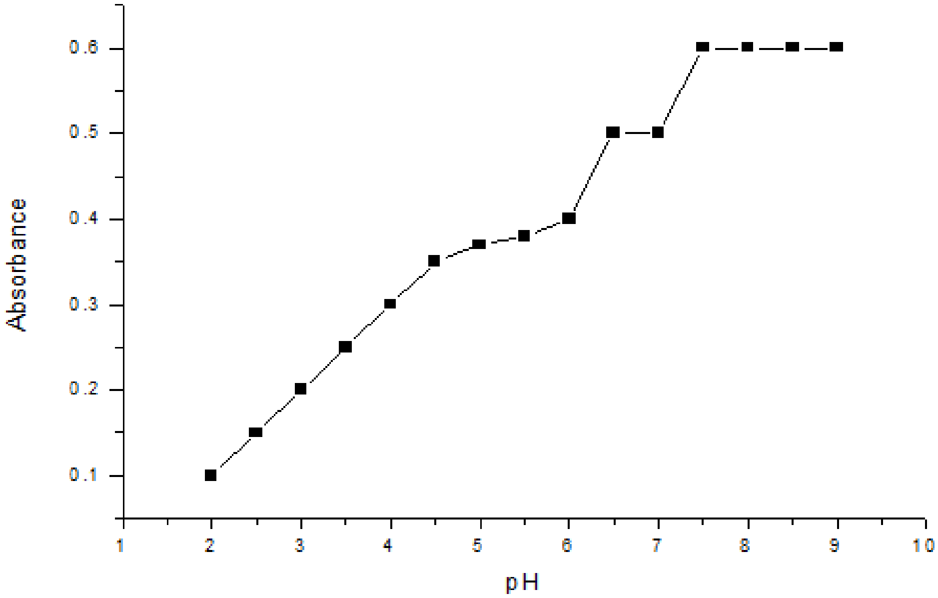
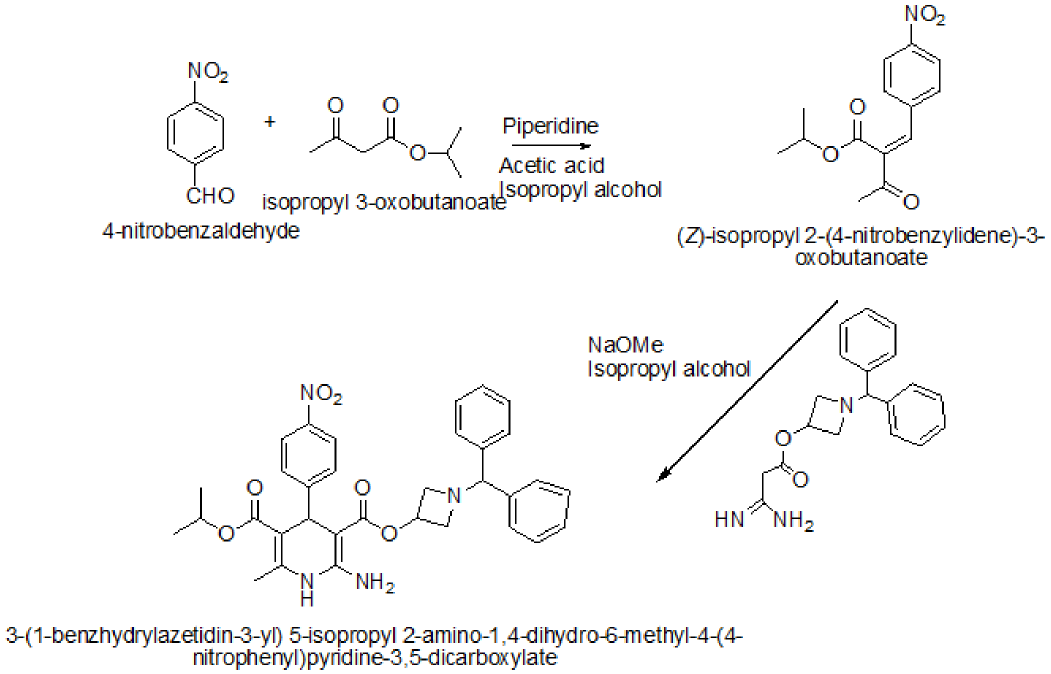


Table 5 Comparison of the present method with other spectrophotometric methods for the determination of Nickel

Reagent	λ_{Max}/nm	Optimum pH range	Beer's law validity range, ppm	Molar absorptivity/l mol^{-1} cm^{-1}	M:L	Remarks	Ref
Salicylaldehyde 3-Oxobutanoylhydrazone	410	5-10	1	0.5-0.3	1:1	Less sensitive	19
2-(2-Quinolylazo)-5-diethylaminoaniline	590	6.0	0.03-0.05	0.02-0.7	1:1	Interference no. of metal ionsand poor senstivity and selectivity	20
2-(2-Quinolylazo)-5-dimethylaminoaniline	590	7-9	$1.32x10^5$	$1.32x10^5$	1:1	Less sensitive more reagent consumption	21
PAP with XAD-16	445	9.0	0.01-0.05	$1.34x10^4$	-	Sensitive,easily available,	22
3 BPANPC	445	7.5	0.030	0.3-0.8	1:1	Selective ,sensitive and Inexpensive reagent	Present method



Scheme 1 preparation of the 3 BPANPC **ligand**

3.5 Application of the Spectrophotometric method for the determination of Ni (II) with present method

The proposed spectrophotometric method for the determination of Ni (II) has been employed for water and alloy samples. The analytical data summarised in Table 5 suggest that the percentage recovery of Ni(II) from water and alloy samples ranges from 95.0 % to 99.8 % which is more reliable and sensitive method.

3.6 Conclusions

The proposed spectrophotometric method is simple, highly sensitive and selective for the determination of Ni (II) in water and food samples.The limit of detection of the proposed method is superior to other methods. The method has additional advantage over method owing to it's.

i. Proposed method is highly sensitive due to the stabilization of coloured complex for more than 6 days formed by interactions of the metal ion with newly procured reagent.

ii. Low reagent consumption, elimination of the analytical error and statistical analysis which made the method to be more sensitive and selective.

iii. Low reagent consumption, elimination of the analytical error, less interference and statistical analysis which made the method to be more sensitive and selective.

References

1. Sen-Gupta, J. G. *Anal. Chimica Acta* **1972**, *58*, 23-37
2. Scaccia, S. *Talanta* **1999**, *49*, 467-472
3. Economou, A.; Fielden, P. R. *Talanta* **1998**, *46*, 1137-1146
4. Frolin, M.; Contiero, E.; Calliari, I. *Annali di Chimica* **1991**, *81*,395-416
5. Fu, Y.; Wang, W. G.; Xie, K. J.; Zhao, Q. R.; Bi, Y. M. *Fenxi Huaxue* **1998**, *26*, 431-434
6. Ren, Y. L.; Zhang, X. B.; Ren, Y. G.; Wang, M. C.; Xu, G. A. *Fenx Huaxue* **1997**, *25*, 301.
7. Galas, W.; Trzcionka, J. *ChemicaAnalityczna (Warsaw)* **1997**, *42*,697-702
8. Muddukrishna, S. N.; Holzbecher, J.; Ryan, D. E. *J. Radioanl. Nucl. Chem.* **1991**, *148*, 27-32.
9. Suresh, G.; Dhanalakshimi, P.; Naidu, N. V. N. *International J. Of Current Sciences* **2003**, *23*(3), 83-85.
10. Yang, G.; Lin, H.; Ma, C.; Zhao, J. *Hauxue Shiji* **1986**, *274*(5), 14-18.
11. Alikhodzhaev, A. K.; Pachadzha, D. N.; Yusupov, M.; Yu, Z. *Ana. Khim.* **1985**, *40*(1), 2021
12. Gonzalez Armas, A.; Gonzalez Diaz, V.; Perez Tryillo, J. P.; Garcia Montelongo, F. *Anal. Quim. Sec. B* **1982**, *78*(5), 351-356

13. Chen, M.; Lin, Y.; Li, J. *Fenxi Huaxue* **1984**, *12*(5), 405-408
14. Zhu, Y.; Jian, W.; Ten, E.; Wei, F.; Zhonycio, K. *Jishu. Daxue Xue Bao.* **1991**, *21*(1), 17-23
15. Bandyopadyay, G.; Roy, B. C.; Sha, M. B. *J. Indian Chem. Soc.* **1986**, *63*(7), 707-709
16. Babaiah, O. *Ph.D. Thesis*, S. K. University; Anantapur, A.P. India, 1997.
17. Lokhande, R. S.; Chaudhary, A. B.; Nirupa, S. *Asain J. Chem*. **2002**, *14*(1), 149-152
18. Ma, Q. L.; Su, M. H.; Wang, Z. H.; Nie, L. H.; Liang, S. C.; Ma, H. M. *Anal. Chim. Acta* **2001**, *439*, 73-79
19**.** Qiufen Hu, Guangyu Yang, Zhangjie Huang, JiayuanYin; Bull.Korean Chem.Soc., **25**, 545-548, **2004**.
20. Prakash Jagtap, Alexei Degterev, SungwoonChoi, Junying Yuan, D**.**Gregory**;** Abstracts published,July 3**, 2006**.
21. S.K.Kumar, P.S.Rao, L.Krishnaiah, B.Jayaraj,Chiranjeevi; P.Anal Sci., **20(6)**, 951-953, Jun **2004**.
22. P.Yamini, K.Vijaya Kumar, R.Kishore Kumar, V.Govinda, P.Venkateswarlu; Anal. chem., **20(6),** 1-7, **2012**