

CHAPTER II

EXTRACTION-SPECTROPHOTOMETRIC
DETERMINATION OF NICKEL(II) WITH
N-HYDROXY-N,N-DIPHENYLBENZAMIDINE
AND 1-(2-PYRIDYLAZO)-2-NAPHTHOL

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II)
WITH N-HYDROXY-N, N'-DIPHENYLBENZAMIDINE AND 1-(2-PYRIDYLAZO)-
2-NAPHTHOL

SUMMARY

A simple and sensitive extraction-spectrophotometric method for the determination of nickel(II) is described. It is based on the extraction of nickel(II) with hydroxyamidines (HOAs) and simultaneous colour reaction with 1-(2-pyridylazo)-2-naphthol(PAN) at pH 8.0 ± 0.2 . The red coloured complex, so formed, is quantitatively extracted with various organic solvents. The molar absorptivity of the complex in chloroform with seven hydroxyamidines lie in the range of $(4.89 - 7.83) \times 10^4$ $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 560-570 nm. Among these, the simplest, N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) is selected for all experimental work. The molar absorptivity of the Ni(II)-HDPBA-PAN complex is 7.83×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 570 nm. The system follows Beer's law upto 0.7 $\mu\text{g/ml}$ in chloroform. The limit for detection of the metal is found to be 0.008 $\mu\text{g/ml}$ aqueous solution.

The reproducibility of the method was checked by finding relative standard deviation for ten replicate measurements, each containing 0.3 $\mu\text{g/ml}$ of Ni(II) and it is found to be $\pm 1.3\%$. The present method does not suffer from rigid control of experimental conditions. The method is free from the interferences of most of the common metal ions like Cu(II),

Zn(II), Pb(II), Mn(II) etc. The present method is precise and easy to follow. It has been applied successfully for the determination of nickel(II) in metallurgical and industrial samples.

Nickel is one of the oldest alloying elements. It occurs in the earth's crust at a level of 0.016%. Nickel is widely distributed in plant, animal tissues, igneous rocks, plasma, vegetables, etc.¹ The commercially important ores and alloys of nickel are pentlandite, pyrrhotite, chalcopyrites and kupronickel.² It is mainly used in ferro alloys, coins, electronics, batteries, gas turbine, etc.^{3,4} Industrial exposure of nickel compound produces dermatitis (nickel itch). It also produces pulmonary eosinophilia and paroxymal asthmatic attack.⁵

Many spectrophotometric methods have been reported for the determination of nickel. Of these, dimethylglyoxime method⁶⁻⁹ is most popular and used widely for the determination of nickel. The classical dimethylglyoxime method is based on the determination of nickel as nickeldimethylglyoximate in ammoniacal medium. But the sensitivity of this method is not enough and it suffers from interferences of common metal ions like Cu, Fe, Co and Mn. To enhance the sensitivity of the classical dimethylglyoxime method, bromine has been used as an oxidizing agent.^{6,10} However, this method is not suitable because it does not give reproducible results, and requires back extraction, it is also time consuming. Several methods using oxime^{6,7,11-14} have been reported but they also suffer from both i.e. lack of sensitivity as well as selectivity.

Various other spectrophotometric methods have been reported for the determination of nickel with reagents like

4-methyl-3-hydrazinopyridazine,¹⁵ 2-(5-methyl-2-isoxazol-3-ylazo)-4-chlorophenol,¹⁶ 2-[2-(3,5-dibromopyridyl)azo]-5-dimethylaminobenzoic acid,¹⁷ 2-hydroxy-1-naphthaldoxime,¹⁸ diacetyl-monoxime glycinimine,¹⁹ 3-(4-methoxyphenol)-2-mercaptopropenoic acid,²⁰ bis-salicylidene-o-phenylenediamine,²¹ 1,4-dihydroxyanthraquinone,²² piperidine dithiocarbamate,²³ pyrrolidinedicarbodithioic acid,²⁴ 1-allyl-3-(2-pyridyl)thiourea,²⁵ N-methylpiperazinedithiocarbamate.²⁶ But most of these methods, require rigid control of pH, prior separation of nickel, order of addition of reagent and they suffer from poor sensitivity. Moreover, the selectivity of some of the methods reported above, is also poor due to the serious interferences of one or more metal ions viz. Co, Zn, Cu and Mn which are found commonly associated with the real samples.

Many methods have been reported with quite sensitive colour reaction employing a number of chromogenic reagents like 1-(2-pyridylazo)-2-naphthol,²⁷⁻³¹ and its derivative³² or with surfactant^{33,34} 4-(2-pyridylazo) resorcinol^{27,35} and with surfactant,^{36,37} 1-(2-thiazolylazo)-2-naphthol with³⁸ or without polysorbate 80,³⁹ TAN-3, 6-S,^{40,41} 1-(1,2,4-triazolyl-3-azo)-2-naphthol,⁴² xylenol orange in presence of surfactants,^{43,44} or with benzylamine,⁴⁵ and sulphur containing reagents.⁴⁶⁻⁶⁸ However, these methods are often time consuming, indirect and suffer from disadvantages of maintaining a narrow pH range, require back extraction and less stability of the complex. In the above reported methods interferences from several metal ions are also serious drawback.

In the present investigation, nickel(II) is extracted with N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) in presence of 1-(2-pyridylazo)-2-naphthol(PAN) at pH 8.0 ± 0.2 . The method is fairly sensitive and quite selective. The method is reproducible and has been applied satisfactorily for the determination of nickel(II) in metallurgical and industrial samples.

EXPERIMENTAL

APPARATUS - A Carl Zeiss Jena 'Spekol' with EK-5 attachment and matched quartz cells of 1-cm optical path length, was used for all absorbance measurements. A Systronic digital pH-meter type 335 was employed for the measurements of pH values of the solutions.

SATANDARD NICKEL(II) SOLUTION - A stock solution of nickel(II) was prepared by digestion of a weighed amount of nickel metal (99.98% purity) in 5 ml concentrated nitric acid. The excess of nitric acid was removed by heating the dried mass with concentrated hydrochloric acid. The solution was heated upto dryness. The dried mass was dissolved in 1 ml of 10 M hydrochloric acid and diluted to 100 ml with distilled water. The solution was standardized gravimetrically using dimethylglyoxime.⁶⁹ Working standard solution was prepared by appropriate dilution of the stock solution.

CHLOROFORM - AR Grade chloroform was used for all extraction work.

HYDROXYAMIDINES(HOAs) - Hydroxyamidines were synthesized as described in the literature.⁷⁰ Their 0.6%(w/v) or $\approx 2.0 \times 10^{-2}$ M solution in chloroform was used for extraction purpose.

1-(2-PYRIDYLAZO)-2-NAPHTHOL(PAN) - A 0.1%(w/v) or 4.0×10^{-3} M solution of PAN in 95%(v/v) ethanol was used.

BUFFER SOLUTION- A sodium hydroxide-boric acid buffer solution of pH 8.0 was prepared as described in the literature.⁷¹

SOLUTION OF DIVERSE IONS - The solution of diverse ions were prepared as described in the literature.⁷² A 1 mg/ml solution of the appropriate ions was used.

SODIUM TARTRATE SOLUTION - A 20% (w/v) or 0.87 M sodium tartrate solution was used as a masking agent for Fe(III).⁴²

All chemicals used were of Analytical Reagent grade (S D Fine Chem./E. Merck).

PROCEDURE

An aliquot of the test solution containing upto 7.0 μg Ni(II) is placed in a 125-ml separatory funnel. The pH of the aqueous solution is maintained at 8.0 ± 0.2 with buffer solution in a total volume of 10 ml. To the above solution, 3 ml of PAN is added. This solution is shaken vigorously for 2 min with 5 ml chloroform solution of HDPBA. The organic layer is separated and the aqueous phase is washed with 1 x 2 ml fresh portion of chloroform. The combined extracts are dried over anhydrous sodium sulphate ($\sim 2\text{g}$). The total organic phase is made upto 10 ml with chloroform in a 10-ml volumetric flask. The absorbance of the complex is measured against reagent blank at λ_{max} 570 nm.

RESULTS AND DISCUSSION

ABSORPTION SPECTRA

The absorption spectra of the metal complex formed with seven different hydroxyamidines (HOAs) and 1-(2-pyridylazo)-2-naphthol (PAN) in chloroform against their respective reagent blanks and the reagent blank of N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) along with PAN against chloroform are shown in Figure 2.1a. All the complexes exhibit maximum absorption between 560-570 nm. The sensitivity of the complex with HDPBA is comparatively greater than the different hydroxyamidines (HOAs) (Table 2.1). Therefore, it is chosen for all experimental work. The reagent blank of HDPBA along with PAN shows some absorption at the λ_{\max} of the metal complex. Hence, all absorbance measurements were carried out by using it as a reference. The metal concentration does not affect the position of absorption maxima, shown in Figure 2.1b.

EFFECT OF SOLVENTS

Various organic solvents such as 1-pentanol, ethyl acetate, isobutyl methyl ketone, benzene, toluene, xylene, carbon tetrachloride, cyclohexane and chloroform were tested for the extraction of the complex. All these solvents, except carbon tetrachloride and cyclohexane extract the complex quantitatively (Table 2.2, Figure 2.2). But chloroform was selected as the best solvent due to the highest colour sensitivity and selectivity of the complex.

TABLE 2.1 EFFECT OF NATURE OF HYDROXYAMIDINES ON THE ABSORBANCE OF THE Ni(II)-HOA-PAN COMPLEXES IN CHLOROFORM + ETHANOL MIXTURE

$C_{Ni(II)}$	=	5.1×10^{-6} M (3.0 μ g/10 ml organic phase)
pH	=	8.0 \pm 0.2
C_{HOAs}	\approx	2.0×10^{-2} M
C_{PAN}	=	1.2×10^{-3} M

Hydroxyamidines (HOAs)	$\begin{bmatrix} \text{Ph} - \text{C} = \text{N} - \text{Ph}' \\ \\ \text{Ph}'' - \text{N} - \text{OH} \end{bmatrix}$			λ_{max} nm	Molar absorptivity $l \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$
	Ph''	Ph'	Ph		
N-Hydroxy-N, N'-diphenylbenzamide	C_6H_5	C_6H_5	C_6H_5	570	7.83
N-Hydroxy-N-phenyl-N'-(3-chlorophenyl)-benzamide	C_6H_5	3-Cl- C_6H_4	C_6H_5	570	7.44
N-Hydroxy-N-(4-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide	4-Cl- C_6H_4	3-Cl- C_6H_4	2-Cl- C_6H_4	565	7.34
N-Hydroxy-N-(4-chlorophenyl)-N'-(2-methylphenyl)-2-chlorobenzamide	4-Cl- C_6H_4	2-CH ₃ - C_6H_4	2-Cl- C_6H_4	570	6.26
N-Hydroxy-N-(2-chlorophenyl)-N'-(4-chlorophenyl)-2-chlorobenzamide	2-Cl- C_6H_4	4-Cl- C_6H_4	2-Cl- C_6H_4	560	5.67
N-Hydroxy-N-(3-chlorophenyl)-N'-(2-methylphenyl)-benzamide	3-Cl- C_6H_4	2-CH ₃ - C_6H_4	C_6H_5	570	5.48
N-Hydroxy-N-(2-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide	2-Cl- C_6H_4	3-Cl- C_6H_4	2-Cl- C_6H_4	560	4.89

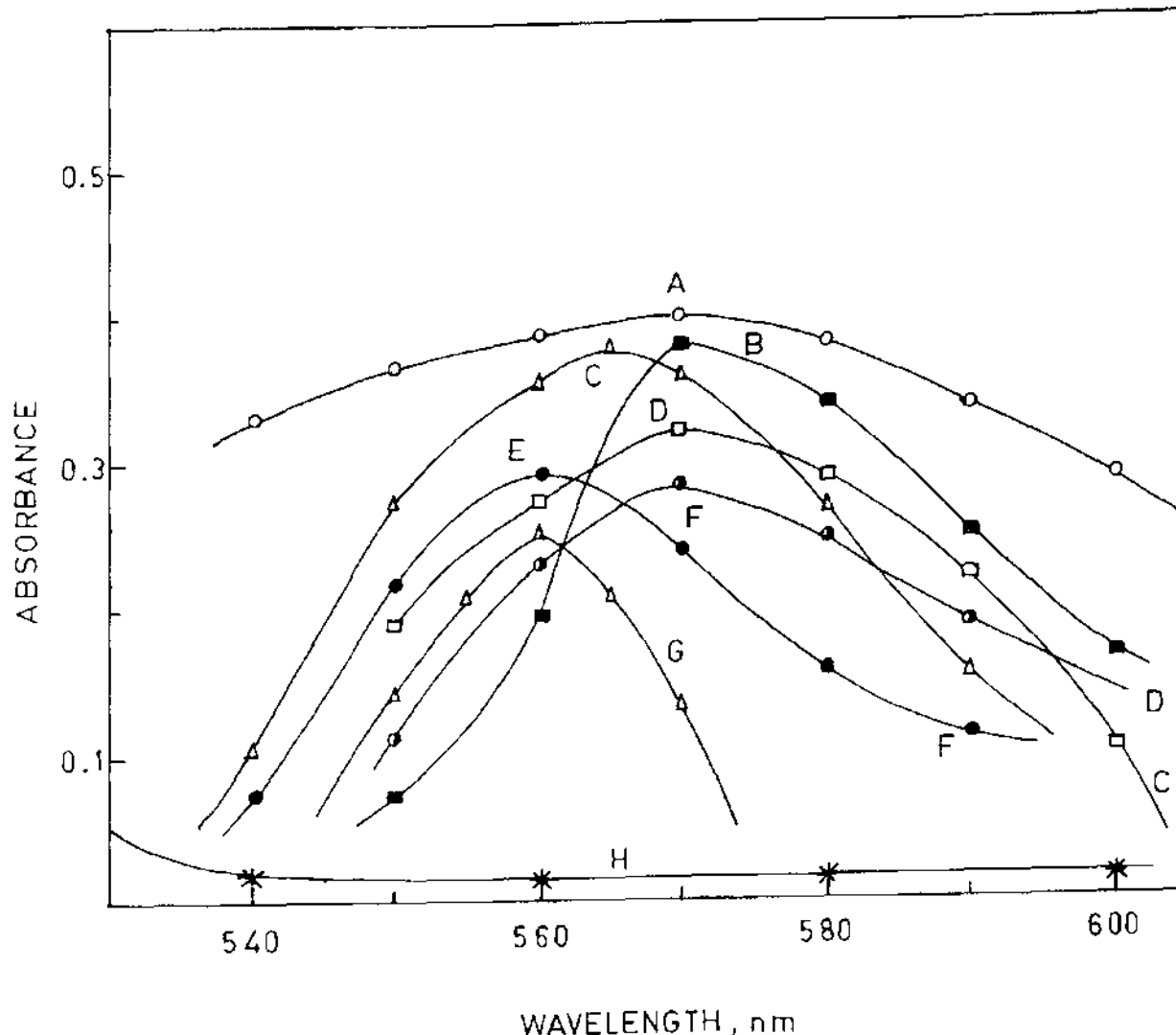


FIG.2.1 a. ABSORPTION SPECTRA OF NICKEL(II) COMPLEX WITH DIFFERENT HYDROXYAMIDINES(HOAs) AND PAN AGAINST THEIR RESPECTIVE REAGENT BLANKS IN CHLOROFORM + ETHANOL MIXTURE

$$C_{Ni(II)} = 5.1 \times 10^{-6} \text{ M} ; \text{pH} = 8.0 \pm 0.2 ;$$

$$C_{HOAs} \approx 2.0 \times 10^{-2} \text{ M} ; C_{PAN} = 1.2 \times 10^{-3} \text{ M}.$$

- [A] N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE
- [B] N-HYDROXY-N-PHENYL-N'-(3-CHLOROPHENYL)-BENZAMIDINE
- [C] N-HYDROXY-N-(4-CHLOROPHENYL)-N'-(3-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [D] N-HYDROXY-N-(4-CHLOROPHENYL)-N'-(2-METHYLPHENYL)-2-CHLOROBENZAMIDINE
- [E] N-HYDROXY-N-(2-CHLOROPHENYL)-N'-(4-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [F] N-HYDROXY-N-(3-CHLOROPHENYL)-N'-(2-METHYLPHENYL)-BENZAMIDINE
- [G] N-HYDROXY-N-(2-CHLOROPHENYL)-N'-(3-CHLOROPHENYL)-2-CHLOROBENZAMIDINE
- [H] REAGENT BLANK OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE

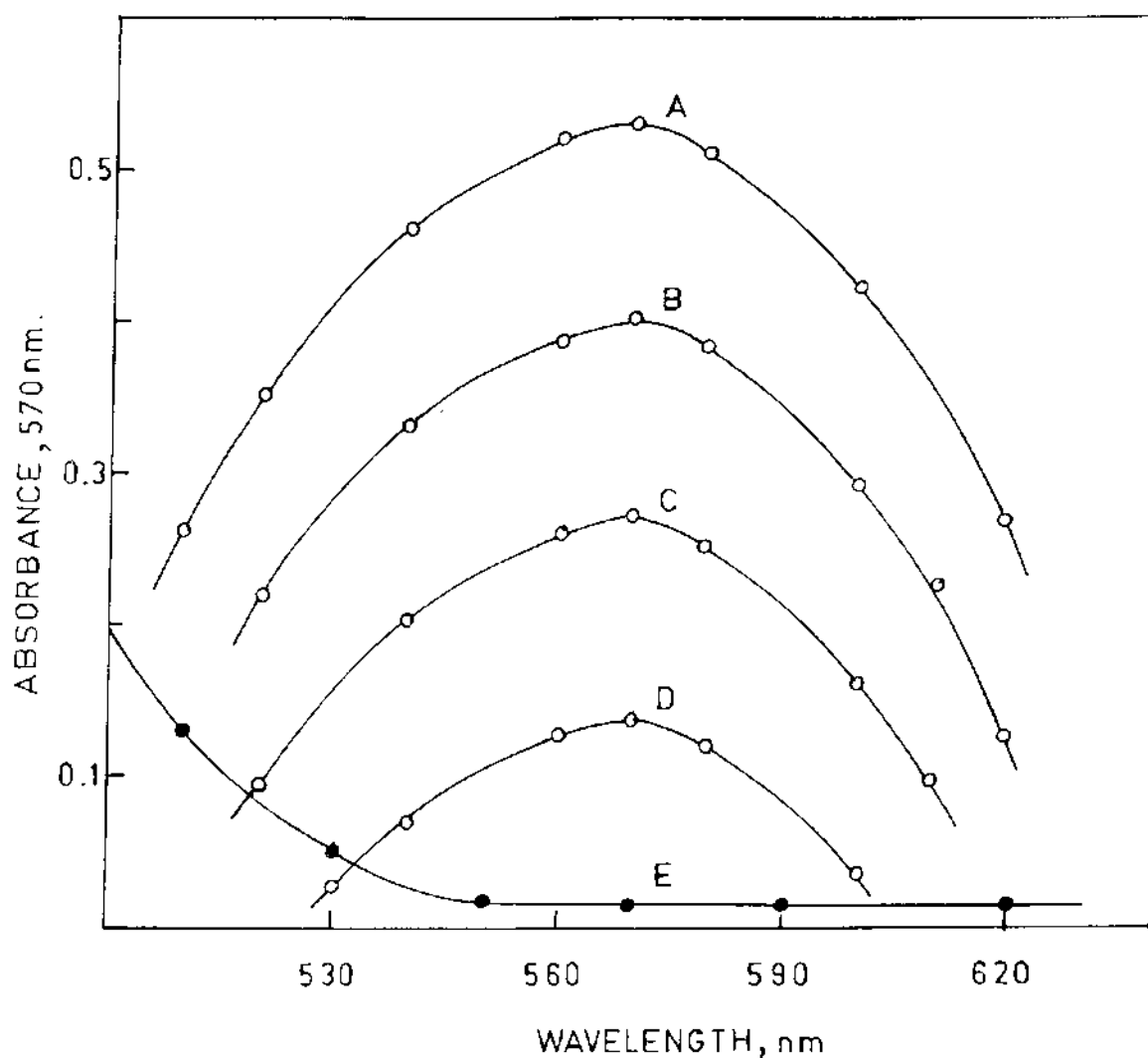


FIG. 2.1 b. EFFECT OF METAL CONCENTRATION ON THE POSITION OF λ_{\max} OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

- [A] $C_{Ni(II)} \approx 6.8 \times 10^{-6}$ M (4.0 μ g/10 ml organic phase)
 [B] $C_{Ni(II)} \approx 5.1 \times 10^{-6}$ M (3.0 μ g/10 ml organic phase)
 [C] $C_{Ni(II)} \approx 3.4 \times 10^{-6}$ M (2.0 μ g/10 ml organic phase)
 [D] $C_{Ni(II)} \approx 1.7 \times 10^{-6}$ M (1.0 μ g/10 ml organic phase)
 [E] REAGENT BLANK

EFFECT OF pH

The influence of pH of the aqueous phase on the extraction of the complex was studied. It was found that the pH range of 7.0-9.0 was essential for quantitative extraction and full colour development of the complex (Table 2.3, Figure 2.3). Therefore, subsequent determination were carried out at pH 8.0 ± 0.2 using borate buffer.

EFFECT OF N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE (HDPBA)

The effect of HDPBA solution, made in chloroform, on the extraction of the metal was studied and it was observed that minimum of 1.9×10^{-2} M HDPBA was necessary for complete formation of the complex and upto 2.4×10^{-2} M HDPBA solution had no adverse effect on the absorbance of the complex (Table 2.4, Figure 2.4). Hence, all extractions were performed with 2.0×10^{-2} M HDPBA solution.

EFFECT OF 1-(2-PYRIDYLAZO)-2-NAPHTHOL (PAN)

The effect of PAN concentration on the colour development of the complex was examined. It was found that $(0.8-1.6) \times 10^{-3}$ M PAN solution was enough for maximum colour development of the complex. Lower concentration of PAN gave incomplete complexation while excess of PAN concentration increased the intensity of the blank (Table 2.5, Figure 2.5). Hence, all experiments were carried out at 1.2×10^{-3} M PAN solution.

EFFECT OF DILUTION AND TEMPERATURE

The volume ratio of organic to aqueous phase is an important factor for the extraction of the complex. Therefore,

TABLE 2.2 EFFECT OF SOLVENTS ON THE ABSORBANCE OF THE Ni(II)-HDPBA-PAN COMPLEX

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml organic phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

Solvent	λ_{max} nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$
Chloroform	570	7.83
Isobutyl methyl ketone	560	6.26
Xylene	560	6.26
Toluene	570	4.20
Benzene	570	3.72
Ethyl acetate	570	4.01
1-Pentanol	560	3.91
Cyclohexane	-	No extraction
Carbon tetrachloride	-	No extraction

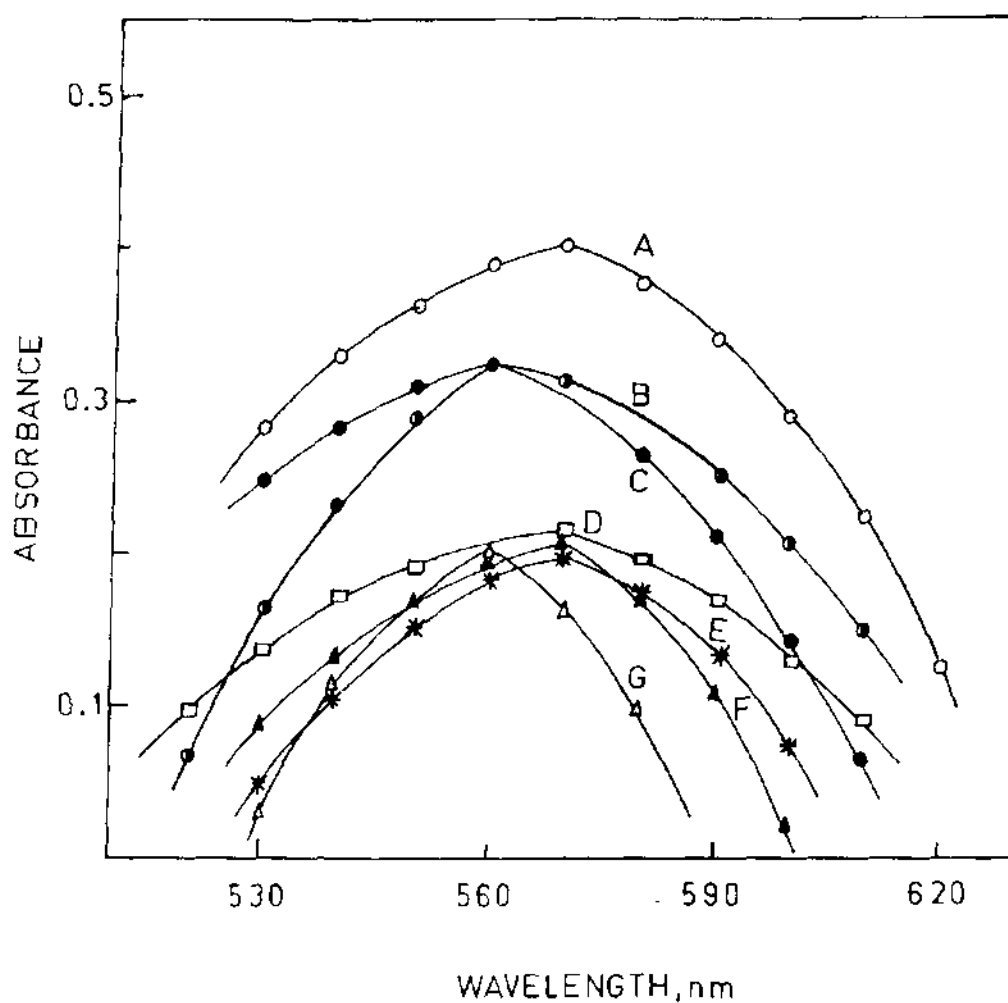


FIG. 2.2 EFFECT OF SOLVENTS ON THE ABSORBANCE AND λ_{\max} OF THE Ni(II)-HDPBA-PAN COMPLEX

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M};$$

$$\text{pH} = 8.0 \pm 0.2;$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M};$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}.$$

[A] CHLOROFORM [B] ISOBUTYL METHYL KETONE
 [C] XYLENE [D] TOLUENE [E] BENZENE
 [F] ETHYL ACETATE [G] 1-PENTANOL

TABLE 2.3 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION AND COLOUR DEVELOPMENT OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

pH of the aqueous phase	Absorbance at 570 nm
5.0	0.24
6.0	0.32
6.5	0.36
7.0	0.40
7.5	0.40
8.0	0.40
9.0	0.40
9.5	0.37
10.0	0.34
11.0	0.30

TABLE 2.4 EFFECT OF HDPBA CONCENTRATION ON THE ABSORBANCE OF Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

Concentration of HDPBA, M $\times 10^{-2}$	Absorbance at 570 nm
1.4	0.36
1.6	0.37
1.9	0.40
2.0	0.40
2.2	0.40
2.4	0.40
2.6	0.35
2.8	0.30

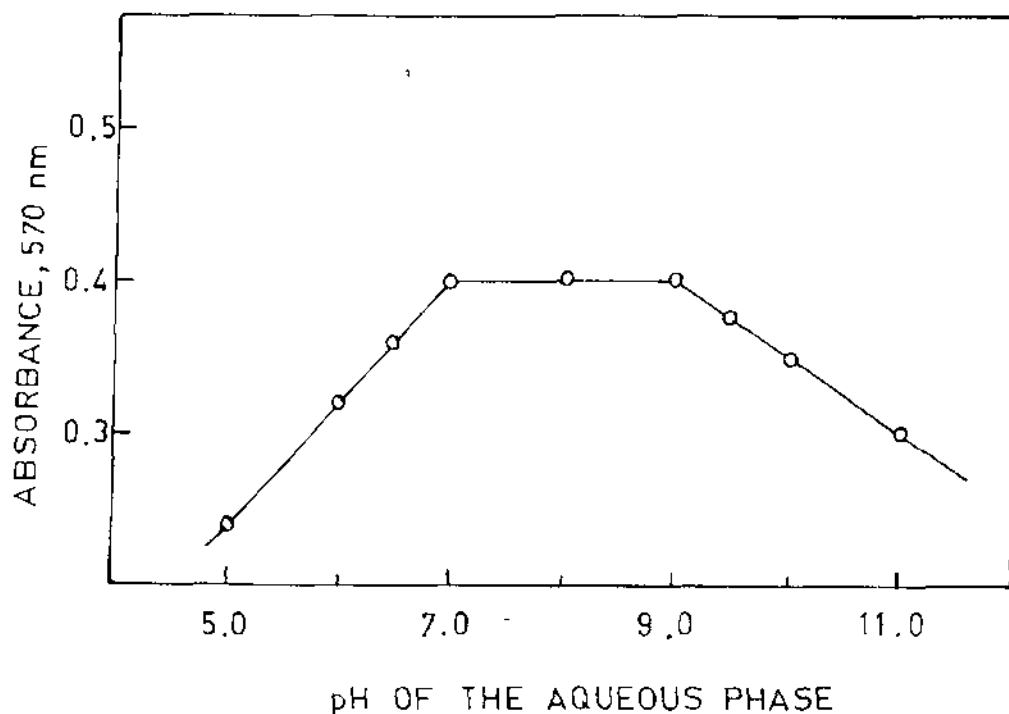


FIG. 2.3 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION AND COLOUR DEVELOPMENT OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M}; C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}; C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M.}$$

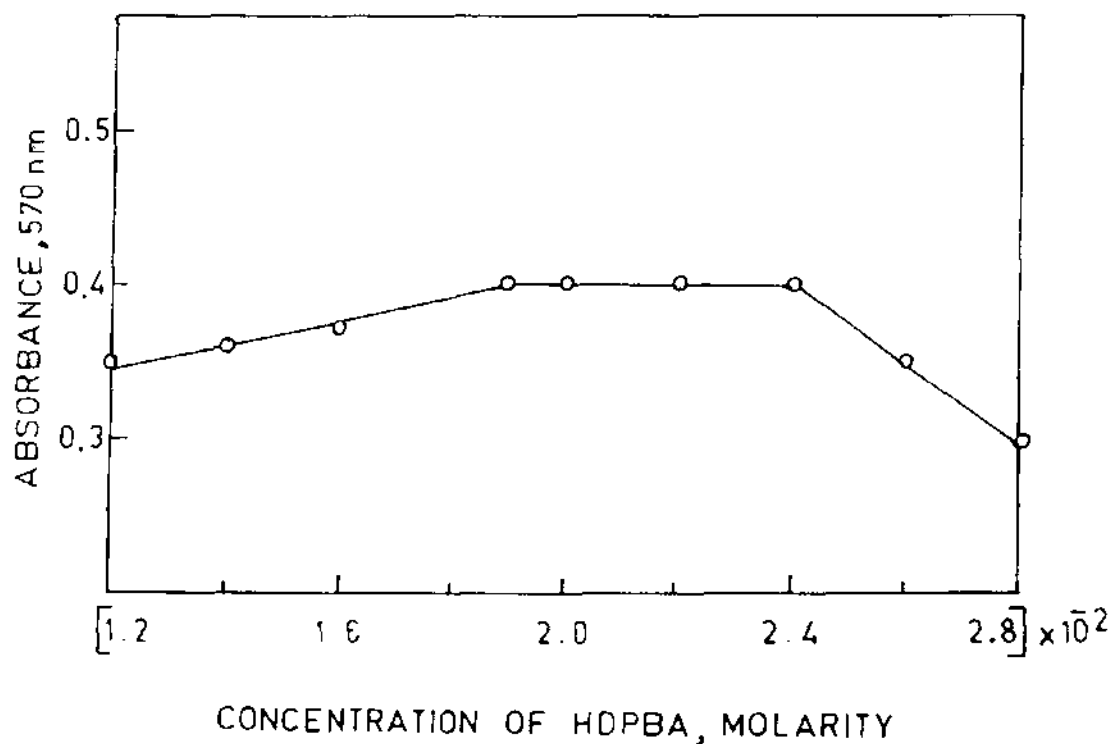


FIG. 2.4 EFFECT OF HDPBA CONCENTRATION ON THE ABSORBANCE OF Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M}; \text{pH} = 8.0 \pm 0.2; C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M.}$$

the effect of volume ratio on the absorbance was examined. The absorbance remained constant when the volume ratio of organic to aqueous phase was varied between 2:1 to 1:8 (Table 2.6, Figure 2.6). For the uniformity in all experiments the volume of the aqueous phase was always kept to 10 ml before the extraction of the analyte in organic phase. The colour intensity of the complex was unaffected by variation of temperature of the aqueous phase from 20 - 35°C (Table 2.7). Therefore, all extractions were carried out at room temperature $25 \pm 2^\circ\text{C}$.

EFFECT OF ELECTROLYTES

The effect of electrolytes such as NaCl/KCl/NH₄Cl/NH₄NO₃, and (NH₄)₂SO₄ has been studied for the extraction of the metal complex. No change on the absorbance of the complex was observed when the ionic strength of these electrolytes in the aqueous phase was upto 2 M.

EFFECT OF EXTRACTION TIME, STABILITY OF THE COMPLEX AND ORDER OF ADDITION OF REAGENTS

The minimum shaking time for maximum extraction of the complex was found to be 2 min at room temperature $25 \pm 2^\circ\text{C}$. Prolonged shaking had no adverse effect on the extraction of the complex. The absorbance of the complex was stable upto 24 hr. The order of addition of reagents in the procedure was not critical.

TABLE 2.5 EFFECT OF PAN CONCENTRATION ON THE FORMATION AND COLOUR DEVELOPMENT OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

Concentration of PAN, M $\times 10^{-3}$	Absorbance at 570 nm
0.4	0.32
0.6	0.34
0.8	0.40
1.0	0.40
1.2	0.40
1.4	0.40
1.6	0.40
1.7	0.35
1.8	0.29

TABLE 2.6 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION AND ABSORBANCE OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 3.0 \mu\text{g}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

Volume ratio of organic to aqueous phase	Absorbance at 570 nm
2 : 1	0.40
1 : 1	0.40
1 : 2	0.40
1 : 4	0.40
1 : 6	0.40
1 : 8	0.40
1 : 9	0.36
1 : 10	0.32

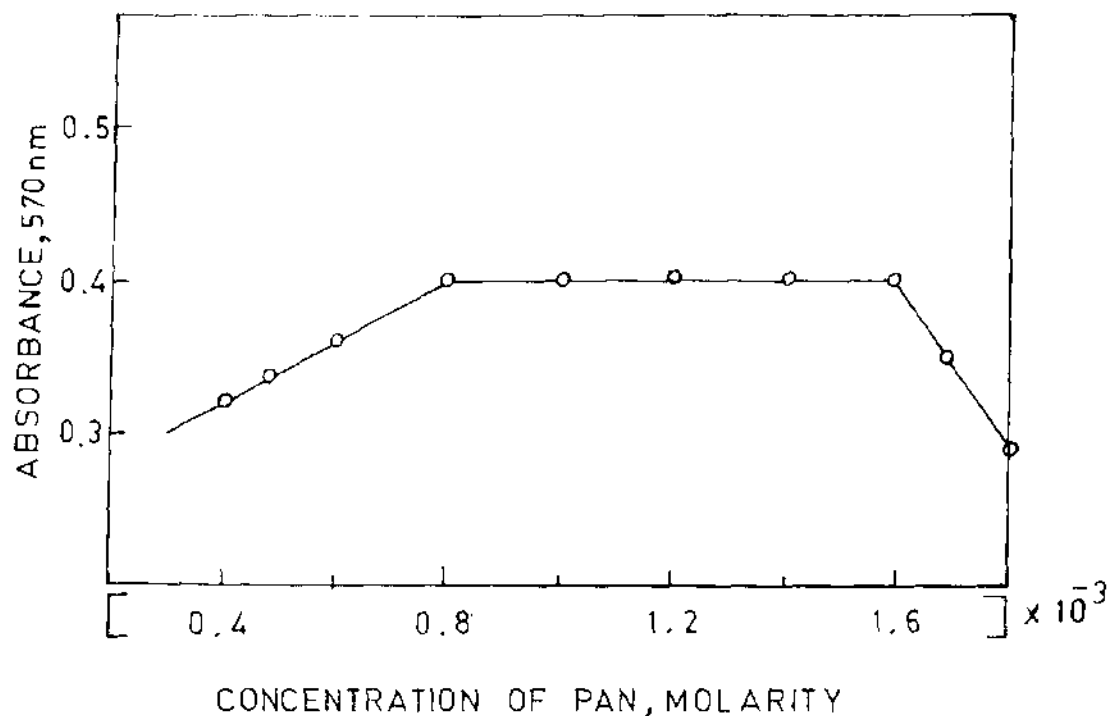


FIG. 2.5 EFFECT OF PAN CONCENTRATION ON THE FORMATION AND COLOUR DEVELOPMENT OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M}; \text{ pH} = 8.0 \pm 0.2; C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M.}$$

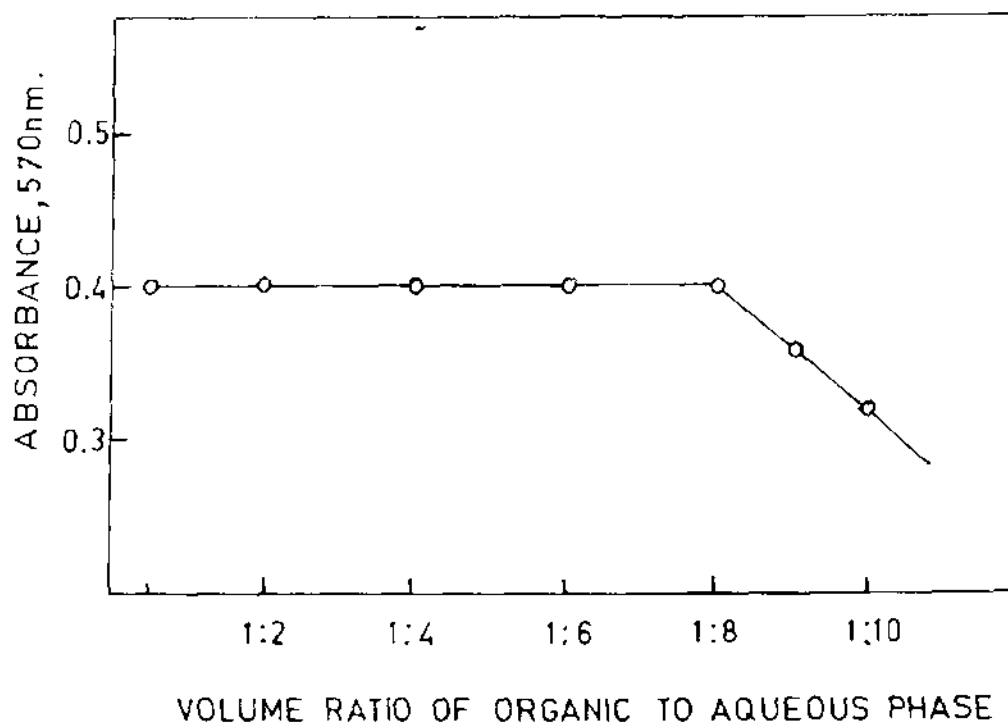


FIG. 2.6 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION AND ABSORBANCE OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 3.0 \mu\text{g}; \text{ pH} = 8.0 \pm 0.2; C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}; \\ C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M.}$$

TABLE 2.7 EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE ON THE COLOUR INTENSITY OF THE Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

Temperature of the aqueous phase, °C	Absorbance at 570 nm
10	0.34
15	0.37
20	0.40
25	0.40
30	0.40
35	0.40
40	0.34
45	0.32

BEER'S LAW, CORRELATION COEFFICIENT, MOLAR ABSORPTIVITY AND DETECTION LIMIT

The system confirms to Beer's law upto 0.7 ppm (7.0 $\mu\text{g}/10$ ml organic solution) with correlation coefficient⁷³ value of 0.99 (Table 2.8, Figure 2.7). The optimum concentration range for the determination of nickel is evaluated from calibration curve and it is found to be between 0.15 -0.53 ppm (1.5-5.3 $\mu\text{g}/10$ ml organic solution). The molar absorptivity of the complex with seven different hydroxyamidines lie in the range of $(4.89 - 7.83) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 560 -570 nm. The molar absorptivity of the Ni(II)-HDPBA-PAN complex in chloroform is found to be $7.83 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 570 nm. The sensitivity in terms of Sandell's definition⁶ is $0.00075 \mu\text{g}/\text{cm}^2$ of nickel(II), for an absorbance unit of 0.001. The detection limit of the metal is $0.008 \mu\text{g}/\text{ml}$ aqueous solution.

PRECISION OF THE METHOD AND CONFIDENCE LIMIT

Precision of the method was checked by taking ten replicate measurements, each containing $3.0 \mu\text{g}$ of Ni(II)/10 ml aqueous phase. A mean absorbance and standard deviation values were calculated to be 0.40 and ± 0.0053 , respectively. The relative standard deviation of the method was found to be $\pm 1.3 \%$. The confidence limit⁷³ of the method in terms of mean absorbance and molar absorptivity at 95% probability were found to be (0.40 ± 0.004) and $(7.83 \pm 0.08) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ respectively (Table 2.9).

TABLE 2.8 CALIBRATION CURVE DATA AND CORRELATION COEFFICIENT FOR THE DETERMINATION OF NICKEL(II) AS Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

No. of obser- vation	Concentration of Ni(II) in organic solution Xi = $\mu\text{g}/10 \text{ ml}$	Absorbance at 570 nm Yi	Correlation coefficient r
	1.0	0.13	
	2.0	0.27	
	3.0	0.40	
7	4.0	0.53	0.99
	5.0	0.67	
	6.0	0.80	
	7.0	0.94	

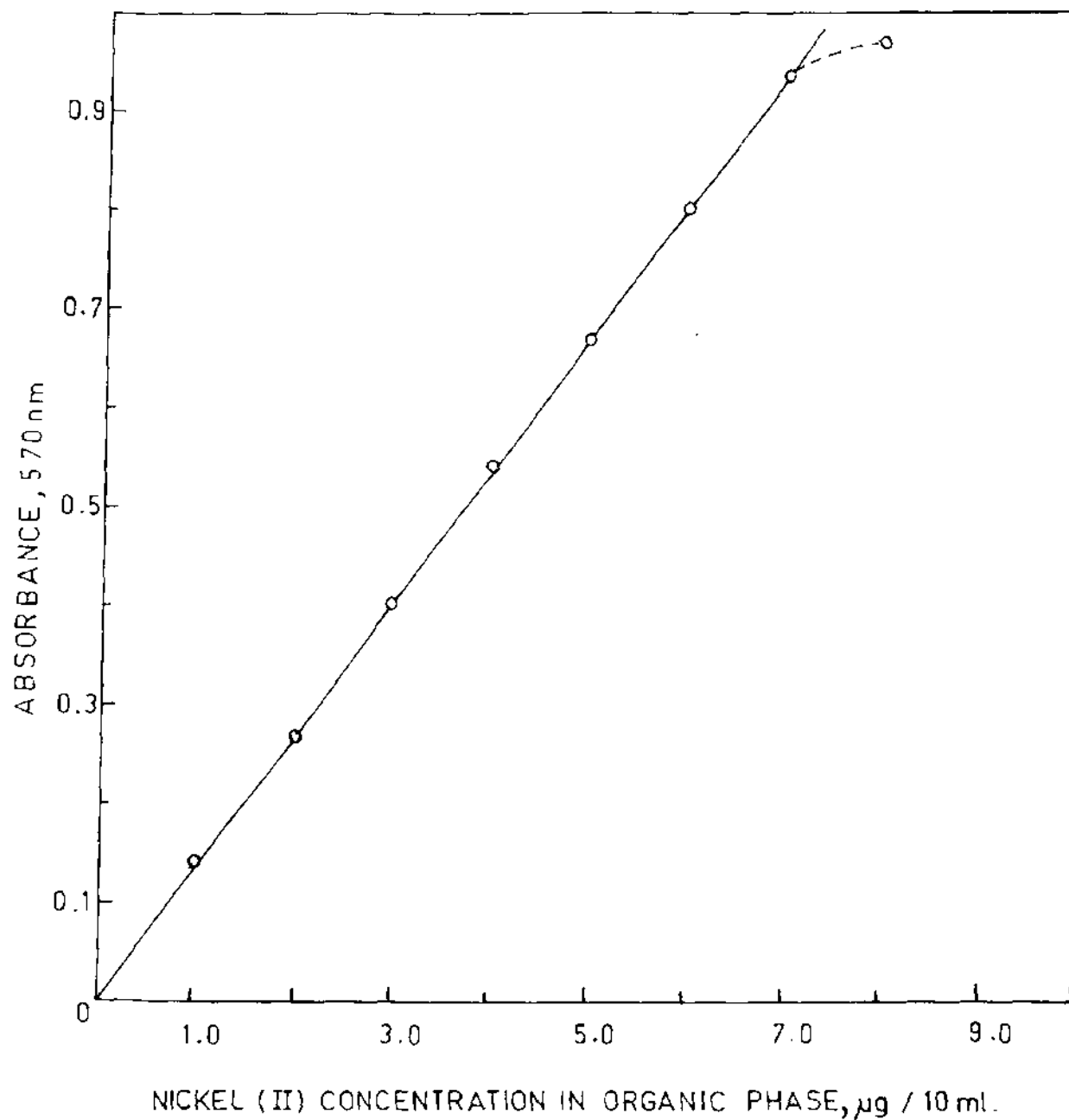


FIG. 2.7 CALIBRATION CURVE FOR THE DETERMINATION OF NICKEL(II) AS Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

TABLE 2.9 DETERMINATION OF PRECISION OF THE METHOD

$$C_{Ni(II)} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{HDPBA} = 2.0 \times 10^{-2} \text{ M}$$

$$C_{PAN} = 1.2 \times 10^{-3} \text{ M}$$

No. of obser- vation	Absorbance at 570 nm	Mean absorbance	Standard deviation	Relative standard deviation	Value of 't' at 95% confi- dence level	Confidence limit	$\left[\bar{x} \pm \frac{t_s}{\sqrt{N}} \right]$
N		\bar{x}	$\pm S$	$\pm, \%$			
	0.40						
	0.40						
	0.41						
	0.40						
10	0.40	0.40	0.0053	1.3	2.262	(0.40±0.004)	(7.83±0.08)
	0.40						
	0.41						
	0.40						
	0.40						
	0.40						

EFFECT OF DIVERSE IONS

The effect of various ions on the determination of 0.3 $\mu\text{g/ml}$ Ni(II) was studied as in the above described procedure. No metal ions, except Fe(III), interfere in the present method. The interference due to Fe(III) could be removed by adding 1 ml of 20% (w/v) sodium tartrate solution prior to the extraction of the metal. The tolerance limit of various ions are summarised in Table 2.10.

TABLE 2.10 EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 3.0
 μg NICKEL(II)

ION	Added as	Tolerance limit [#] mg
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.03 ^a
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.06
Phosphate	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.06
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	0.15
W(VI)	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.75
Mn(II)	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	1.0
Sb(III)	$(\text{SbO})\text{KC}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$	1.0
Bi(III)	$\text{Bi}_2(\text{SO}_4)_3$	1.0
Zr(IV)	$\text{ZrO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$	1.0
Sn(IV)	SnCl_4	1.0
Hg(IV)	HgCl_2	1.2
Ce(IV)	$\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	1.2
Os(VI)	Na_2OsO_4	1.3
Re(VII)	KReO_4	1.3
U(VI)	$\text{UO}_2(\text{NO}_3)_2$	1.5
Fe(II)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	2.0
Mn(VII)	KMnO_4	2.5
Co(II)	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	4.0
Ti(IV)	$\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	4.0

Contd..

TABLE 2.10 (Contd.)

ION	Added as	Tolerance limit [#] mg
Mg(II)	MgCl ₂ · 6H ₂ O	5.0
Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	5.0
Persulphate	Na ₂ S ₂ O ₈	6.0
Cr(III)	Cr ₂ (SO ₄) ₃ Al ₂ (SO ₄) ₃ · 24H ₂ O	8.0
V(V)	NH ₄ VO ₃	8.0
Ca(II)	CaCl ₂ · H ₂ O	12
Cu(II)	CuSO ₄ · 5H ₂ O	12
Ba(II)	BaCl ₂	12
Oxalate	Na ₂ C ₂ O ₄	15
Cyanide	KCN	16
Bromide	KBr	16
EDTA	Na ₂ -EDTA	20
Tartrate	Na ₂ C ₄ H ₄ O ₆ · 2H ₂ O	300

[#] Causing error in absorbance less than $\pm 2\%$.

a Masked with 1 ml of 20% (w/v) Na-tartrate solution

STOICHIOMETRY OF THE COMPLEX

In order to find out the ratio of metal to HDPBA and PAN in Ni(II)-HDPBA-PAN complex in chloroform, curve-fitting method has been applied. The data obtained indicated that one molecule of each of HDPBA and PAN reagent was necessary for the formation of 1:1:1, Ni(II)-HDPBA-PAN complex.

PROCEDURE

[A] DETERMINATION OF THE RATIO OF HDPBA

An aliquot of the test solution containing 3.0 μg Ni(II) was placed in a 125-ml separatory funnel. The pH of the aqueous solution was maintained at 8.0 ± 0.2 with buffer solution, by keeping a total volume of 10 ml aqueous phase. To the above solution 3 ml of PAN was added. The mixture was shaken vigorously for 2 min with varying known amounts of chloroform solution of HDPBA. The organic extract was taken in a 10-ml volumetric flask and dried as above. The absorbance of the organic extract was measured against reagent blank at λ_{max} . The reagent blank was prepared in the similar manner.

A graph was plotted between the logarithmic value of distribution ratio of metal ($D = A_{\text{eq}}/A_{\text{max}} - A_{\text{eq}}$) versus log molar concentration of the N-hydroxy-N, N'-diphenylbenzamidine (HDPBA). The slope of the curve was found to be 1.1 which is close to integer 1. This shows that one molecule of HDPBA is necessary for each metal ion in the complex formation (Table 2.11, Figure 2.8).

TABLE 2.11 CURVE - FITTING METHOD FOR THE DETERMINATION OF NICKEL(II) TO HDPBA RATIO IN Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M}$$

Concentration of HDPBA in organic phase, M $\times 10^{-2}$	Log M	$D = \frac{A_{\text{eq}}}{A_{\text{max}} - A_{\text{eq}}}$	Log D
1.4	-1.85	9.00	0.95
1.2	-1.92	7.00	0.85
1.0	-2.00	5.67	0.75
0.7	-2.15	3.44	0.54

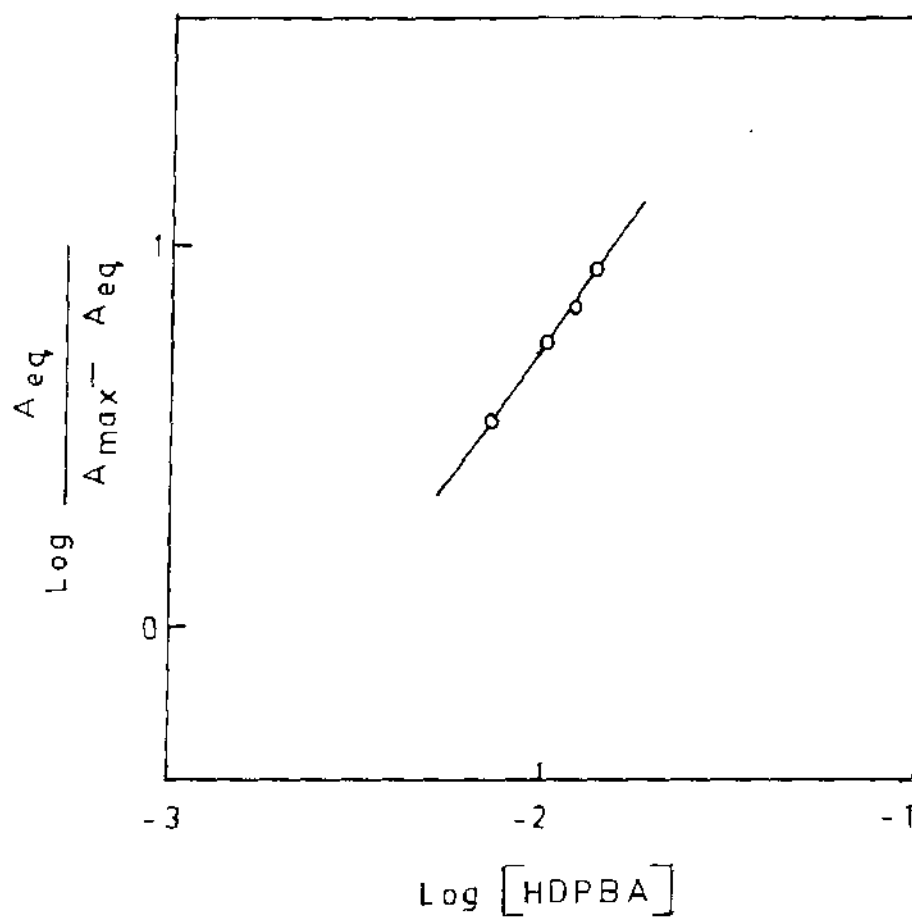


FIG. 2.8 CURVE-FITTING METHOD FOR THE DETERMINATION OF NICKEL(II) TO HDPBA RATIO IN Ni(II)-HDPBA-PAN COMPLEX, FORMED IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Ni(II)}} = 5.1 \times 10^{-6} \text{ M};$$

$$\text{pH} = 8.0 \pm 0.2;$$

$$C_{\text{PAN}} = 1.2 \times 10^{-3} \text{ M};$$

$$\lambda_{\text{max}} = 570 \text{ nm.}$$

[B] DETERMINATION OF THE RATIO OF PAN

An aliquot of the test solution containing 3.0 μg Ni(II) was placed in a 125-ml separatory funnel. The pH of the aqueous solution was adjusted to 8.0 ± 0.2 , by keeping a constant volume of 10 ml. A known concentration of PAN solution was added in the aqueous solution. The aqueous solution was shaken with 5 ml of HDPBA solution of chloroform for 2 min. This procedure was repeated with a varying known concentration of PAN solution, to obtain a series of data. The organic extract was separated and transferred to a 10-ml volumetric flask. The absorbance of the complex was measured against reagent blank at λ_{max} 570 nm as in the above described procedure. The reagent blank in each cases were prepared in a similar manner.

The slope of the curve was calculated by plotting the graph between logarithmic value of distribution ratio of metal ($D = A_{\text{eq}}/A_{\text{max}} - A_{\text{eq}}$) versus log molar concentration of PAN and it was found to be 0.95 which is close to 1. This value indicates that one molecule of PAN is required for each nickel(II) in the complex formation (Table 2.12, Figure 2.9).

N-Hydroxy-N,N'-diphenylbenzamidine(HDPBA) is used as a monobasic bidentate reagent. The nickel(II) reacts with HDPBA to give a 1:2, Ni(II)-HDPBA greenish solid complex which has been reported by Satyanarayana et al.⁷⁴ 1-(2-Pyridylazo)-2-naphthol (PAN) reacts with nickel(II) to give 1:2, Ni(II)-PAN complex but according to Betteridge et al.⁷⁵ nickel complex of PAN showed anomalous behaviour and preliminary experiments

TABLE 2.12 CURVE - FITTING METHOD THE FOR DETERMINATION OF NICKEL(II) TO PAN RATIO IN Ni(II)-HDPBA-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{Ni(II)} = 5.1 \times 10^{-6} \text{ M (3.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 8.0 \pm 0.2$$

$$C_{HDPBA} = 2.0 \times 10^{-2} \text{ M}$$

Concentration of PAN in organic phase, M $\times 10^{-3}$	Log M	$D = \frac{A_{eq}}{A_{max} - A_{eq}}$	Log D
0.52	-3.28	5.15	0.70
0.40	-3.40	4.00	0.60
0.28	-3.55	2.80	0.45
0.20	-3.70	2.07	0.30

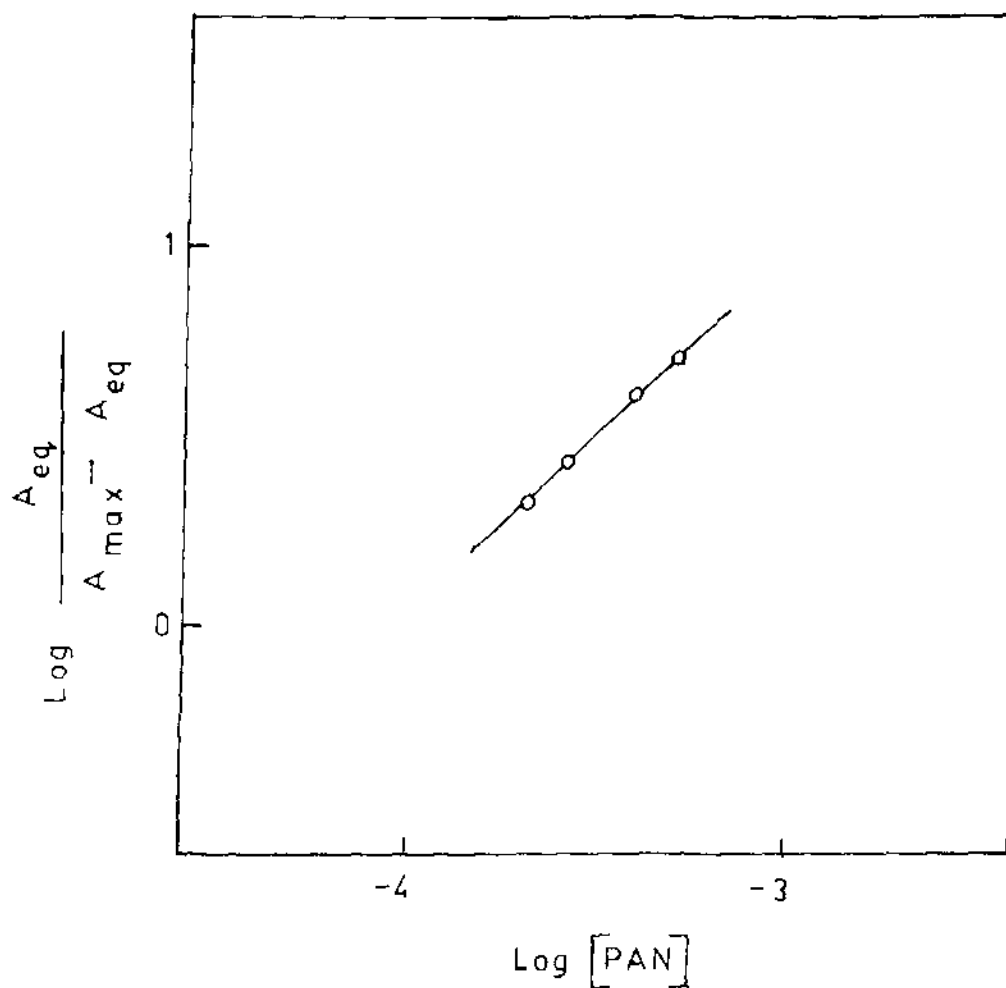


FIG.2.9 CURVE-FITTING METHOD FOR THE DETERMINATION OF NICKEL(II) TO PAN RATIO IN Ni(II)-HDPBA-PAN COMPLEX, FORMED IN CHLOROFORM + ETHANOL MIXTURE

$$C_{Ni(II)} = 5.1 \times 10^{-6} \text{ M};$$

$$\text{pH} = 8.0 \pm 0.2;$$

$$C_{HDPBA} = 2.0 \times 10^{-2} \text{ M};$$

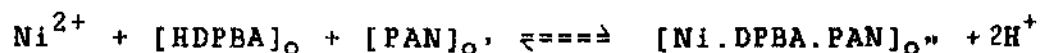
$$\lambda_{\text{max}} = 570 \text{ nm.}$$



T 12749

T.12749

indicate that only one proton is released and one PAN molecule is taken up by the metal ion. In the present investigation, the extracted ternary complex is a mixed ligand complex in nature because in the presence of PAN one molecule of HDPBA is replaced from 1:2, Ni(II)-HDPBA complex by one molecule of PAN. Thus, 1:1:1 Ni(II)-HDPBA-PAN complex is formed and its reaction mechanism can be written as



Where abbreviations HDPBA and PAN, and subscripts o, o' and o'' denote N-hydroxy-N,N'-diphenylbenzamide, 1-(2-pyridylazo)-2-naphthol, chloroform, ethanol and chloroform + ethanol mixture, respectively.

TABLE 2.13 DETERMINATION OF NICKEL(II) IN METALLURGICAL AND INDUSTRIAL SAMPLES

Sample	Composition		Ni(II) found	Relative standard deviation [*]
		%		
SAE 8630 Steel ^a	C	0.30		
	Ni	0.42	0.40	1.3
	Mo	0.20		
	Mn	0.82		
	Cr	0.82		
Brass metal (5f) ^b	Zn	24.20		
	Sn	1.85		
	Pb	2.52	0.16	1.3
	Fe	0.31		
	Mo	0.12		
	P	0.06		
	Ni	0.17		
Coal ash ^c	-		0.012(0.013) ^{**}	1.6(1.5) ^{**}

a. Obtained from Himmat Steel Foundary, Kumhari, Durg, India.

b. Obtained from Bureau of Analysed Samples Ltd., England.

c. Obtained from Mandhar Cement Factory, Raipur(M.P.)

* Average of six determinations.

** Determined by AAS.

APPLICATION OF THE METHOD

The present method has been applied successfully for the determination of nickel(II) in following standard samples and coal ash. The results are shown in Table 2.13. The digestion of the samples are given below -

- [1] Steel sample - A weighed amount of steel sample was dissolved in 10 ml of warm 50% nitric acid, boiled to expel oxides of nitrogen.⁷⁶ The solution was cooled and made upto the mark with distilled water in a 250-ml volumetric flask. The nickel content was determined as in the above described procedure after the addition of 1 ml of 20% (w/v) sodium tartrate solution.
- [2] Brass metal - A known amount of Brass metal was dissolved in 40% nitric acid.⁷⁷ The solution was evaporated to a small volume and after dilution to 100 ml with distilled water, precipitated tin oxide were filtered off. The Precipitate was thoroughly washed with dilute nitric acid. The filterate was again evaporated to dryness and diluted with distilled water. The solution was transferred to a 250-ml volumetric flask and diluted to the volume. The analyte content was determined as in the previously described procedure after the addition of 1 ml of 20% (w/v) sodium tartrate solution.
- [3] Coal ash - A weighed amount of coal ash in a platinum dish was treated with 1 ml of sulphuric acid, 10 ml of nitric acid, 5 ml of perchloric acid and 10 ml of hydrochloric acid.⁷⁸ The mixture was then heated on a hot

plate and evaporated almost to dryness. The residue was dissolved in 20 ml of 1 M hydrochloric acid by heating for 30 min and the solution was cooled to room temperature, transferred into a 100-ml volumetric flask and diluted to the mark with distilled water. The nickel content was determined as in the proposed method.

COMPARISON WITH OTHER METHODS

Various spectrophotometric methods have been reported for the determination of nickel(II) in various kinds of samples. The spectral characteristics of all the methods are compared with the present method (Table 2.14). The comparison shows that the present method is highly sensitive and quite selective than the other established methods.

TABLE 2.14 COMPARATIVE STUDY OF SOME SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF NICKEL

Reagents	pH/Acidity	Solvent	λ_{\max} nm	Molar absorp- tivity $l\ mol^{-1}\ cm^{-1}$	Remarks	Refer- ence
Dimethylglyoxime	5.5- 9.6	Chloroform	375	-	Fe,Cu,EDTA and bi-carbonate interfere seriously.	8
Dimethylglyoxime + Bromine	9.0-10.0	Chloroform	442	-	Back extraction re- quired,time consu- ming,Mn interfere.	10
1-(2-Pyridylazo)- 2-naphthol	4.6	Chloroform	580	51400	Critical pH, Co and Fe interfere,low sensitivity.	28
1-(2-Pyridylazo)- 2-naphthol+Triton X-100+Sulphydryl- acetic acid	6.0-10.0	-	589.3	56000	Low sensitivity,Su- lfhydrylacetic acid is used as acceler- ater in complex formation	33
2-(2-Pyridylazo)- 5-methoxyphenol	7.5-10.0	Chloroform	520	113000	Selectivity is poor, triple extraction required, time consuming.	32
4-(2-Pyridylazo)- resorcinol+Tetra- decyldimethylben- zylammonium chloride	8.5- 9.5	Chloroform	500	70000	Pb,Cr,Co interfere, Interference from V, Fe,Mo,Ti,Zr and Sb are removed by diff- erent masking agents.	36
1-(1,2,4-Triazolyl -3-azo)-2-naphthol	4.8- 5.4	Chloroform	523	37000	Cd,Co,Fe,Cu,Hg,V, etc. interfere.	42
2-(2-Thiazolylazo) -p-cresol	5.9	Water	580	26000	Cu,Bi,Sn,Mn,Cd,Mo, Pb,Al,Fe and Co interfere.	60
Rubeanic acid + Quinoline	7.5- 9.0	90% (v/v) Al- coholic solution	390	8400	Cu,Cd,Pb,Fe,Mn,Co, Pd,Al,Cr and Bi interfere.	66

Contd..

TABLE 2.14 Contd.

Reagents	pH/Acidity	Solvent	λ_{\max} nm	Molar absorp- tivity $l \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks	Refer- ence
N-Methylpiperazi- nedithiocarbamate +Microcrystalline naphthalene	6.0- 9.5	Dimethyl formamide	390	3025	Poor sensitivity.	26
3-(4-Methoxyphe- nyl)-2-mercapto- propenoic acid	10.0-12.0	Water	400	19500	Cu, Co and Pd interfere.	20
3-Hydroxy-3-iso- propyl-1-p-chlo- rophenyl triazene	8.0- 8.4	Ethanol	415	2387	Co,Cu,Zn,Cr,Phosph- ate,oxalate,moly- bdate interfere, se- nsitivity is poor.	65
5-Methyl furfu- ral-1-phthalazi- nohydrazone	7.2-10.4	-	503	37000	Co,Cr,Cu and citrate interfere, heating necessary.	59
Diacetyl Monoxime Glycinimine	8.5-11.0	Aq. ethanol	450	17000	Many metal ions are precipitated.	19
N-Hydroxy-N, N'- diphenylbenzamidine +1-(2-Pyridylazo)- 2-naphthol.	7.0- 9.0	Chloroform + Ethanol	570	78300	Fe(III) interfere but can be masked by adding sodium tartrate solution.	Present Method

CONCLUSION

A new extraction-spectrophotometric method for the determination of nickel(II) at trace levels has been described. In this method, N-hydroxy-N, N'-diphenylbenzamidine (HDPBA) and 1-(2-pyridylazo)-2-naphthol (PAN) reagents react with metal ion to form an intense red coloured complex which is extractable into chloroform. All analytical parameters, such as pH, reagent concentration, effect of volume ratio of organic to aqueous phase, etc. have been examined. The method was found free from the rigid control of experimental conditions. The present method is superior in terms of sensitivity and selectivity in comparison to the classical dimethylglyoxime and PAN methods, and other established methods. The method is reproducible and has been applied successfully to the determination of nickel(II) in metallurgical and industrial samples.

REFERENCES

1. I.M. Kolthoff and P.J. Erving, "Treatise on Analytical Chemistry", Part II, Vol. 2, John Wiley and Sons, INC., New York 1962.
2. M. Sittig, "Toxic Metals Pollutions Control and Worker Protection", Noyes Data Corporation, New Jersey, USA 1976.
3. F.W. Oehme, "Toxicity of Heavy Metals in the Environment" Part II, Marcel Dekker, New York 1979.
4. N.N. Greenwood and A. Earnshaw, "Chemistry of Elements" 1st Ed., Pergamon press, Oxford 1984.
5. N.I. Sax, "Industrial Pollution", Van Nostrand Reinhold Company, New York 1974.
6. E.B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed. INC., New York 1959.
7. E. Upor, M. Mohai and Gy. Novak, "Photometric Methods in Inorganic Trace Analysis", Vol. 20, Elsevier Science Publishers B.V., Amsterdam 1985.
8. T. Fuginaga, M. Satake and T. Yonekubo; Jpn. Analyst 20, 1255, 1971.
9. K.S. Pakhomova, L.P. Valkova and V.V. Gorshkov; Zh. Anal. Khim. 19, 1085, 1964.
10. E. Kentner, D. Bruce Armitage and H. Zeitlin; Anal. Chim. Acta 45, 343, 1969.
11. A.Gahler, A. Mitchel and M. Mellon; Anal. Chem. 23, 500, 1951.
12. I.V. Glinskaya and I. Yu. Merisov; Zh. Anal. Khim. 37, 650, 1982.
13. K. Ueda and M. Nozaki; Yamamoto, Yoshikazu Kanazawa Daigaku Kogakubu Kiyo 13, 103, 1980; Chem. Abstr. 95, 113823 e, 1981.
14. M. Kamini, S.K. Sindhwani and R.P. Singh; Analisis 10, 390, 1982.
15. M. Morishita, H. Ichiba, K. Shimodaira, H. Yamada, H. Izuka and M. Katayanagi; Bunseki Kagaku 31, 203, 1982; Chem. Abstr. 97, 48803 u, 1982.
16. A. Gonzalez Armas, V. Gonzalez Diaz, J.P. Perez Trujillo and F. Garcia Montelongo; An. Quim Ser. B 78, 351, 1982, Chem. Abstr. 98, 100422 f, 1983.

17. M. Furukawa and S. Shibata; *Anal. Chim. Acta* 140, 301, 1982.
18. K. Uesugi and S. Yamaguchi; *Microchem. J.* 27, 71, 1982; *Chem. Abstr.* 96, 134969 p, 1982.
19. P. Riyazuddin; *Analyst* 105, 1196, 1980.
20. A. Izquierdo and J. Carrasco; *Analyst* 109, 605, 1984.
21. J. Aggett and A.R. Richardson; *Analyst* 105, 1118, 1980.
22. H.R. Singh, M.R. Sudersana, N. Wasi and M. Satake; *Asian J. Chem.* 3, 248, 1991.
23. A. Kumar and M. Jain; *Chem. Anal.* 37, 73, 1992.
24. A. Kumar, M.F. Hussain, M. Satake and B.K. Puri; *Chim. Acta Turc.* 11, 337, 1983; *Chem. Abstr.* 101, 83154 f, 1984.
25. S.K. Hawa, B.K. Sharma and S.P. Mathur; *Orient J. Chem.* 2, 51, 1986; *Chem. Abstr.* 104, 161184 u, 1986.
26. A. Kumar, M. Jain and B.K. Puri; *Chim. Acta Turc.* 18, 155, 1990; *Chem. Abstr.* 115, 293852 x, 1991.
27. H.A. Flaschka and A.J. Barnard, "Chelates in Analytical Chemistry", Marcel Dekker, New York 1972.
28. Y. Zhu and L. Zhang; *Huaxue Shijie* 23, 77, 1982; *Chem. Abstr.* 100, 114113 c, 1984.
29. M.I. Bulatov, I.N. Evtukhovich and N.P. Mukhovichova; *IZV. Vyssh. Uchebn. Zaved., Khim. Khim. Technol.* 31, 49, 1988; *Anal. Abstr.* 51, 8B56, 1989.
30. K. Kasiura and Z. Sytniewska; *Chem. Anal.* 13, 177, 1968.
31. S. Shibata; *Anal. Chim. Acta* 23, 367, 1960.
32. K. Ohshita, H. Wada and G. Nakagawa; *Anal. Chim. Acta* 124, 193, 1981.
33. Y. Yuan; *Fenxi Ceshi Tongbao* 4, 41, 1985; *Chem. Abstr.* 105, 145262 h, 1986.
34. M. Ruan; *Fenxi Shiyanshi* 5, 34, 1986; *Anal. Abstr.* 49, 11B75, 1987.
35. I.V. Pyatnitskii and S.G. Mamuliya, K.I. Grigalashvili and L.L. Kolomiets; *Ukr. Khim. Zh.* 50, 977, 1984; *Chem. Abstr.* 102, 38976 k, 1985.
36. T. Yotsuyanagi, R. Yamashita, H. Hoshino, K. Aomura, H. Sato and N. Masuda; *Anal. Chim. Acta* 82, 431, 1976.

37. X. Li and W. Shi; Fenxi Shiyanshi 7, 7, 1988; Anal. Abstr 51, 10B48, 1989.
38. H. Cao; Lihua Jianyan, Huaxue Fence 24, 216, 1988; Anal. Abstr. 51, 4B143, 1989.
39. J. Miura and M. Satake; Fukui Daigaku Kogakubu Kenkyu Hokoku 26, 259, 1978; Anal. Abstr. 36, 2B205, 1979.
40. A.I. Busev, T.N. Zholondovskaya, L.S. Krysina and A. Barinova; Zh. Anal. Khim. 29, 1758, 1794.
41. T.V. Marchak, G.D. Brykina and T.A. Belyavskaya; Zh. Anal. Khim. 36, 513, 1981.
42. J. Cacho and C. Nerin; Anal. Chim. Acta 131, 277, 1981.
43. J. Kobylecka; Chem. Anal. 31, 825, 1986; Chem. Abstr. 107, 69827 v, 1987.
44. E. Zheng; Yejin Fenxi 9, 54, 1989; Chem. Abstr. 113, 108325 a, 1990.
45. V.Y. Sukhan, V.F. Gorlach and T.M. Lokhan'ko; Ukr. Khim. Zh. 54, 847, 1988; Chem. Abstr. 111, 145871 e, 1989.
46. F. Salinas, J.C. Jimenez Sanchez and J.L. Lemus; Bull. Soc. Chim. Belg. 95, 293, 1986; Chem. Abstr. 105, 53752 q, 1986.
47. A.V. Reddy and Y.K. Reddy; Talanta 33, 617, 1986.
48. K.G. Reddy, K.M.M.S. Prakash, K.H. Reddy and D.V. Reddy; Acta Cienc. Indica, [ser.] Chem. 10, 175, 1984; Chem. Abstr. 103, 64046 x, 1985.
49. N.S. Reddy and D.V. Reddy; Acta Cienc. Indica, [ser.] Chem. 10, 65, 1984; Chem. Abstr. 103, 64047 y, 1985.
50. H.S. Gowda, S.M. Ahmed and K.N. Thimmaiah; Curr. Sci. 52, 360, 1983.
51. M. Roman Ceba, J.A. Munoz Leyva and J.C. Jimenez Sanchez; An. Quim. 78, 64, 1982; Chem. Abstr. 97, 48857 q, 1982.
52. H.S. Gowda, K.N. Thimmaiah and S.M. Ahmed; Indian J. Chem. Sect. A 21, 327, 1982.
53. H. Akaiwa, H. Kawamoto and E. Hiyamuta; Bunseki Kagaku 31, E117, 1982; Chem. Abstr. 96, 173554 u, 1982.
54. T.V. Petrova, S.B. Savvin and T.G. Dzherayan; Zh. Anal. Khim. 35, 695, 1980.
55. C.K. Bhaskare, Devi Surekha and M.B. Chavan; J. Shivaji Univ. : Sci. 17, 47, 1977; Chem. Abstr. 93, 197065 z, 1980.

56. M.L. Cluett and J.H. Yoa; *Anal. Chem.* 29, 1265, 1957.
57. R.L. Heller and J.C. Guyon; *Talanta* 17, 865, 1970.
58. G.S. Katiyar and B.C. Chaldar; *Indian J. Chem. Sect. A* 22, 1084, 1983.
59. H. Ishii, T. Odashima and T. Imamura; *Analyst* 107, 885, 1982.
60. S.L.C. Ferreira; *Talanta* 35, 485, 1988.
61. A. Gonzalez Armas and V. Gonzalez Diaz; *An. Quim.* 84, 89, 1988; *Anal. Abstr.* 50, 10B238, 1988.
62. T. Pal, A. Ganguly and A. Pal; *J. Indian Chem. Soc.* 65, 655, 1988.
63. M. Morishita and M. Katayanagi; *Bunseki Kagaku* 30, 460, 1981; *Chem. Abstr.* 95, 107952 a, 1981.
64. J. Gimenez Plaza and J.M. Bocanegra Garces; *Rev. Soc. Quim. Mex.* 25, 488, 1981; *Chem. Abstr.* 96, 134958 j, 1982.
65. R. Bhatt, M.K.S. Chhangani, A.K. Goswami and D.N. Purohit; *Asian J. Chem.* 5, 773, 1993.
66. M.B. Saha and A.K. Chakraborty; *J. Indian Chem. Soc.* 60, 281, 1983.
67. J. Feng, Y. Peng, B. Zhang and S. Tong; *Fenxi Huaxue* 20, 1188, 1992; *Chem. Abstr.* 118, 93373 s, 1993.
68. S.C. Sharma and M.P. Tyagi; *Orient. J. Chem.* 113, 129, 1990; *Chem. Abstr.* 113, 183911 s, 1990.
69. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis" 4th Ed., Longmans, London p. 480, 1962.
70. K. Satyanarayana and R.K. Mishra; *Anal. Chem.* 46, 1609, 1974.
71. N.A. Lange, "Hand Book of Chemistry" 10th Ed., McGraw Hill, New York p. 972, 1967.
72. P.W. West; *J. Chem. Educ.* 18, 528, 1941.
73. G.D. Christian, "Analytical Chemistry" 4th Ed., John Wiley and Sons, New York 1986.
74. K. Satyanarayana and R.K. Mishra; *Indian J. Chem.* 18, 295, 1975.
75. D. Betteridge, Q. Fernando and H. Frelser; *Anal. Chem.* 35, 294, 1975.

76. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 4th Ed., Longmans, London p. 748, 1962.
77. K.S. Patel and R.K. Mishra; J. Indian Chem. Soc. 55, 462, 1978.
78. T. Katami, T. Hayakawa, M. Furukawa and S. Shibata; Analyst 109, 731, 1984.