

CHAPTER III

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

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NAPHTHOL

SUMMARY

A new and convenient method for the extraction-spectrophotometric determination of cobalt(II) at trace levels has been described. It is based on the prior selective extraction of cobalt(II) with seven different hydroxyamidines (HOAs) and simultaneous colour reaction with 1-(2-pyridylazo)-2-naphthol(PAN) at pH range 8.0 - 12.0. The red coloured complex, so formed, is extractable in chloroform. The molar absorptivity of these complexes, when different hydroxyamidines (HOAs) were used as extractant, lie in the range of $(2.06 - 3.18) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 535 - 550 nm. The parent compound N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) is selected for all experimental work because of easier synthesis and greater sensitivity of the complex. The molar absorptivity of the red coloured Co(II)-PAN complex after coupling Co(II)-HDPBA complex with PAN is $3.18 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at absorption maxima 550 nm. The Sandell's sensitivity of the method is $0.0018 \mu\text{g}/\text{cm}^2$.

The system follows Beer's law in terms of cobalt(II) upto $1.5 \mu\text{g}/\text{ml}$ organic solution. The detection limit of the method for the determination of cobalt(II) is $0.02 \mu\text{g}/\text{ml}$ aqueous solution. The relative standard deviation of the method for ten replicate measurements, each containing

1.0 $\mu\text{g/ml}$ cobalt(II) is $\pm 1.2\%$. Various analytical parameters such as effect of reagent concentration, solvent, volume ratio of organic to aqueous phase, diverse ions, etc. have been studied. The present method has been applied successfully for the determination of cobalt(II) in vitamin B12 samples.

Cobalt is a vital trace element for man and animal.¹ The average concentration of cobalt in the earth's crust is 23 ppm. It is wide spread in nature at trace amount.² The important cobalt minerals are sulfides, arsenides and oxidised compound.³ It is used mainly in alloy, catalyst, varnish, etc.^{4,5} Small amounts of cobalt is used in the prevention of pernicious anemia.⁶ It exerts hazardous effects on living organism when exposed even in small quantities. Excess intake of cobalt produces polycythemia, cardiomyopathy, diarrhoea, etc.⁷.

Of the various known reagents for the spectrophotometric determination of cobalt(II), thiocyanate, o-nitrosocresol, nitroso-R salt and picolinaldehyde-4-phenyl-3-thiosemicarbazone are commonly employed. In the thiocyanate^{8,9} and modified thiocyanate method,¹⁰⁻¹⁵ the molar absorptivity of the complex is less, a large amount of reagent is required for full colour development and common metal ions e.g. Fe, Cr, Cu, U, Bi and Ni interfere. The alkaline earth metals also give precipitates in these methods. The method using nitroso-R salt^{8,16-18} is sensitive but not very specific and it is often necessary to carry out a preliminary separation. The excess of reagent is required for masking Cu and Ni. Common metal ions like Cu, Fe, Cr, U, Ni, Ti, etc. are masked by adding various masking agents. However, ammonium ion interfere seriously.¹⁸ The interference are also observed when Fe, Mn, Cd ions, etc. are present.^{16,17} o-Nitrosocresol¹⁹ and picolinaldehyde-4-phenyl-3-thiosemicarbazone,²⁰ are reported to be sensitive reagents. But o-nitrosocresol is a liquid and not very stable. Moreover, the selectivity of both the reagents is poor.

Several sensitive reagents and azo compounds have been reported for the spectrophotometric determination of cobalt such as eriochrome azurol B, 4,4'-bipyridyl with cetyltrimethyl ammonium bromide,²¹ 5-methoxy-2-nitrosophenol,²² 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,²³ 3-(4'-methyl-2'-thiazolylazo)-2,6-diaminopyridine,²⁴ 5-(5-chloro-2-pyridylazo) toluene-2,4-diamine,²⁵ 3-substituted 5-hydroxy-5-D-arabino tetrahydroxybutyl thiazolidine-2-thione,²⁶ 2-[2-(3,5-dibromopyridylazo)]-5-dimethylamino benzoic acid.²⁷ All these reagents give highly sensitive colour reactions but they suffer from serious interferences of a large number of metal ions viz. Cu, Fe, Cd, Zr, Ti, U, DCTA, EGTA, etc. In most of these methods the pH is critical, interfering metal ions are separated by anion exchange resin techniques, and selectivity is also poor. A large number of reagents containing thio groups²⁸⁻⁴⁰ have also been employed, but they face practical difficulties like poor sensitivity, requirement of heating on water bath for 5 to 25 min, and interference due to large number of metal ions.

Numerous dyes and reagents have been used for the spectrophotometric determination of cobalt such as 4-(2-pyridylazo) resorcinol,⁴¹ 1-(2-pyridylazo)-2-naphthol⁴² or together with surfactant,⁴³ crystal violet + nitroso-R salt,⁴⁴ brilliant green + thiocyanate,⁴⁵ 4,4'-dimethoxybenzil monoxime,⁴⁶ picramazochrom,⁴⁷ ethylenediamine-N,N'-bis(o-hydroxyphenylacetic acid),⁴⁸ dibenzoylmethane,⁴⁹ 4-bromodibenzoylmethane,⁵⁰ acetylacetone + hydroxylamine,⁵¹ p-methylisonitrosoacetophenone,⁵² 4-methylbenzoyl methane,⁵³ phenyltriazene

derivatives with^{54,55} or without tetraphenylborate and naphthalene,^{56,57} nitroso-NW acid.⁵⁸ Out of these reagents, some are highly sensitive but require a considerable time and large excess of reagent for full colour development.⁴¹⁻⁴⁴ With some other reagents^{41,42,47-58} various analytical problems such as narrow pH range^{45,52,53} short range of Beer's law,⁴⁴⁻⁴⁷ poor reproducibility of results,⁵⁸ less colour intensity of the complex,^{41-43,47-58} and interference of metals are encountered.^{42,56-58}

In addition to these, other spectrophotometric methods⁵⁹⁻⁷⁰ have been reported which are less sensitive and selective. Although the selectivity of these methods are improved by using different techniques and masking agents. However, in doing so, the methods become tedious.

In the present investigation, cobalt(II) is extracted with chloroform solution of N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) and then the organic extract is reacted with 1-(2-pyridylazo)-2-naphthol (PAN) at pH 10.0 ± 0.2 . The absorbance of the coloured complex, so formed, is measured at λ_{\max} 550 nm. The method is free from the interferences of most of the common metal ions which are found associated with cobalt. It has been applied successfully for the determination of cobalt in vitamin B12 samples.

EXPERIMENTAL

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

STANDARD COBALT(II) SOLUTION - A stock solution of cobalt(II) was prepared by dissolving a weighed amount of cobalt(II) chloride hexahydrate in 100 ml of 1 M hydrochloric acid. Working standard solution was prepared by appropriate dilution of the stock solution. The solution was standardized gravimetrically using 1-nitroso-2-naphthol.⁷¹

CHLOROFORM - Purified chloroform was used for all experimental work.

HYDROXYAMIDINES(HOAs) - Hydroxyamidines were synthesized as described in the literature.⁷² A 0.2% (w/v) or $\approx 6.9 \times 10^{-3}$ M solution of these reagents 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 ammonia-ammonium chloride buffer solution of pH 10.0 was prepared as described in the literature.⁷³

SOLUTION OF DIVERSE IONS - The solution of diverse ions were prepared as described in the literature.⁷⁴ A 1 mg/ml solution of the appropriate ions was used.

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

PROCEDURE

[A] EXTRACTION OF COBALT(II) WITH HDPBA

An aliquot of the test solution containing upto 30.0 μg Co(II) is placed in a 125-ml separatory funnel. The pH of the aqueous solution is maintained at 10.0 ± 0.2 with buffer solution in a total volume of 10 ml. This solution is vigorously shaken with 5 ml of HDPBA solution in chloroform. After shaking the solution for 2 min, the organic layer is separated from the aqueous phase. The aqueous phase is washed with 1 x 2 ml fresh portion of chloroform. All the extracts are dried over anhydrous sodium sulphate (≈ 2 g) and transferred to a 10-ml volumetric flask. The organic solution is made upto the mark with chloroform. The absorbance of the yellow coloured complex is measured against reagent blank at λ_{max} 400 nm.

[B] COLOUR REACTION OF THE EXTRACT WITH PAN

The organic extract of Co(II)-HDPBA complex obtained as above, containing upto 15.0 μg Co(II), is reacted with 2 ml of ethanolic PAN solution. The red coloured complex is dried over anhydrous sodium sulphate (≈ 2 g). The organic solution is transferred to a 10-ml volumetric flask and made upto the mark with chloroform. The absorbance of the red coloured complex is measured against reagent blank at λ_{max} 550 nm.

RESULTS AND DISCUSSION

[A] EXTRACTION OF COBALT(II) WITH N-HYDROXY-N,N'-DIPHENYL-BENZAMIDINE (HDPBA)

ABSORPTION SPECTRA

The absorption spectra of Co(II)-HDPBA complex exhibits maximum absorbance around 400 nm, whereas reagent blank of this complex shows negligible absorbance at absorption maxima. The position of the λ_{max} at different metal concentration remains unchanged, shown in figure 3.1.

EFFECT OF SOLVENTS

Various water immiscible organic solvents such as benzene, toluene, xylene, carbon tetrachloride, chloroform, 1-pentanol and isobutyl methyl ketone were tested. No extraction has been seen in carbon tetrachloride and isobutyl methyl ketone, whereas all other solvents extract the complex quantitatively (Table 3.1, figure 3.2). The greater sensitivity and higher colour intensity of the complex in chloroform has been observed as compared to other solvent. Hence, chloroform was selected as most effective solvent for extraction and colour development of the complex.

EFFECT OF pH

The extraction of the complex was examined at different pH values. It was found that Co(II)-HDPBA complex was extracted quantitatively at the pH range of 8.0-12.0 (Table 3.2, Figure 3.3). Hence, all extractions were carried out at pH 10.0 ± 0.2 using ammonia-ammonium chloride buffer solution.

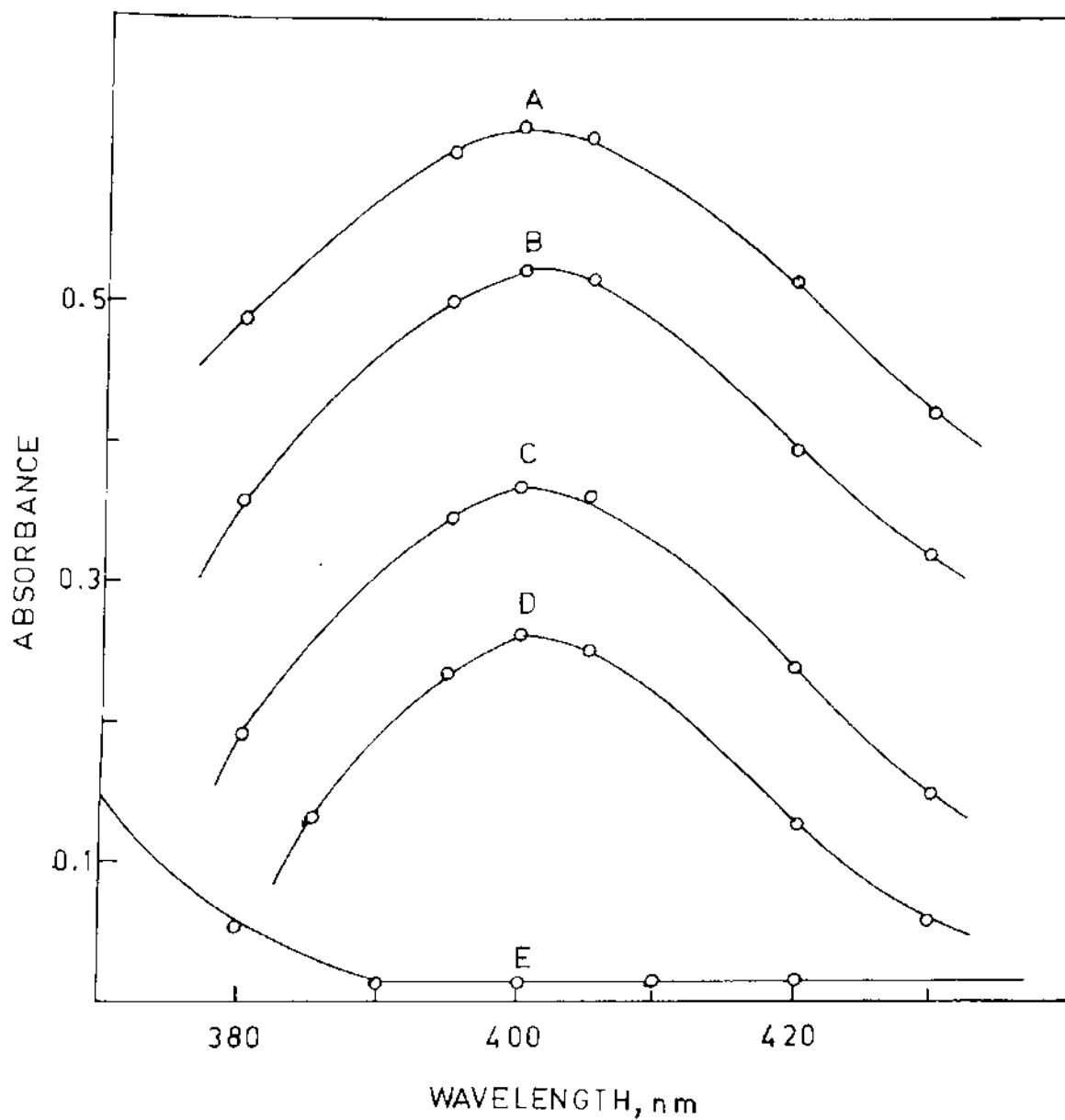


FIG. 3.1 EFFECT OF METAL CONCENTRATION ON THE POSITION OF λ_{\max} OF THE Co(II)-HDPBA COMPLEX IN CHLOROFORM

[A] $C_{\text{Co(II)}} \approx 4.1 \times 10^{-5}$ M (24.0 $\mu\text{g}/10$ ml organic phase)

[B] $C_{\text{Co(II)}} \approx 3.4 \times 10^{-5}$ M (20.0 $\mu\text{g}/10$ ml organic phase)

[C] $C_{\text{Co(II)}} \approx 2.3 \times 10^{-5}$ M (14.0 $\mu\text{g}/10$ ml organic phase)

[D] $C_{\text{Co(II)}} \approx 1.7 \times 10^{-5}$ M (10.0 $\mu\text{g}/10$ ml organic phase)

[E] REAGENT BLANK

TABLE 3.1 EFFECT OF SOLVENTS ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M (20.0 } \mu\text{g/10 ml organic phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$$

Solvent	λ_{max} nm	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$
Chloroform	400	1.53
Benzene	380	1.30
Toluene	390	1.18
1-Pentanol	400	1.18
Xylene	400	0.94
Carbon tetrachloride	-	No extraction
Isobutyl methyl ketone	-	No extraction

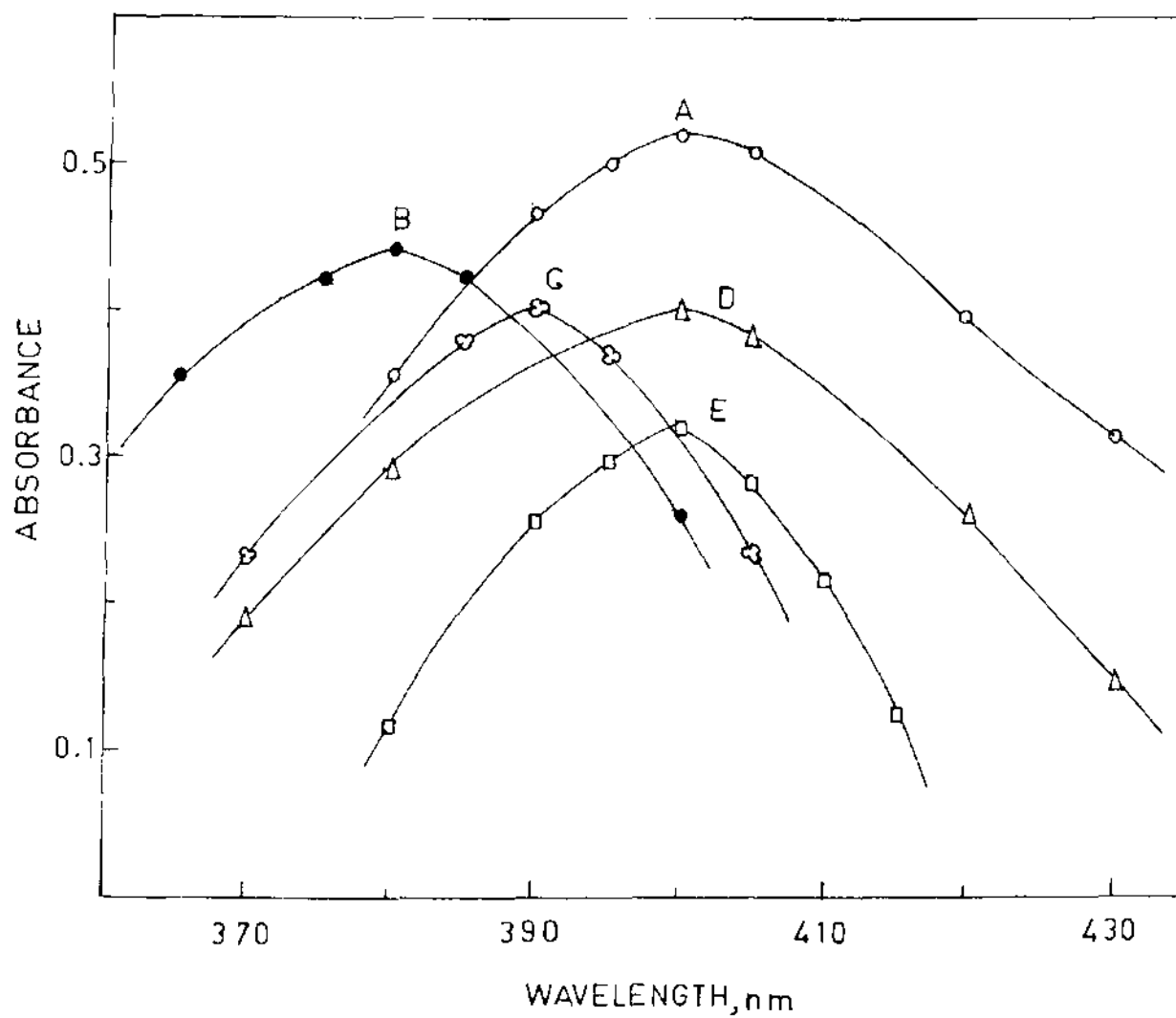


FIG. 3.2 EFFECT OF SOLVENTS ON THE ABSORBANCE AND λ_{\max} OF THE Co(II) -HDPBA COMPLEX

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M};$$

$$\text{pH} = 10.0 \pm 0.2;$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}.$$

- | | |
|----------------|----------------|
| [A] CHLOROFORM | [B] BENZENE |
| [C] TOLUENE | [D] 1-PENTANOL |
| [E] XYLENE | |

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

The effect of HDPBA concentration on the extraction of the metal was studied and it was found that minimum of 0.52×10^{-2} M HDPBA solution is necessary for maximum extraction of the metal complex. An increased concentration upto 1.0×10^{-2} M HDPBA could be used without any adverse effect on the absorbance value of the complex (Table 3.3, Figure 3.4). In practice, therefore 0.69×10^{-2} M solution of HDPBA in chloroform was used.

EFFECT OF DILUTION, TEMPERATURE AND ELECTROLYTES

The influence of volume ratio of organic to aqueous phase was studied. It was found that the absorbance of the yellow complex remains unchanged when the volume ratio of organic to aqueous phase was varied between 2:1 to 1:6 (Table 3.4, Figure 3.5). Hence, 1:2 volume ratio of organic to aqueous phase was chosen for all extractions. The extraction of the complex was independent of the temperature of aqueous phase in the range of 15 - 40°C (Table 3.5).

The capability of the extraction of complex was unaffected when the extraction was carried out in the presence of upto 1 M electrolytes viz. $\text{NH}_4\text{Cl}/\text{KCl}/\text{NaCl}/(\text{NH}_4)_2\text{SO}_4$.

EFFECT OF EXTRACTION TIME, STABILITY OF THE COMPLEX, BEER'S LAW AND MOLAR ABSORPTIVITY

The Co(II) -HDPBA complex was found to be extracted completely within a shaking period of 2 - 3 min in chloroform.

TABLE 3.2 EFFECT OF pH OF THE AQUEOUS PHASE ON THE ABSORBANCE OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M (20.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$$

pH of the aqueous phase	Absorbance at 400 nm
7.0	0.43
7.5	0.47
8.0	0.52
9.0	0.52
10.0	0.52
11.0	0.52
12.0	0.52
12.5	0.48
13.0	0.44

TABLE 3.3 EFFECT OF HDPBA CONCENTRATION ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M (20.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

Concentration of HDPBA, M $\times 10^{-2}$	Absorbance at 400 nm
0.30	0.43
0.45	0.49
0.52	0.52
0.69	0.52
0.80	0.52
1.00	0.52
1.05	0.47
1.10	0.40

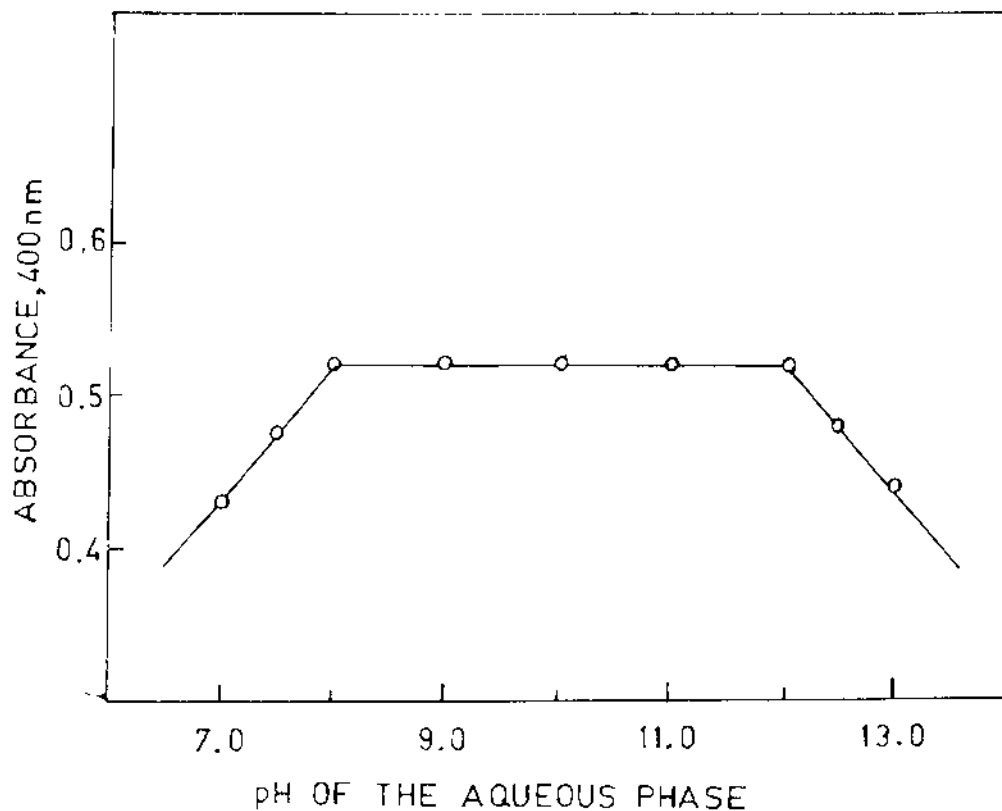


FIG. 3.3 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M}; C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M.}$$

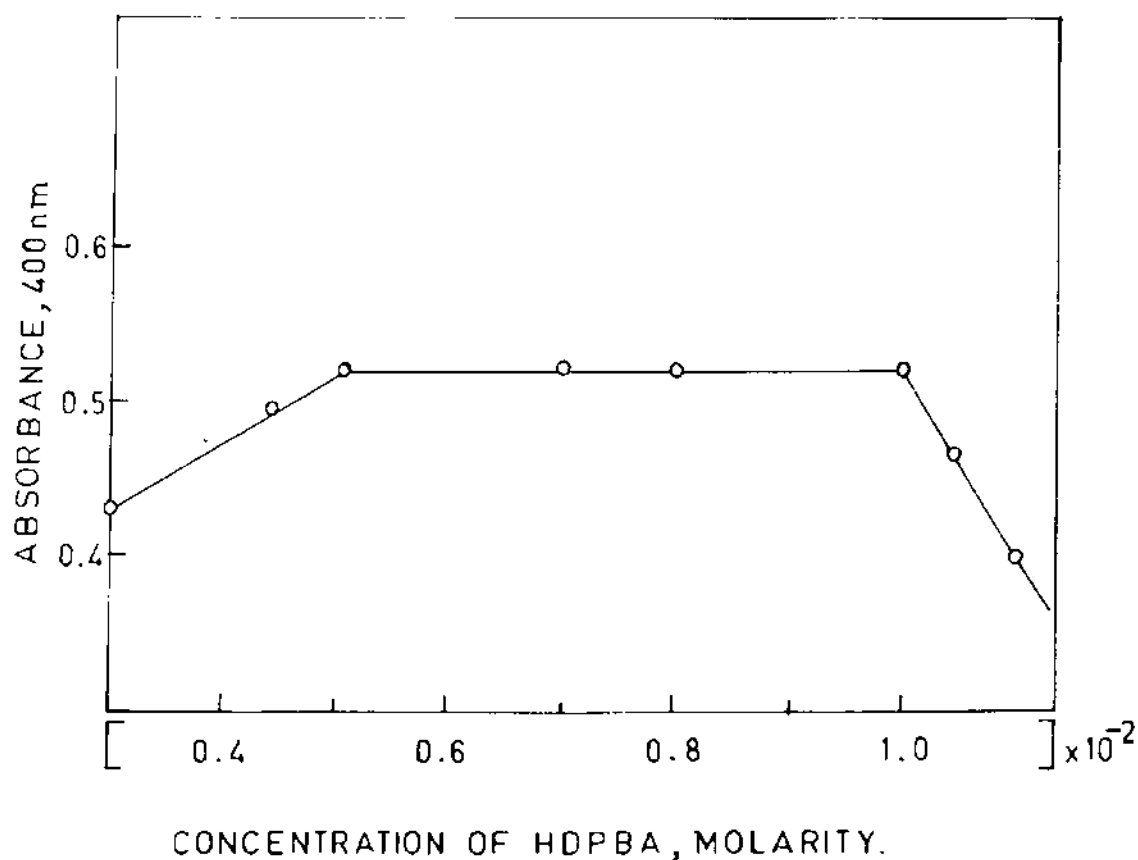


FIG. 3.4 EFFECT OF HDPBA CONCENTRATION ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M}; \text{pH} = 10.0 \pm 0.2.$$

TABLE 3.4 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 20.0 \mu\text{g}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$$

Volume ratio of organic to aqueous phase	Absorbance at 400 nm
2 : 1	0.52
1 : 1	0.52
1 : 2	0.52
1 : 3	0.52
1 : 4	0.52
1 : 5	0.52
1 : 6	0.52
1 : 7	0.49
1 : 8	0.45

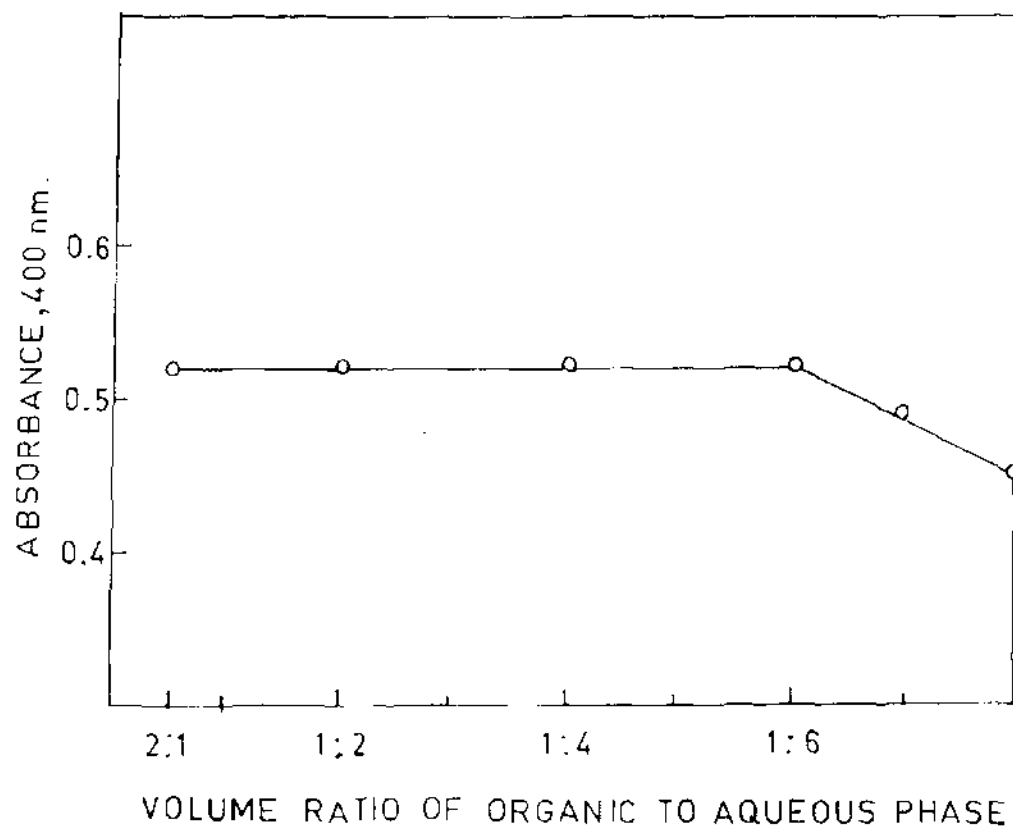


FIG. 3.5 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION OF Co(II)-HDPBA COMPLEX IN CHLOROFORM

$C_{\text{Co(II)}} = 20.0 \mu\text{g}$; $\text{pH} = 10.0 \pm 0.2$; $C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$.

TABLE 3.5 EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE ON THE EXTRACTION OF Co(II)-HDFBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M (20.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{HDFBA}} = 6.9 \times 10^{-3} \text{ M}$$

Temperature of the aqueous phase, °C	Absorbance at 400 nm
8	0.45
10	0.48
15	0.52
20	0.52
25	0.52
30	0.52
35	0.52
40	0.52
45	0.44
50	0.36

Prolonged shaking time had no adverse effect on the extraction of metal complex. The complex was found to be stable upto 12 hr at room temperature $25 \pm 2^\circ\text{C}$. The system confirms to Beer's law upto 3.0 ppm (30.0 $\mu\text{g}/10$ ml organic solution). The molar absorptivity of the Co(II)-HDPBA complex is 1.53×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 400 nm.

[B] COLOUR REACTION OF THE EXTRACT WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL (PAN)

The chloroform extract of Co(II)-HDPBA reacts with ethanolic solution of PAN at pH 10.0 ± 0.2 to form a red coloured Co(II)-PAN complex.

ABSORPTION SPECTRA

The absorption spectra of Co(II)-PAN complex obtained after the extraction of metal ion with different hydroxyamidines (HOAs) and subsequent reaction with 1-(2-pyridylazo)-2-naphthol (PAN) exhibits maximum absorbance at absorption maxima around 535 - 550 nm against their respective reagent blanks and the reagent blank of N-hydroxy-N,N'-diphenylbenzamidine (HDPBA) and PAN are shown in Figure 3.6. The sensitivity of the Co(II)-PAN complex obtained after the extraction of metal ion with HDPBA is higher than the other hydroxyamidines. Therefore, it is selected for all extraction work (Table 3.6). The position of λ_{max} is unaffected on the variation of metal concentration, shown in Figure 3.7.

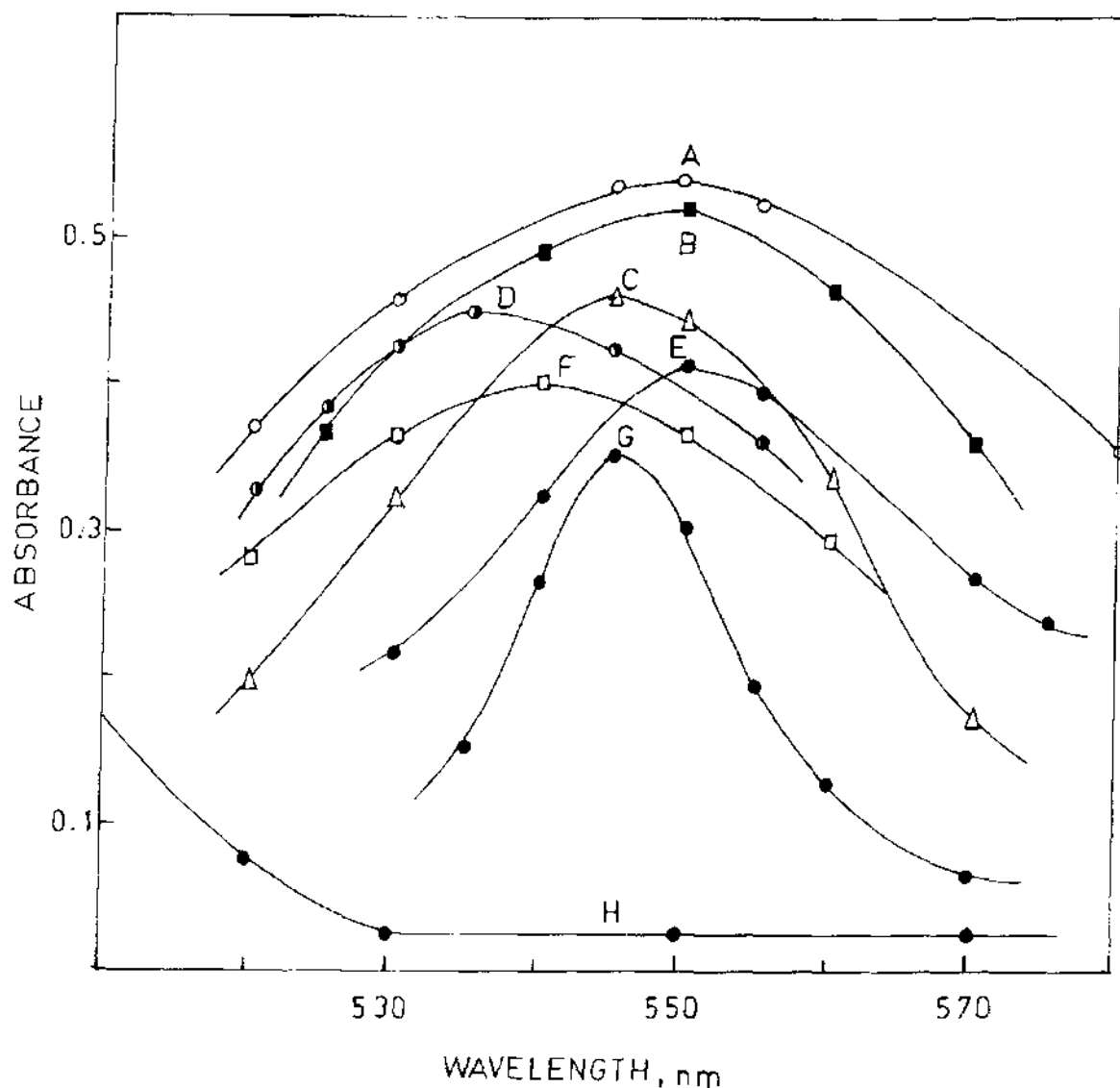


FIG. 3.6 ABSORPTION SPECTRA OF COBALT(II) COMPLEX WITH DIFFERENT HYDROXYAMIDINES(HOAs) AND PAN AGAINST THEIR RESPECTIVE REAGENT BLANKS IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M}; \text{ pH} = 10.0 \pm 0.2;$$

$$C_{\text{HOAs}} \approx 6.9 \times 10^{-3} \text{ M}; C_{\text{PAN}} = 0.8 \times 10^{-3} \text{ M}.$$

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

TABLE 3.6 EFFECT OF NATURE OF HYDROXYAMIDINES ON THE ABSORBANCE OF THE Co(II)-HOA/PAN COMPLEXES IN CHLOROFORM + ETHANOL MIXTURE

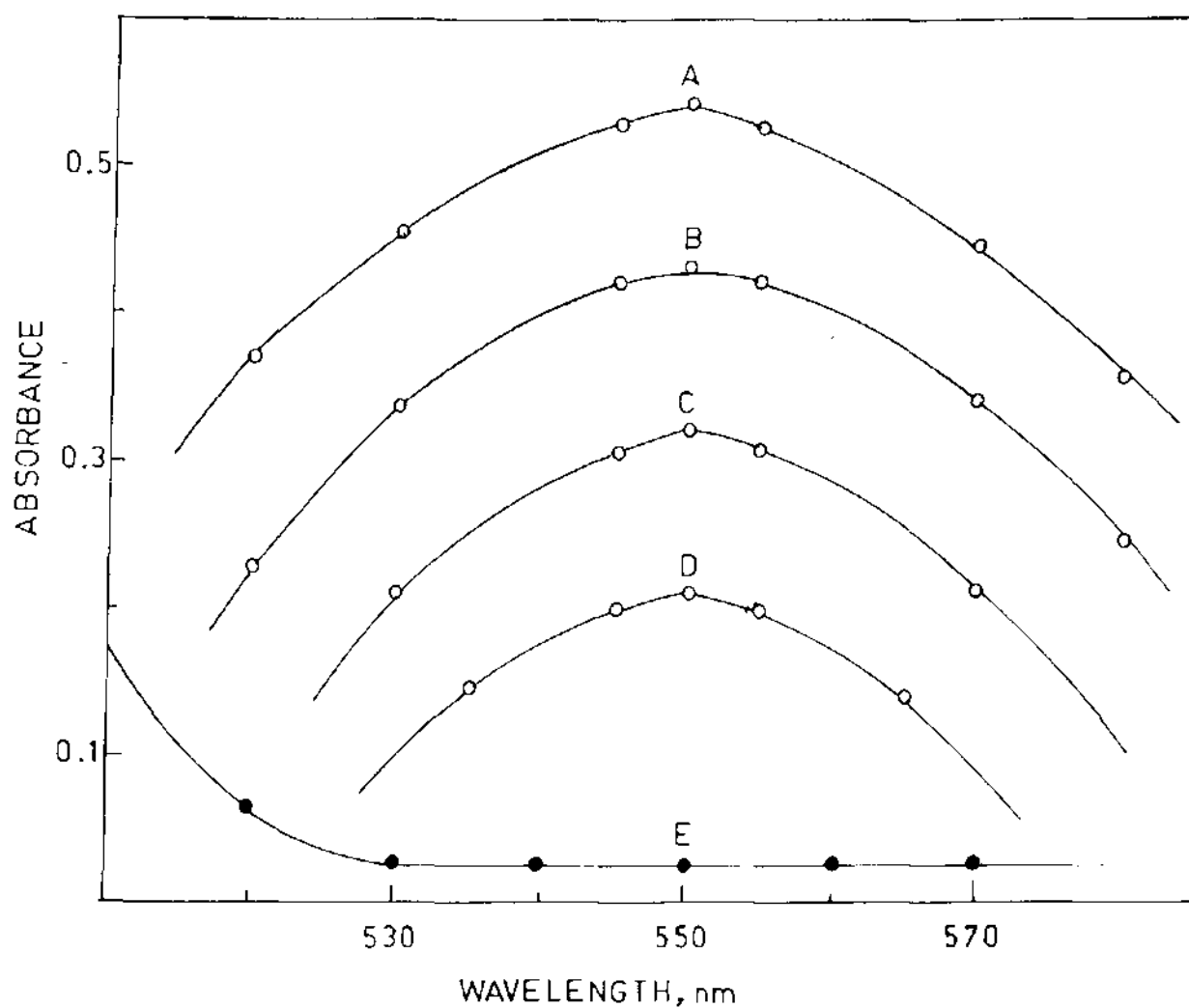
$$C_{Co(II)} = 1.7 \times 10^{-5} \text{ M (10.0 } \mu\text{g/10 ml organic phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{HOAs} \approx 6.9 \times 10^{-3} \text{ M}$$

$$C_{PAN} = 0.8 \times 10^{-3} \text{ M}$$

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 $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$
	Ph''	Ph'	Ph		
N-Hydroxy-N, N'-diphenylbenzamide	-C ₆ H ₅	-C ₆ H ₅	-C ₆ H ₅	550	3.18
N-Hydroxy-N-(3-chlorophenyl)-N'-(2-methylphenyl) benzamide	3-Cl-C ₆ H ₄	2-CH ₃ -C ₆ H ₄	-C ₆ H ₅	550	3.06
N-Hydroxy-N-phenyl-N'-(3-chlorophenyl) benzamide	-C ₆ H ₅	3-Cl-C ₆ H ₄	-C ₆ H ₅	545	2.71
N-Hydroxy-N-(2-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide	2-Cl-C ₆ H ₄	3-Cl-C ₆ H ₄	2-Cl-C ₆ H ₄	535	2.65
N-Hydroxy-N-(4-chlorophenyl)-N'-(2-methylphenyl)-2-chlorobenzamide	4-Cl-C ₆ H ₄	2-CH ₃ -C ₆ H ₄	2-Cl-C ₆ H ₄	550	2.41
N-Hydroxy-N-(4-chlorophenyl)-N'-(3-chlorophenyl)-2-chlorobenzamide	4-Cl-C ₆ H ₄	3-Cl-C ₆ H ₄	2-Cl-C ₆ H ₄	540	2.35
N-Hydroxy-N-(2-chlorophenyl)-N'-(4-chlorophenyl)-2-chlorobenzamide	2-Cl-C ₆ H ₄	4-Cl-C ₆ H ₄	2-Cl-C ₆ H ₄	545	2.06



IG.3.7 EFFECT OF METAL CONCENTRATION ON THE POSITION OF λ_{\max} OF THE Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

[A] $C_{\text{Co(II)}} \approx 1.7 \times 10^{-5}$ M (10.0 $\mu\text{g}/10$ ml organic phase)

[B] $C_{\text{Co(II)}} \approx 1.4 \times 10^{-5}$ M (8.0 $\mu\text{g}/10$ ml organic phase)

[C] $C_{\text{Co(II)}} \approx 1.0 \times 10^{-5}$ M (6.0 $\mu\text{g}/10$ ml organic phase)

[D] $C_{\text{Co(II)}} \approx 0.7 \times 10^{-5}$ M (4.0 $\mu\text{g}/10$ ml organic phase)

[E] REAGENT BLANK

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

The effect of PAN concentration on the colour development of the metal complex was examined and it was found that $(0.4 - 1.2) \times 10^{-3}$ M PAN in ethanol were needed for the formation of red coloured complex (Table 3.7, Figure 3.8). Therefore, 0.8×10^{-3} M PAN was selected for all experimental work.

STANDING TIME AND STABILITY OF THE COMPLEX

The colour development of the complex was found instantaneous. The red coloured complex was stable upto 12 hr at room temperature $25 \pm 2^\circ\text{C}$.

BEER'S LAW, CORRELATION COEFFICIENT AND MOLAR ABSORPTIVITY

The Co(II)-PAN complex, when HDPBA is used as extractant, adheres to the Beer's law upto 1.5 ppm (15.0 $\mu\text{g}/10$ ml organic solution). The correlation coefficient⁷⁵ for the calibration curve data is found to be 0.99 (Table 3.8, Figure 3.9). The optimum concentration range evaluated from Beer's law is found to be between 0.4-1.3 ppm (4.0-13.0 $\mu\text{g}/10$ ml organic solution). The molar absorptivity of the coloured complexes with seven hydroxyamidines, after the colour reaction with 1-(2-pyridylazo)-2-naphthol(PAN) lie in the range of $(2.06-3.18) \times 10^4$ $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 535-550 nm. The molar absorptivity of the red coloured Co(II)- HDPBA/PAN complex in chloroform, in terms of cobalt, is 3.18×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 550 nm. The sensitivity of the complex in terms of

TABLE 3.7 EFFECT OF PAN CONCENTRATION ON THE ABSORBANCE OF THE
Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M (10.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$$

Concentration of PAN, M $\times 10^{-3}$	Absorbance at 550 nm
0.2	0.36
0.3	0.45
0.4	0.54
0.6	0.54
0.8	0.54
1.0	0.54
1.2	0.54
1.4	0.46
1.6	0.37

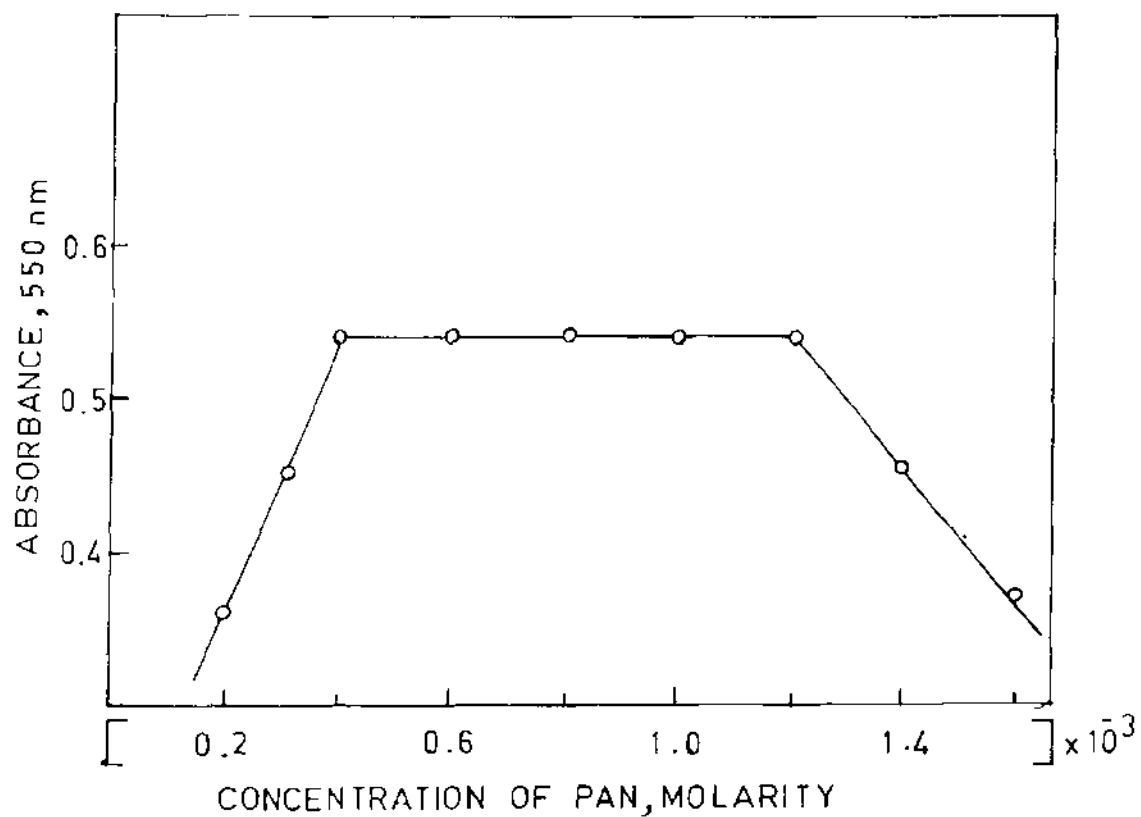


FIG. 3.8 EFFECT OF PAN CONCENTRATION ON THE FORMATION AND ABSORBANCE OF Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M}; \text{ pH} = 10.0 \pm 0.2.$$

TABLE 3.8 CALIBRATION CURVE DATA AND CORRELATION COEFFICIENT FOR THE DETERMINATION OF COBALT(II) AS Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$\text{pH} = 10.0 \pm 0.2$$

$$\text{CPAN} = 0.8 \times 10^{-3} \text{ M}$$

No. of obser- vation	Concentration of Co(II) in organic solution Xi = $\mu\text{g}/10 \text{ ml}$	Absorbance at 550 nm Yi	Correlation coefficient r
	1.0	0.05	
	2.0	0.12	
	4.0	0.22	
	6.0	0.32	
10	8.0	0.43	0.99
	10.0	0.54	
	12.0	0.64	
	13.0	0.72	
	14.0	0.75	
	15.0	0.80	

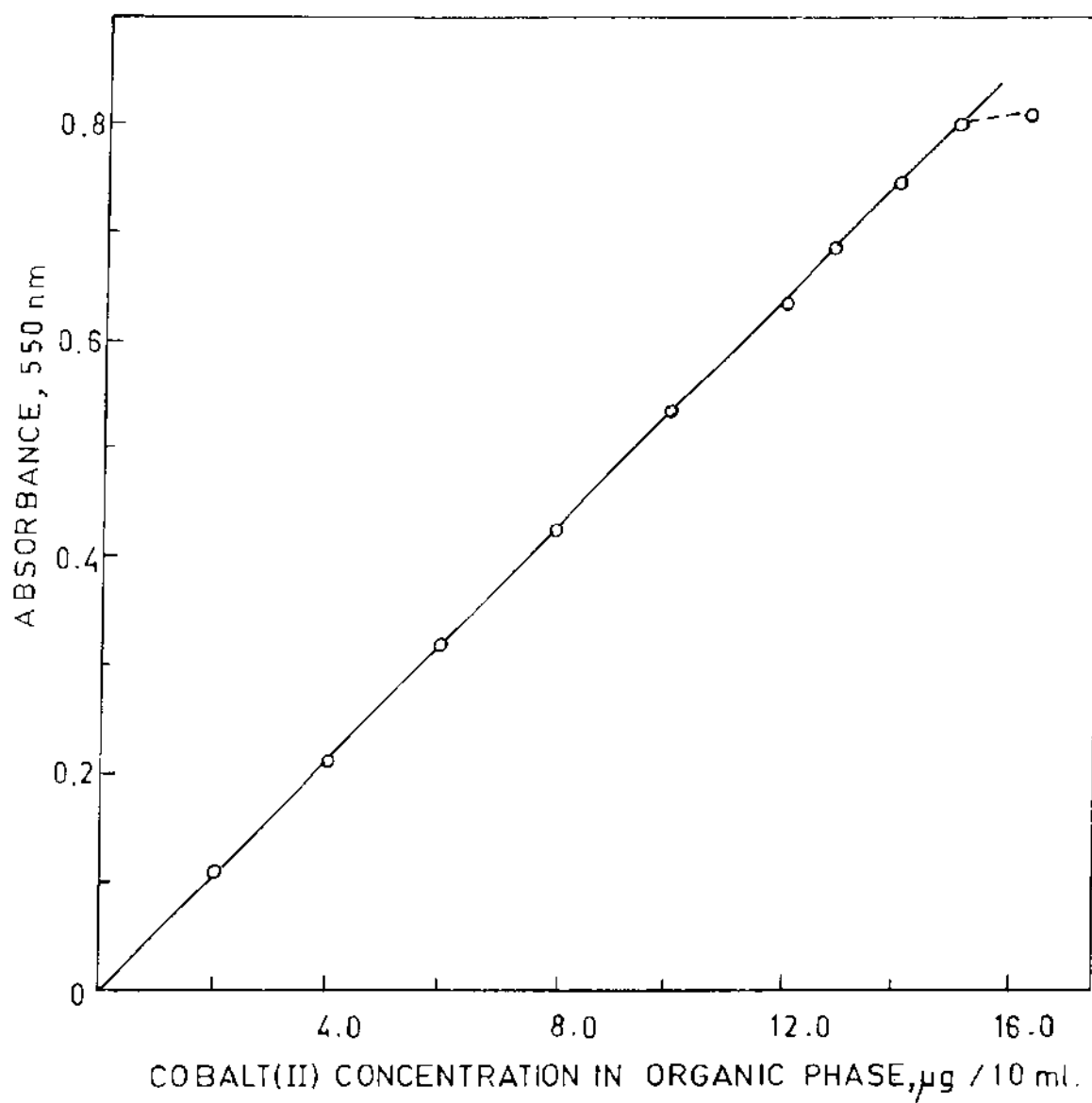


FIG. 3.9 CALIBRATION CURVE FOR THE DETERMINATION OF COBALT(II) AS Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

Sandell's definition⁷⁶ is $0.0018 \mu\text{g}/\text{cm}^2$ of cobalt(II), for $\log I_0/I = 0.001$ absorbance unit.

PRECISION OF THE METHOD AND DETECTION LIMIT

The precision of the method was checked by measuring the absorbance of ten replicate analysis at a level of $10.0 \mu\text{g Co(II)}/10\text{ml}$ aqueous solution. A mean absorbance and standard deviation values were calculated to be 0.54 and ± 0.0066 , respectively. The relative standard deviation of the method was found to be $\pm 1.2\%$. The confidence limit,⁷⁵ in terms of mean absorbance and molar absorptivity of the system were found to be (0.54 ± 0.005) and $(3.18 \pm 0.03) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively at 95% probability (Table 3.9). The detection limit of the method was $0.02 \mu\text{g}/\text{ml}$ aqueous solution.

EFFECT OF DIVERSE IONS

The effect of diverse ions on the determination of Co(II) was determined in chloroform as in the early described procedure. Many metal ions which are commonly associated with cobalt did not interfere. Only the serious interference due to Ni(II) was observed but it could be masked by the addition of EDTA solution prior to the extraction. The tolerance limit of various diverse ions are summarised in Table 3.10.

TABLE 3.9 DETERMINATION OF PRECISION OF THE METHOD

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M (10.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{PAN}} = 0.8 \times 10^{-3} \text{ M} \quad *$$

No. of obser- vation	Absorbance at 550 nm	Mean absorbance	Standard deviation	Relative standard deviation	Value of 't' at 95% confi- dence level	Confidence limit	$\left[r = \left(\bar{x} + \frac{ts}{\sqrt{N}} \right) \right]$
N		\bar{x}	$\pm S$	$\pm, \%$			
	0.54						
	0.54						
	0.55						
	0.54						
10	0.53	0.54	0.0066	1.2	2.262	(0.54±0.005)	(3.18±0.03)
	0.54						
	0.54						
	0.55						
	0.54						
	0.53						

TABLE 3.10 EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 10.0
 μg COBALT(II)

ION	Added as	Tolerance limit [#] mg
Ni(II)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.01 ^a
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.02
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	0.02
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.02
Cd(II)	$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	0.5
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.5
Sn(II)	SnCl_2	0.6
Mn(II)	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.8
Mo(VI)	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0.8
U(VI)	$\text{UO}_2(\text{NO}_3)_2$	0.8
Sb(III)	$(\text{SbO})\text{KC}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$	1.0
Os(VI)	Na_2OsO_4	1.0
As(V)	$\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$	1.5
Cyanide	KCN	1.5
Sulphate	K_2SO_4	2.5
Phosphate	$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	2.5
Ag(I)	AgCl	5.0
Fluoride	NaF	5.5
Persulphate	$\text{K}_2\text{S}_2\text{O}_8$	8.0

Contd..

TABLE 3.10 (Contd.)

ION	Added as	Tolerance limit [#] mg
Oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	8.0
Pd(II)	PdCl_2	10
Bromide	NaBr	10
Ca(II)	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	12
Chloride	KCl	12
Ba(II)	BaCl_2	20
Mg(II)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20
EDTA	$\text{Na}_2\text{-EDTA}$	28
Sr(II)	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	30
Tartrate	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	30

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

a Masked with 1 ml of 2% (w/v) EDTA solution.

COMPOSITION AND REACTION MECHANISM

Curve-fitting method was applied to establish the ratio of metal to ligand in the optimum experimental condition. The results obtained show that a 1:2 Co(II)-HDPBA/PAN complexes are formed.

PROCEDURE

[A] DETERMINATION OF THE RATIO OF HDPBA

The test solution containing 20.0 μg Co(II) was placed in a 125-ml separatory funnel. The pH of the aqueous solution was adjusted at 10.0 ± 0.2 , by keeping a total volume of 10 ml. Different known concentration of HDPBA solutions in chloroform were added and the metal was extracted as in the procedure described above. The absorbance of the complex was measured against respective reagent blanks, prepared in a similar manner at λ_{max} . The distribution ratio and thus its logarithmic value of the metal was calculated as described earlier in Chapter II.

A graph was plotted between logarithmic value of distribution ratio and log molar concentration of HDPBA gave a slope of 1.9 which is close to integer 2. This data indicates that for complexation two molecules of HDPBA is required for each cobalt(II) (Table 3.11, Figure 3.10).

[B] DETERMINATION OF THE RATIO OF PAN

The test solution containing 10.0 μg of Co(II) was placed in a 125-ml separatory funnel. The pH of the aqueous

TABLE 3.11 CURVE -FITTING METHOD FOR THE DETERMINATION OF COBALT(II) TO HDPBA RATIO IN Co(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M (20.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

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
0.40	-2.40	9.40	0.97
0.35	-2.45	6.43	0.80
0.28	-2.55	3.95	0.60
0.24	-2.62	3.16	0.50

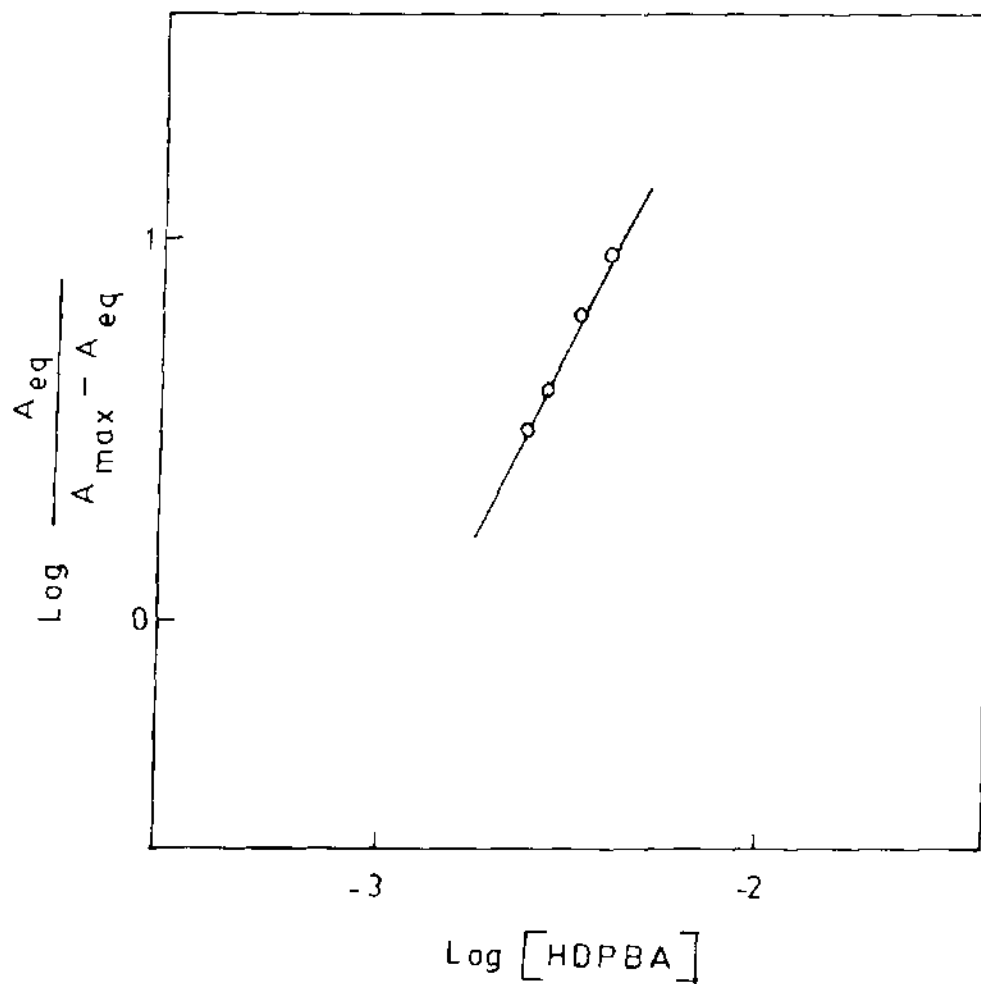


FIG. 3.10 CURVE-FITTING METHOD FOR THE DETERMINATION OF COBALT(II) TO HDPBA RATIO IN Co(II)-HDPBA COMPLEX, FORMED IN CHLOROFORM

$$C_{\text{Co(II)}} = 3.4 \times 10^{-5} \text{ M};$$

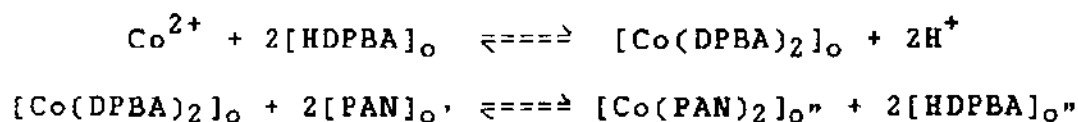
$$\text{pH} = 10.0 \pm 0.2;$$

$$\lambda_{\text{max}} = 400 \text{ nm.}$$

solution was maintained at 10.0 ± 0.2 using ammonia-ammonium chloride buffer in a final volume of 10 ml. The metal ion was extracted with HDPBA as in the procedure described above. The chloroform extract of Co(II)-HDPBA was then reacted with varying known concentration of PAN in ethanol and a series of data were evaluated by measuring the absorbance of red coloured complex at absorption maxima. The distribution ratio of the metal ion was computed as in chapter II.

The graph was plotted between logarithmic value of distribution ratio, D versus log molar concentration of PAN. The slope of the curve was obtained to be 2.0. Hence, it appears that on the addition of PAN to the Co(II)-HDPBA extract, the two molecules of HDPBA from Co(II)-HDPBA complex is replaced by two molecules of PAN in the organic solvent (Table 3.12, Figure 3.11). This type of complex formation in organic medium is suggested by Cheng et al.⁷⁷

The overall reaction mechanism, on the basis of results obtained, can be expressed as :



Where abbreviations HDPBA and PAN, and subscripts o, o' and o'' denote N-hydroxy-N,N'-diphenylbenzamidine, 1-(2-pyridyl-azo)-2-naphthol, chloroform, ethanol and chloroform + ethanol, respectively.

TABLE 3.12 CURVE -FITTING METHOD FOR THE DETERMINATION OF COBALT(II) TO PAN RATIO IN Co(II)-PAN COMPLEX IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M (10.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 10.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M}$$

Concentration of PAN in organic phase, M $\times 10^{-4}$	Log M	$D = \frac{A_{\text{eq}}}{A_{\text{max}} - A_{\text{eq}}}$	Log D
3.2	-3.50	5.00	0.70
2.4	-3.62	2.86	0.46
2.0	-3.70	2.00	0.30
1.6	-3.80	1.25	0.10

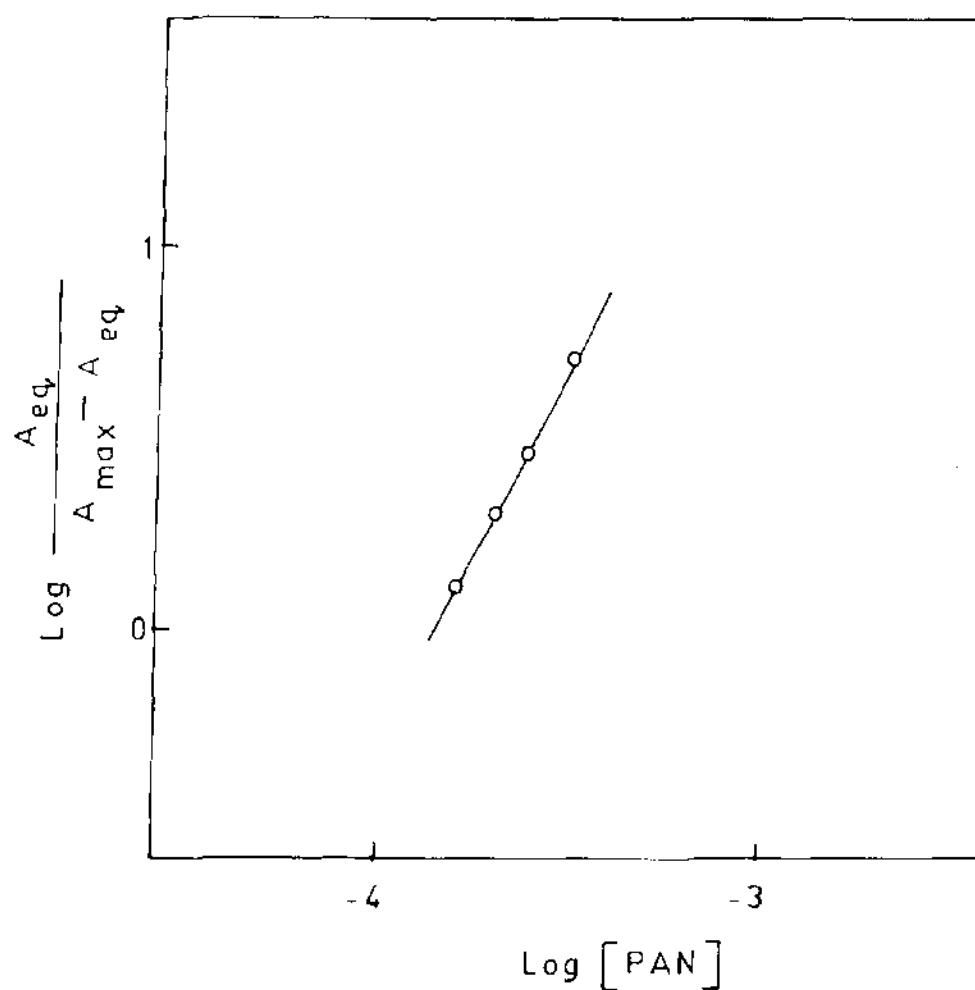


FIG. 3.11 CURVE-FITTING METHOD FOR THE DETERMINATION OF COBALT(II) TO PAN RATIO IN Co(II)-PAN COMPLEX, FORMED IN CHLOROFORM + ETHANOL MIXTURE

$$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ M};$$

$$\text{pH} = 10.0 \pm 0.2;$$

$$C_{\text{HDPBA}} = 6.9 \times 10^{-3} \text{ M};$$

$$\lambda_{\text{max}} = 550 \text{ nm.}$$

APPLICATION OF THE METHOD

The validity of the method was checked by applying it to the determination of cobalt in vitamin B12 samples and the results are shown in Table 3.13. The digestion of the samples are given below :

A 2-3 ml of vitamin B12 samples were decomposed in a covered beaker with nitric acid following a standard procedure⁷⁸ for such samples by heating first at low temperature to avoid violent reaction. The mixture was cooled when reaction subsided and heated again with nitric acid. The temperature was gradually raised and finally the residue was heated to about 400°C on a hot plate. The ash was dissolved in 50% nitric acid and evaporated slowly (1-2 hr) on a steam bath. Finally, the residue was taken in 25 ml water to which nitric acid was added in 0.25 ml portions until a clear solution was obtained on gentle heating. An aliquot of this solution was taken and the analyte content was determined as in the above described procedure after the addition of 2 ml of 5% ascorbic acid solution prior to extraction. The results obtained by the present method was compared with that of standard nitroso-R salt method⁷⁹ and were found to be in good agreement.

TABLE 3.13 DETERMINATION OF COBALT(II) IN VITAMIN B12 SAMPLES

Samples	Cobalt(II) found in ppm		Relative standard deviation [#] ±, %
	Present method	Standard Nitroso R-salt method	
Optineuron	1.4	1.4	1.1
Cobastan - 6	43.1	44.0	1.1
Neuroxin - 12	20.2	20.5	1.2
Neuroplan -12	20.8	21.0	1.2

Average of six determinations

COMPARISON WITH OTHER METHODS

Many spectrophotometric methods have been reported for the determination of cobalt. The various analytical parameters and characteristics of some of the important methods are compared with the present method (Table 3.14). The comparison showed that the present method is more sensitive and quite selective than the previously reported methods.

TABLE 3.14 COMPARATIVE STUDY OF SOME SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COBALT

Reagents	pH/Acidity	Solvent	λ_{\max} nm	Molar absorp- tivity $l\ mol^{-1}\ cm^{-1}$	Remarks	Refer- ence
Nitroso-R salt	8.0	-	520	15000	Fe, Mn, Zn, etc. interfere.	18
Thiocyanate + Cetyl- trimethyl-ammonium bromide	3.5±0.2	Chloroform	625	1920	Cu, Zn and Hg interfere.	12
Nitroso-NW acid	4.5-6.0	Methanol	400	11000	Excess of reagent required, time consuming.	58
1-(2-Pyridylazo)- 2-naphthol	3.0-6.0	Chloroform	640 590	20000 25000	Many metal ions int- erfere and separated by anion exchange resin. Cu interfere seriously.	42
1-(2-Pyridylazo)- 2-naphthol + Triton X-100 + Sodium dodecyl sulphonate	2.4-6.5	Water	620	19000	Fe, Bi, Sn and Al interfere but masked by citrate or oxalate, procedure is time consuming.	43
2-Hydroxy-1-naphth- aldoxime	8.3-9.2	Ethyl acetate	387	11700	Cu, Ni and Fe inter- fere seriously.	60
Morpholine-4-carbo- dithioate + Micro- crystalline naphth- alene	3.0-8.8	-	365	13960	Low sensitivity, Procedure is com- plicated.	37
Maleonitrile Dithi- olate	0.2-0.5 M HCl	Isobutyl methyl ketone	460	5010	Poor sensitivity, Many metal ions interfere.	59

Contd..

Table 3.14 (Contd.)

Reagents	pH/Acidity	Solvent	λ_{\max} nm	Molar absorp- tivity $l \text{ mol}^{-1} \text{ cm}^{-1}$	Remarks	Refer- ence
Potassium o,o-bis- [4'(1-phenyl-3- methyl-4-benzylidene -5-pyrazolone)] di- thiophosphate	8.0 M HCl	Chloroform	417	15400	Heating require on water bath, procedure is time consuming, low sensitivity.	34
2-(3'-Sulphobenzoyl) pyridine benzoylhydra- zone(3-[benzoylhydrazono -(2-pyridyl)methyl] benzenesulphonic acid	5.5	Water	400	21700	Pd, Cyanide and EDTA interfere at all concentrations.	28
Phenanthraquinone Monothiosemicarbazone	6.8-8.5	Aqueous methanol	500	12400	Oxalate, phosphate, cyanide, EDTA, Ni and Pd interfere.	36
2-[2-(3,5-Dibromopyri- dylazo)]-5-dimethyl- aminobenzoic acid	4.0-5.5	Dichloro methane	673	155000	Cu, Fe, Mn and Pd interfere.	27
5,6-Diphenyl-3-(2- pyridyl)-1,2,4-triazine + Tetraphenylborate + Microcrystalline naphthalene	6.5	-	500	4100	Cyanide and EDTA interfere, pH cri- tical, low sens- itivity.	54
p-Methylisonitroso- acetophenone	6.8-7.8	Chloroform	380	23077	Less sensitivity.	52
N-Hydroxy-N,N'-diph- enylbenzamide + 1-(2-Pyridylazo)-2- naphthol	8.0-12.0	Chloroform + Ethanol	550	31800	Ni interfere but masked by EDTA.	pre- sent method

CONCLUSION

In the present investigation, N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) is used as an extracting reagent for cobalt(II). The colour of the extracted complex is further intensified with 1-(2-pyridylazo)-2-naphthol (PAN) for the extraction-spectrophotometric determination of cobalt(II) at trace levels. The present method overcomes all the drawbacks of classical PAN method and other methods. Thus, it proves to be a superior method than the other established methods, owing to its sensitivity and selectivity. It has been applied satisfactorily for the determination of cobalt in vitamin B12 samples.

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