

CHAPTER V

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

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2-NAPHTHOL

SUMMARY

A new extraction-spectrophotometric method for the determination of manganese(II) at trace levels has been investigated. It is based on the extraction of manganese(II) with hydroxyamidines(HOAs) in the pH range of 8.0 - 9.5 and subsequent colour development with 1-(2-pyridylazo)-2-naphthol (PAN) in a borate buffer medium. The molar absorptivity of the resulting complexes lie in the range of $(2.96 - 4.94) \times 10^4$ $\text{l mol}^{-1} \text{cm}^{-1}$ around λ_{max} 545-555 nm. The parent compound N-hydroxy-N,N'-diphenylbenzamidine(HDPBA), the simplest compound, has greater sensitivity than other hydroxyamidines (HOAs). It was therefore, selected for all experimental work. The molar absorptivity of the red coloured complex has been found to be 4.94×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 555 nm. The detection limit of the method is 0.02 $\mu\text{g/ml}$ aqueous solution.

The system follows Beer's law upto 0.7 $\mu\text{g Mn(II)/ml}$ organic solution. Various analytical parameters have been discussed. The relative standard deviation of the method for ten replicate determinations at 0.6 $\mu\text{g/ml}$ of manganese(II) is calculated to be $\pm 1.4\%$. None of the tested ions, except Zn(II) and Pb(II) which were effectively masked with EDTA, interfere. The method has been applied successfully for the determination of manganese(II) at trace levels in environmental samples.

Manganese is an essential micronutrient. It is widely distributed in nature, always in the combined state and its minerals are quite abundant. The average concentration of manganese in the earth's crust is found to be 1000 ppm. The important ores are pyrolusite and psilemelance.^{1,2} It is extensively used as an alloying and cleansing agent for steel, non-ferrous alloys, glass ceramics, oxidizing agents, etc. Isotopic forms of manganese are used in tracer studies.³ Manganese(II) is toxic to human being. The threshold limit value for manganese is 5 mg/m³. Inhalation of manganese dioxide causes chronic manganese poisoning or manganic pneumonia, which affect the central nervous system.²

A large number of spectrophotometric methods have been reported for the determination of manganese in environmental and metallurgical samples at trace levels. The most widely used method for the spectrophotometric determination of low concentration of manganese is the permanganate method.⁴⁻⁹ This method is tedious because chloride has to be removed first and the oxidation should be done at elevated temperature. In the above reported methods cerium and chromium are also oxidized by periodate in acid solution as well as bismuth and tin gives turbidity even in strongly acid solution. Various analytical parameters are critical and followed strictly. Potassium permanganate + tetrabutylammonium chloride¹⁰ and above cited permanganate methods lack sensitivity. The formaldoxime method^{4,11,12} is one such in which interferences from iron can be avoided by selectively decomposing the iron formaldoxime

complex but the conditions for selective decomposition of the iron complex are some what critical.

Various organic reagents have been employed for the spectrophotometric determination of manganese. These reagents are potassium trithiocarbamate,¹³ 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol,¹⁴ 1,10-phenanthroline + tetraiodofluorescein,¹⁵ α ,B,Y,S-tetrakis(4-sulfophenyl)porphine,¹⁶ (5-bromo-2-pyridylazo)-diethylaminophenol¹⁷ and 4,5-dibromophenylfluorone¹⁸ with cetyltrimethylammonium bromide which give highly sensitive colour reaction. However, in these methods careful control of pH is necessary and the Beer's law is followed upto a short range of concentration.

Several reagents containing chromophore azo groups and many other dyes such as 1-(2-quinolyazo)-2, 4, 5-trihydroxybenzene,¹⁹ heterocyclic diamines + 2, 4-dinitrophenylazopyrocatechol,²⁰ khimduchlorophosphonazo I,²¹ 1-(2-pyridylazo)-2-naphthol with²² or without surfactant²³⁻²⁹ and also with emulsifier,³⁰ 4-(2-pyridylazo)-1-naphthol,³¹ 4-(2-pyridylazo)resorcinol + quaternary ammonium salt,³² 4-(2-thiazolylazo)resorcinol,³³ eriochrome black T,³⁴ methyl orange,³⁵ brilliant green,³⁶ formed coloured complexes with metal ion, which are absorbed at higher or lower wavelengths. But in most of these methods,²²⁻³³ the comparable sensitivity exist and many metal ions like Zn, Pb, Cd, Ni, Co, etc. interfere seriously. Moreover, these methods lack in accuracy. In some of these methods^{19-22, 33-36} the rigid control of pH is necessary, heating is required for completion of the reaction, sensitivity

is low and 5 - 10 min waiting time is essential for maximum colour development.

Numerous methods using reagents like sulphur containing group,³⁷⁻⁴⁰ different hydroxamic acids,⁴¹⁻⁴⁶ and others⁴⁷⁻⁵⁸ have been used for the determination of manganese(II) but all these methods suffer from one or more serious experimental problems and also they lack in sensitivity and selectivity as well.

In the present investigation, N-hydroxy-N,N'-diphenylbenzamidinium(HDPBA) is used as an extracting reagent and colour reaction is subsequently developed with 1-(2-pyridylazo)-2-naphthol(PAN). This method is free from the interferences of all common metal ions except Zn and Pb which are masked by the addition of EDTA solution. It gives reproducible results. Thus, present method is sensitive, selective and reproducible.

EXPERIMENTAL

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

STANDARD SOLUTION OF MANGANESE(II) - A stock solution of manganese(II) was prepared by dissolving weighed amount of manganese(II) chloride tetrahydrate in 250 ml double distilled water containing 2 ml of 0.5 M hydrochloric acid. Working standard solution was prepared by dilution of the stock solution and standardized complexometrically.⁵⁹

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

HYDROXYAMIDINES(HOAs) - Hydroxyamidines(HOAs) were synthesized as described in the literature.⁶⁰ Their 0.3%(w/v) or $\approx 1.04 \times 10^{-2}$ M solution in chloroform were used for all extraction purpose.

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

BUFFER SOLUTION - A sodium hydroxide - boric acid buffer solutions of pH 9.0 and 10.0 were prepared as described in the literature.⁶¹

SOLUTION OF DIVERSE IONS - The solution of diverse ions were prepared as described in the literature.⁶² A 1 mg/ml solution of desired ions was used.

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

PROCEDURE

[A] EXTRACTION OF MANGANESE(II) WITH HDPBA

An aliquot of the test solution containing upto 24.0 μg of Mn(II) is transferred to a 125-ml separatory funnel. The pH of the 10 ml final aqueous solution is adjusted at 9.0 ± 0.2 by the addition of barate buffer. The above solution is shaken with 5 ml chloroform solution of HDPBA for 2 min. The organic phase is separated and aqueous phase is washed with 1x2 ml of fresh portion of chloroform. All the organic extracts is collected and dried over anhydrous sodium sulphate ($\sim 2\text{g}$). The combined organic extract is transferred to a 10-ml volumetric flask and made upto the mark with chloroform. The absorbance of the yellow coloured complex is measured at λ_{max} 400 nm against reagent blank. The reagent blank of the sample is prepared in a similar manner.

[B] SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE(II) WITH PAN

The test solution containing upto 10.5 μg of Mn(II) is extracted with HDPBA complex in chloroform and Mn(II) is

stripped to the aqueous phase with 2.0 M hydrochloric acid. The phases are allowed to separate, the organic phase is discarded and 2 ml of PAN solution is added to the aqueous phase. The pH of the aqueous solution is adjusted to 10.0 ± 0.2 by using borate buffer solution and is diluted upto 15 ml with distilled water. The absorbance of the red coloured complex is measured against reagent blank at λ_{\max} 555 nm. The reagent blank is prepared in a similar manner.

RESULTS AND DISCUSSION

[A] EXTRACTION OF MANGANESE(II) WITH N-HYDROXY-N,N'-DIPHENYLBENZAMIDINE (HDPBA)

The absorption spectra of Mn(II) - HDPBA complex shows maximum absorbance at absorption maxima 400 nm against reagent blank. At this wavegength, reagent blank exhibits some absorbance. Hence, it is used as reference for all absorbance measurements. The position of λ_{\max} are unchanged at different metal concentration (Figure 5.1).

EFFECT OF SOLVENTS

Various polar and non-polar organic solvents such as ethyl acetate, benzene, toluene, xylene, chloroform and carbon tetrachloride were tried for the extraction of metal complex (Table 5.1, Figure 5.2). No extraction of the metal complex was seen with xylene and ethyl acetate whereas other solvents extract the complex quantitatively. But chloroform was chosen as the best extracting solvent because it has higher sensitivity and greater selectivity of the complex.

EFFECT OF pH

The metal ion was extracted quantitatively in chloroform with HDPBA as Mn(II)-HDPBA complex from aqueous solution in the pH range of 8.0-9.5 (Table 5.2, Figure 5.3). Therefore, all extractions were carried out at pH 9.0 ± 0.2 using borate buffer solution.

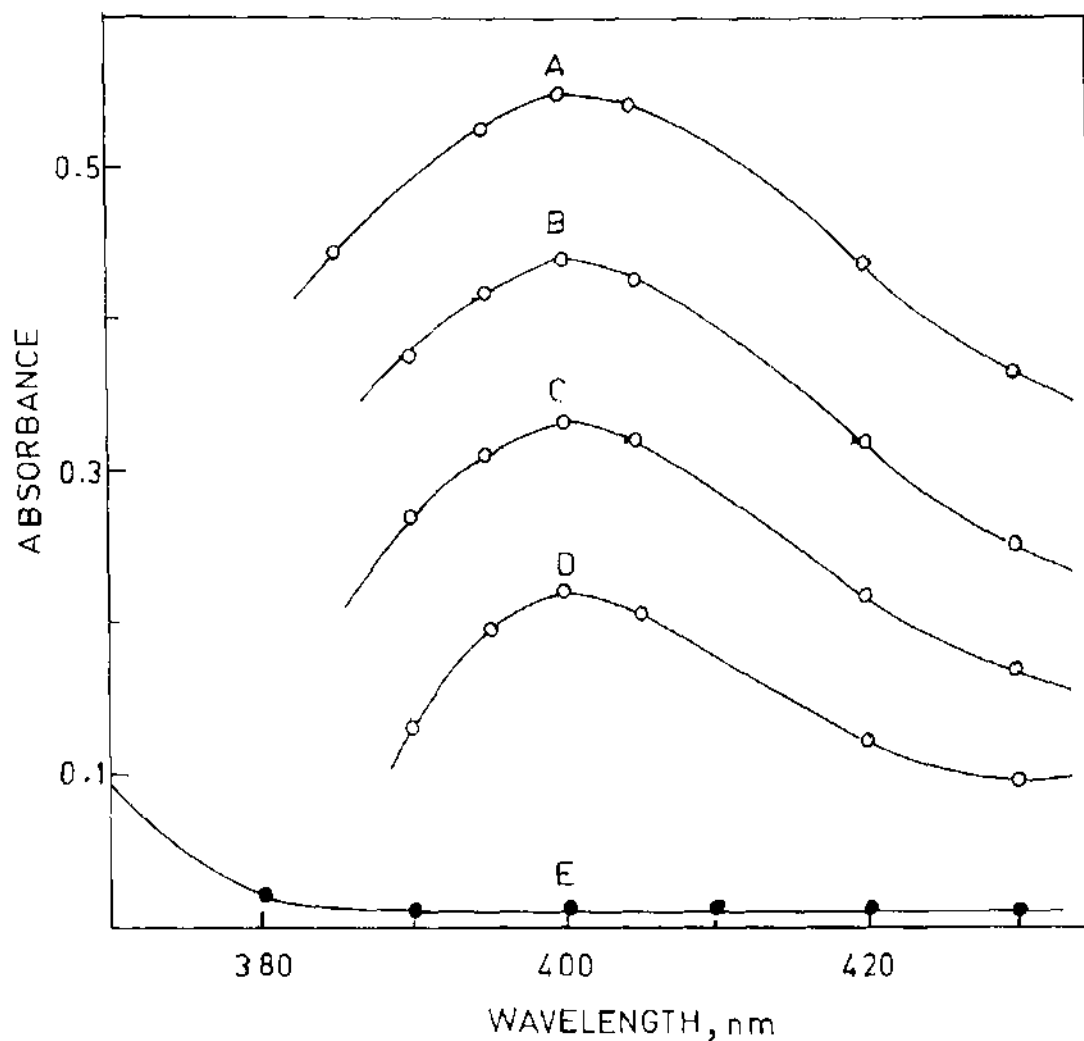


FIG. 5.1 EFFECT OF METAL CONCENTRATION ON THE POSITION OF λ_{\max} OF THE Mn(II)-HDPBA COMPLEX IN CHLOROFORM

[A] $C_{\text{Mn(II)}} \approx 3.64 \times 10^{-5}$ M (20.0 $\mu\text{g}/10$ ml organic phase)

[B] $C_{\text{Mn(II)}} \approx 2.91 \times 10^{-5}$ M (16.0 $\mu\text{g}/10$ ml organic phase)

[C] $C_{\text{Mn(II)}} \approx 2.18 \times 10^{-5}$ M (12.0 $\mu\text{g}/10$ ml organic phase)

[D] $C_{\text{Mn(II)}} \approx 1.46 \times 10^{-5}$ M (8.0 $\mu\text{g}/10$ ml organic phase)

[E] REAGENT BLANK

TABLE 5.1 EFFECT OF SOLVENTS ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M (12.0 } \mu\text{g/10 ml organic phase)}$$

$$\text{pH} = 9.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

| Solvent | λ_{max} nm | Molar absorptivity $l \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$ |
|----------------------|------------------------------|---|
| Chloroform | 400 | 1.51 |
| Benzene | 400 | 1.38 |
| Toluene | 390 | 1.28 |
| Carbon tetrachloride | 380 | 1.24 |
| Xylene | - | No extraction |
| Ethyl acetate | - | No extraction |

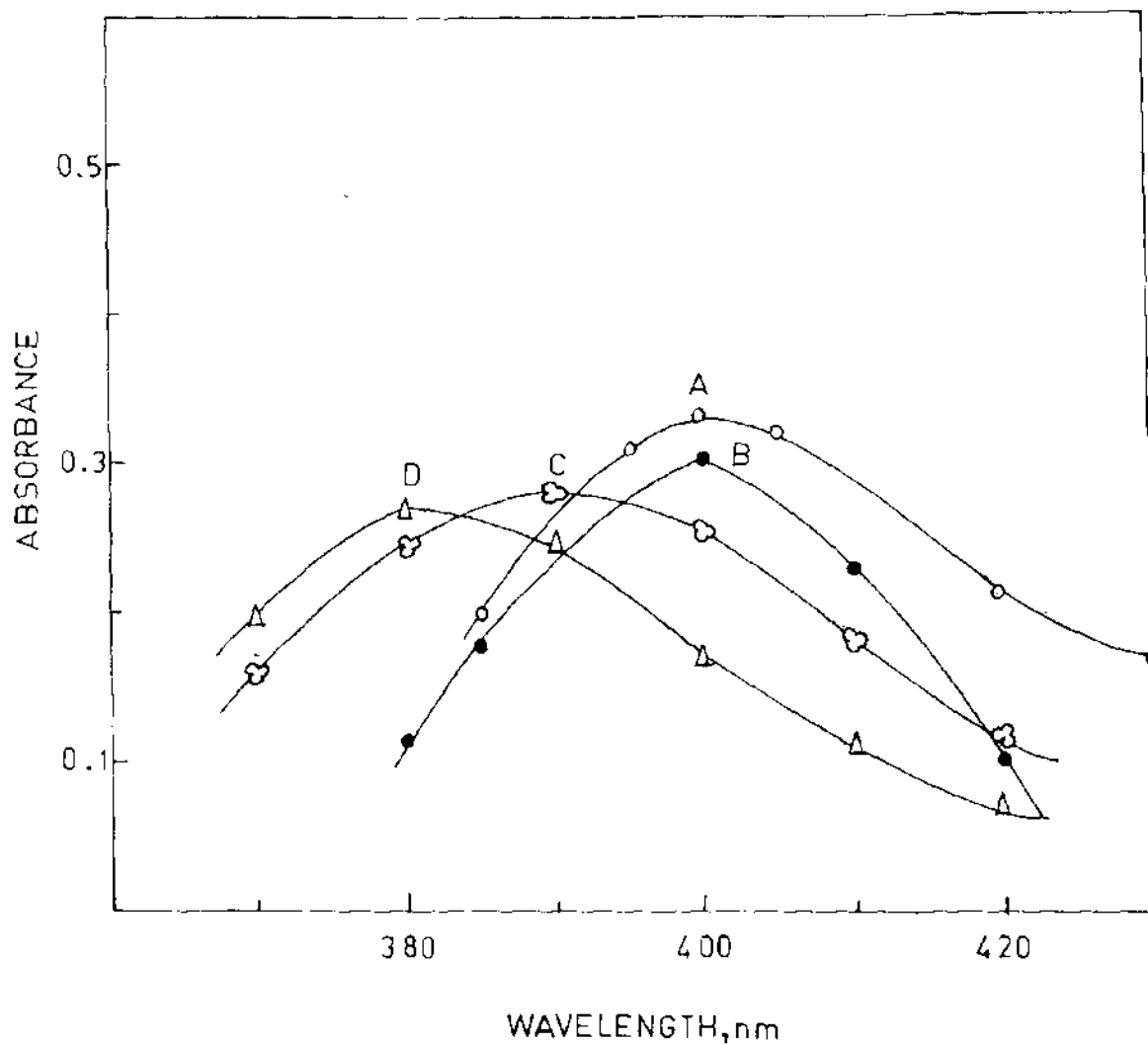


FIG.5.2 EFFECT OF SOLVENTS ON THE ABSORBANCE AND λ_{\max} OF THE $Mn(II)$ -HDPBA COMPLEX

$$C_{Mn(II)} = 2.18 \times 10^{-5} \text{ M};$$

$$pH = 9.0 \pm 0.2;$$

$$C_{HDPBA} = 1.0 \times 10^{-2} \text{ M}.$$

[A] CHLOROFORM

[B] BENZENE

[C] TOLUENE

[D] CARBON TETRACHLORIDE

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

The influence of HDPBA on the extraction of complex was studied and it was found that a minimum of 0.69×10^{-2} M solution of HDPBA in chloroform was needed to obtain a constant and maximum absorbance. Further addition of upto 1.73×10^{-2} M HDPBA did not lead to any change on the extraction of the complex (Table 5.3, Figure 5.4). Hence, all further extractions were carried out at 1.04×10^{-2} M HDPBA solution in chloroform.

EFFECT OF DILUTION, TEMPERATURE AND ELECTROLYTES

No significant changes on the extraction of complex was observed, when the volume ratio of organic to aqueous phase was varied between 2:1 to 1:5 (Table 5.4, Figure 5.5). A complete extraction of the complex was obtained when the temperature of the system was changed between 15 - 30°C (Table 5.5). Therefore, 1:2 volume ratio of organic to aqueous phase was selected throughout the experiment and extractions were performed at room temperature $25 \pm 2^\circ\text{C}$.

The extraction efficiency of the metal complex was unchanged in the presence of upto 2 M electrolytes viz. KCl/NH₄Cl/NaCl.

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

A minimum shaking time of 1-2 min was needed for maximum extraction of the metal complex. The stability of the complex

TABLE 5.2 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M (12.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

| pH of the aqueous phase | Absorbance at 400 nm |
|-------------------------|----------------------|
| 7.0 | 0.27 |
| 7.5 | 0.30 |
| 8.0 | 0.33 |
| 8.5 | 0.33 |
| 9.0 | 0.33 |
| 9.5 | 0.33 |
| 10.0 | 0.28 |
| 10.5 | 0.23 |

TABLE 5.3 EFFECT OF HDPBA CONCENTRATION ON THE ABSORBANCE OF
Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M (12.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 9.0 \pm 0.2$$

| Concentration of HDPBA, M $\times 10^{-2}$ | Absorbance at 400 nm |
|---|-------------------------|
| 0.34 | 0.28 |
| 0.52 | 0.31 |
| 0.70 | 0.33 |
| 1.04 | 0.33 |
| 1.38 | 0.33 |
| 1.56 | 0.33 |
| 1.73 | 0.33 |
| 1.90 | 0.30 |
| 2.25 | 0.25 |

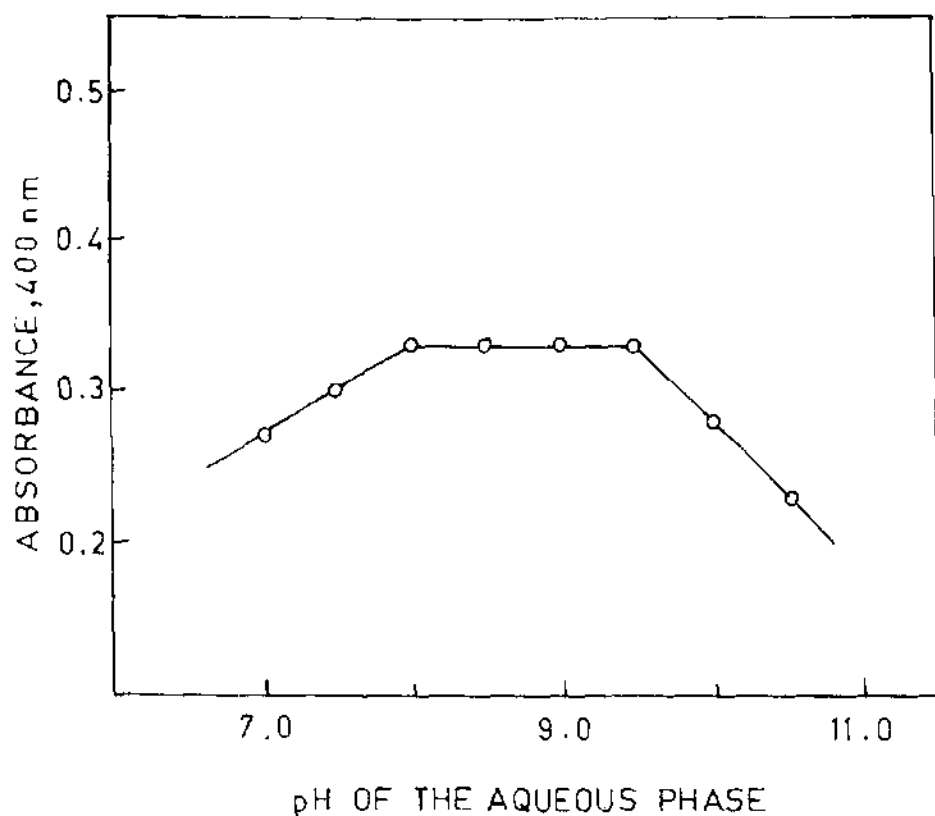


FIG. 5.3 EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M}; C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M.}$$

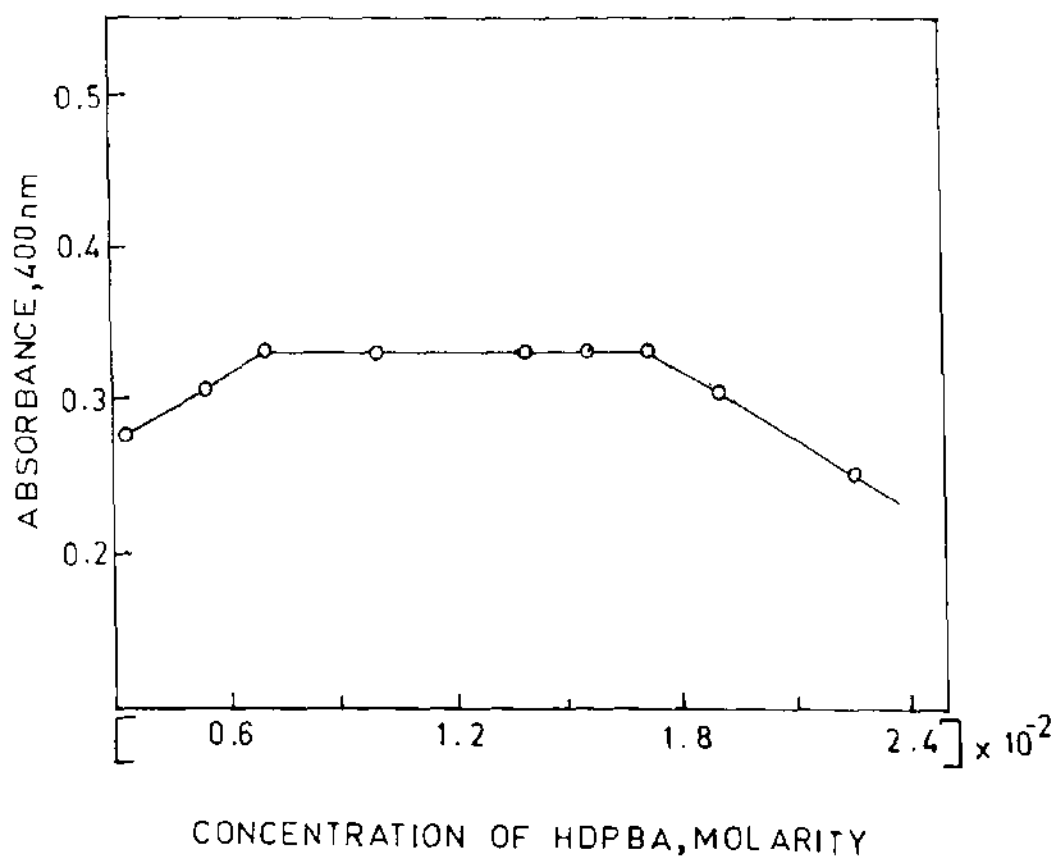


FIG. 5.4 EFFECT OF HDPBA CONCENTRATION ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M}; \text{pH} = 9.0 \pm 0.2.$$

TABLE 5.4 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 12.0 \mu\text{g}$$

$$\text{pH} = 9.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

| Volume ratio of organic to aqueous phase | Absorbance at 400 nm |
|---|-------------------------|
| 2 : 1 | 0.33 |
| 1 : 1 | 0.33 |
| 1 : 2 | 0.33 |
| 1 : 3 | 0.33 |
| 1 : 4 | 0.33 |
| 1 : 5 | 0.33 |
| 1 : 6 | 0.29 |
| 1 : 7 | 0.24 |

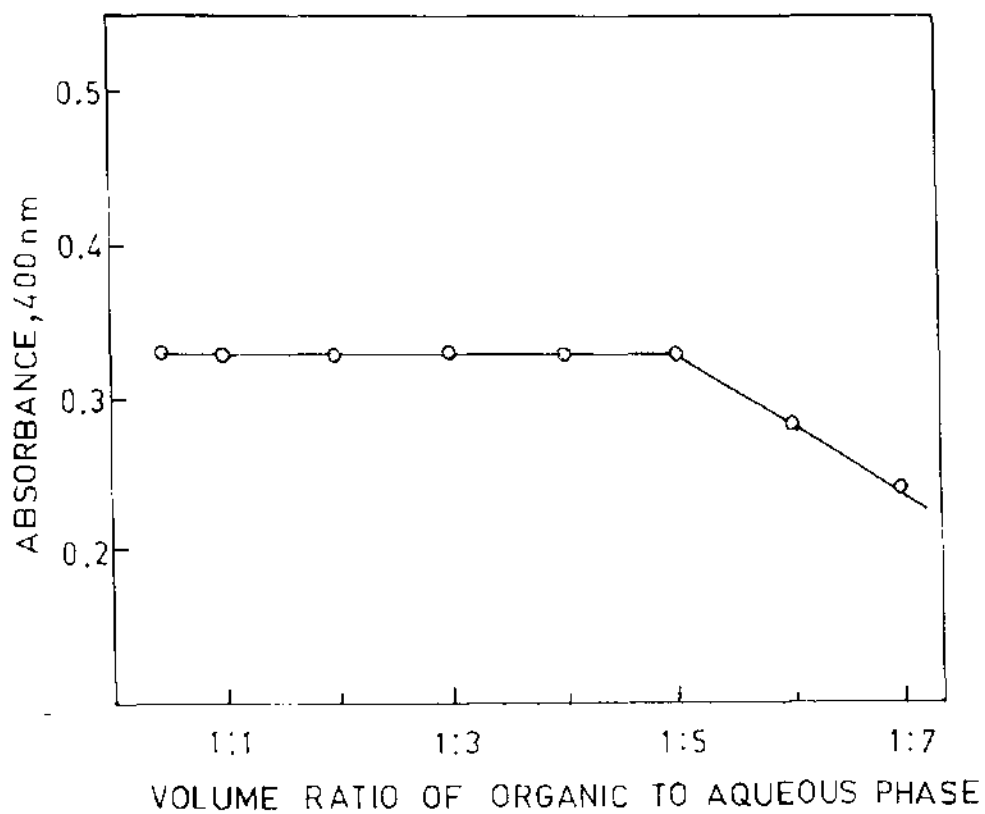


FIG. 5.5 EFFECT OF VOLUME RATIO OF ORGANIC TO AQUEOUS PHASE ON EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$C_{\text{Mn(II)}} = 12.0 \mu\text{g}$; $\text{pH} = 9.0 \pm 0.2$; $C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$.

TABLE 5.5 EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE ON THE EXTRACTION OF Mn(II)-HDPBA COMPLEX IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-6} \text{ M (12.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 9.0 \pm 0.2$$

$$C_{\text{HDPBA}} = 1.0 \times 10^{-2} \text{ M}$$

| Temperature of the aqueous phase, °C | Absorbance at 400 nm |
|--------------------------------------|----------------------|
| 8 | 0.23 |
| 10 | 0.25 |
| 15 | 0.33 |
| 20 | 0.33 |
| 25 | 0.33 |
| 30 | 0.33 |
| 35 | 0.30 |
| 40 | 0.28 |

was found to be 12 hr at room temperature $25 \pm 2^\circ\text{C}$. The Mn(II)-HDPBA system confirms to Beer's law upto 2.4 ppm (24.0 $\mu\text{g}/10$ ml organic solution). The molar absorptivity of this complex, in terms of manganese, is found to be 1.51×10^4 $\text{l mol}^{-1} \text{cm}^{-1}$ at λ_{max} 400 nm.

EFFECT OF ACIDITY

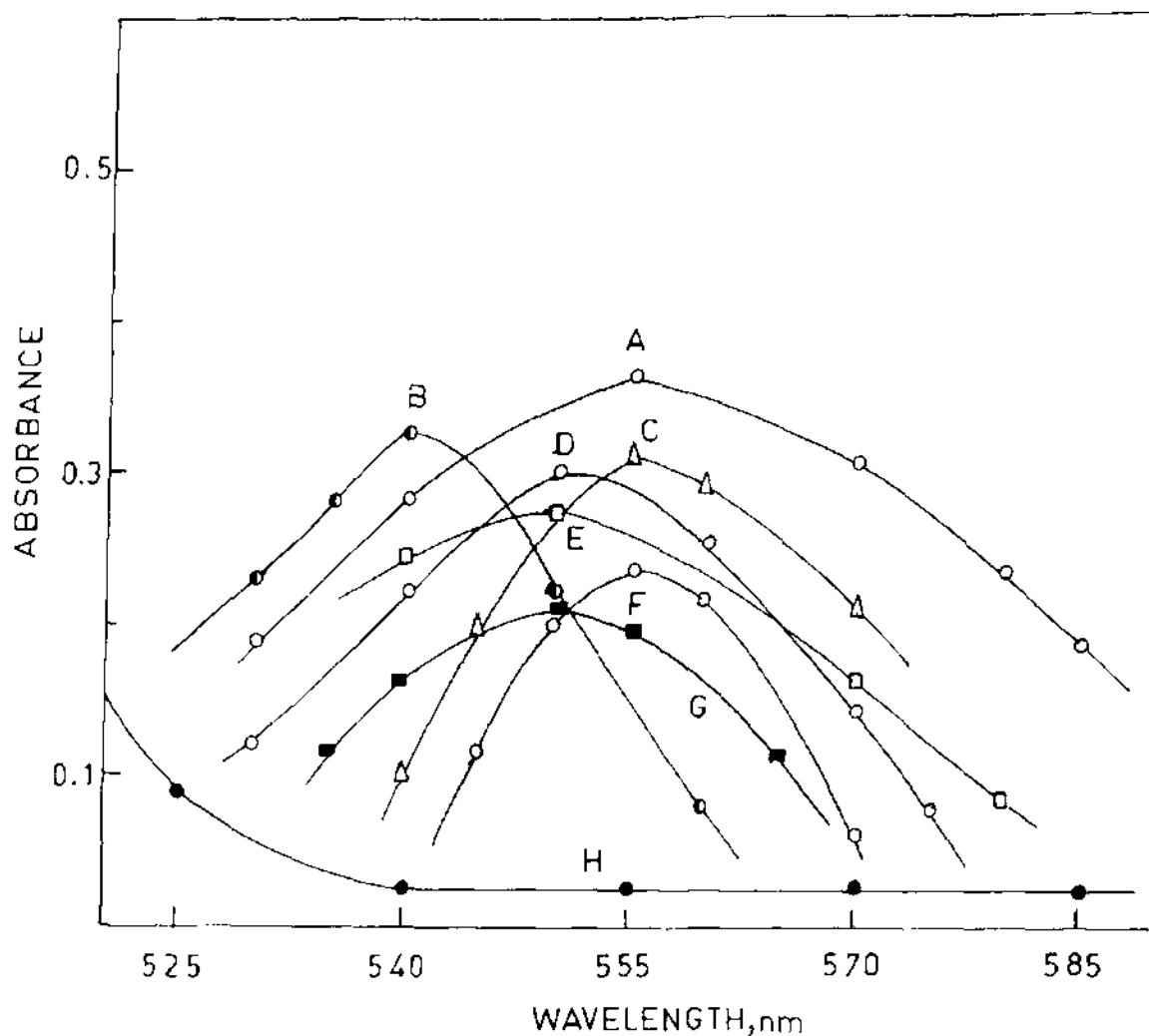
The effect of hydrochloric acid on the stripping of metal from Mn(II)-HDPBA complex was examined. It was found that 1.0 - 3.0 M HCl solution was adequate for stripping the metal ion in the aqueous medium from organic extract. In practice, a 2.0 M HCl solution was selected for all stripping purpose.

[B] SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE(II) WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL (PAN)

Manganese(II) forms a coloured complex with PAN in aqueous medium at $\text{pH } 10.0 \pm 0.2$, after the stripping of the metal ion from Mn(II)-HDPBA complex of the chloroform.

ABSORPTION SPECTRA

The absorption spectra of Mn(II)-PAN complexes, formed after the extraction of metal with seven different hydroxyamidines (HOAs) and subsequent colour reaction of the stripped metal with PAN, exhibit a maximum absorbance around 545 - 555 nm against their respective reagent blanks. The absorption spectra of the Mn(II)-PAN complex and the reagent blank of N-hydroxy-N,N'-diphenylbenzamidinium(HDPBA) are shown in Figure 5.6 a. The sensitivity of the metal complex of HDPBA



6 a. ABSORPTION SPECTRA OF MANGANESE(II) COMPLEX WITH DIFFERENT HYDROXYAMIDINES(HOAs) AND PAN AGAINST THEIR RESPECTIVE REAGENT BLANKS IN WATER + METHANOL MIXTURE

$$C_{Mn(II)} = 7.28 \times 10^{-6} \text{ M}; \text{ pH} = 10.0 \pm 0.2;$$

$$C_{HOAs} \approx 1.0 \times 10^{-2} \text{ M}; C_{PAN} = 0.8 \times 10^{-4} \text{ M}.$$

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

is higher than other hydroxyamidines. Therefore, it is chosen for all experimental work (Table 5.6). The position of λ_{\max} does not change on the variation of metal concentration (Figure 5.6 b).

EFFECT OF pH

The influence of pH on the colour development of the complex was examined and it was found that a pH range of 9.0-11.2 was essential for the complete colour development of the complex (Table 5.7, Figure, 5.7). Therefore, further determinations were performed at pH 10.0 ± 0.2 by using borate buffer solution.

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

For constant and maximum absorbance of the coloured complex, a $(0.53 - 1.06) \times 10^{-4}$ M PAN solutions were necessary (Table 5.8, Figure 5.8). Thus, 0.8×10^{-4} M solution was used for all experimental work.

STABILITY OF THE COMPLEX, STANDING TIME AND ORDER OF ADDITION OF REAGENTS

The absorbance of the red coloured complex is constant upto 6 hr at room temperature ($25 \pm 2^{\circ}\text{C}$). The colour development of the complex is found to be instantaneous. The order, in which reagents were added is not critical in this system.

TABLE 5.6 EFFECT OF NATURE OF HYDROXYAMIDINES ON THE ABSORBANCE OF THE $Mn(II)$ -HOA/PAN COMPLEXES IN WATER + METHANOL MIXTURE

$$C_{Mn(II)} = 7.28 \times 10^{-6} \text{ M (6.0 } \mu\text{g/15 ml aqueous methanol)}$$

$$pH = 10.0 \pm 0.2$$

$$C_{HOAs} \approx 1.0 \times 10^{-2} \text{ M}$$

$$C_{PAN} = 0.8 \times 10^{-4} \text{ M}$$

| Hydroxyamidines (HOAs) | $\begin{array}{c} \left[\begin{array}{c} \text{Ph} - \text{C} = \text{N} - \text{Ph}' \\ \\ \text{Ph}'' - \text{N} - \text{OH} \end{array} \right] \end{array}$ | | | λ_{max} nm | Molar absorptivity $l \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$ |
|--|--|--|------------------------------------|------------------------------|---|
| | Ph'' | Ph' | Ph | | |
| N-Hydroxy-N, N'-diphenylbenzamide | -C ₆ H ₅ | -C ₆ H ₅ | -C ₆ H ₅ | 555 | 4.94 |
| N-Hydroxy-N-phenyl-N'-(3-chlorophenyl) benzamide | -C ₆ H ₅ | 3-Cl-C ₆ H ₄ | -C ₆ H ₅ | 540 | 4.56 |
| 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 | 555 | 4.17 |
| N-Hydroxy-N-(4-chlorophenyl)-N'-(2-chlorophenyl) benzamide | 4-Cl-C ₆ H ₄ | 2-Cl-C ₆ H ₄ | -C ₆ H ₅ | 550 | 3.73 |
| 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 | 550 | 3.62 |
| 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 | 555 | 3.29 |
| 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 | 550 | 2.96 |

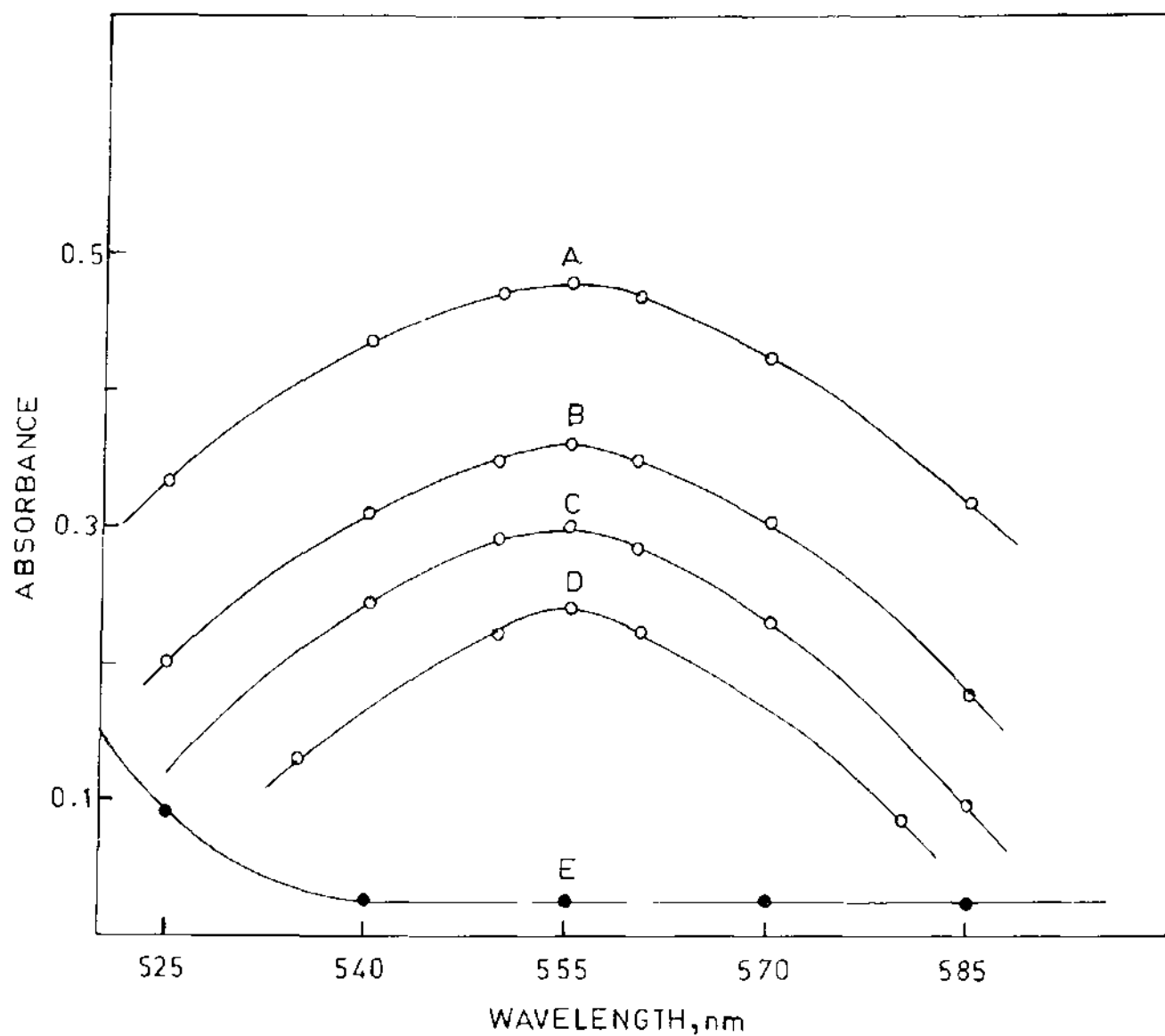


FIG. 5.6 b. EFFECT OF METAL CONCENTRATION ON THE POSITION OF λ_{\max} OF THE $Mn(II)$ -PAN COMPLEX IN AQUEOUS METHANOL

[A] $C_{Mn(II)} \approx 9.70 \times 10^{-6}$ M (8.0 μg /15 ml aqueous methanol)

[B] $C_{Mn(II)} \approx 7.28 \times 10^{-6}$ M (6.0 μg /15 ml aqueous methanol)

[C] $C_{Mn(II)} \approx 6.07 \times 10^{-6}$ M (5.0 μg /15 ml aqueous methanol)

[D] $C_{Mn(II)} \approx 4.85 \times 10^{-6}$ M (4.0 μg /15 ml aqueous methanol)

[E] REAGENT BLANK

TABLE 5.7 EFFECT OF pH OF THE AQUEOUS PHASE ON THE COLOUR DEVELOPMENT OF Mn(II)-PAN COMPLEX IN WATER + METHANOL MIXTURE

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M (6.0 } \mu\text{g/10 ml aqueous phase)}$$

$$C_{\text{PAN}} = 0.8 \times 10^{-4} \text{ M}$$

| pH of the aqueous phase | Absorbance at 555 nm |
|-------------------------|----------------------|
| 7.0 | 0.26 |
| 8.0 | 0.31 |
| 8.5 | 0.33 |
| 9.0 | 0.36 |
| 10.0 | 0.36 |
| 11.2 | 0.36 |
| 11.6 | 0.32 |
| 12.0 | 0.30 |
| 13.0 | 0.22 |

TABLE 5.8 EFFECT OF PAN CONCENTRATION ON THE COMPLEX FORMATION AND ABSORBANCE OF Mn(II)-PAN COMPLEX IN WATER + METHANOL MIXTURE

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M (6.0 } \mu\text{g/10 ml aqueous phase)}$$

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

| Concentration of PAN, M $\times 10^{-4}$ | Absorbance at 555 nm |
|---|-------------------------|
| 0.40 | 0.32 |
| 0.45 | 0.34 |
| 0.53 | 0.36 |
| 0.66 | 0.36 |
| 0.80 | 0.36 |
| 0.93 | 0.36 |
| 1.06 | 0.36 |
| 1.11 | 0.29 |
| 1.33 | 0.23 |

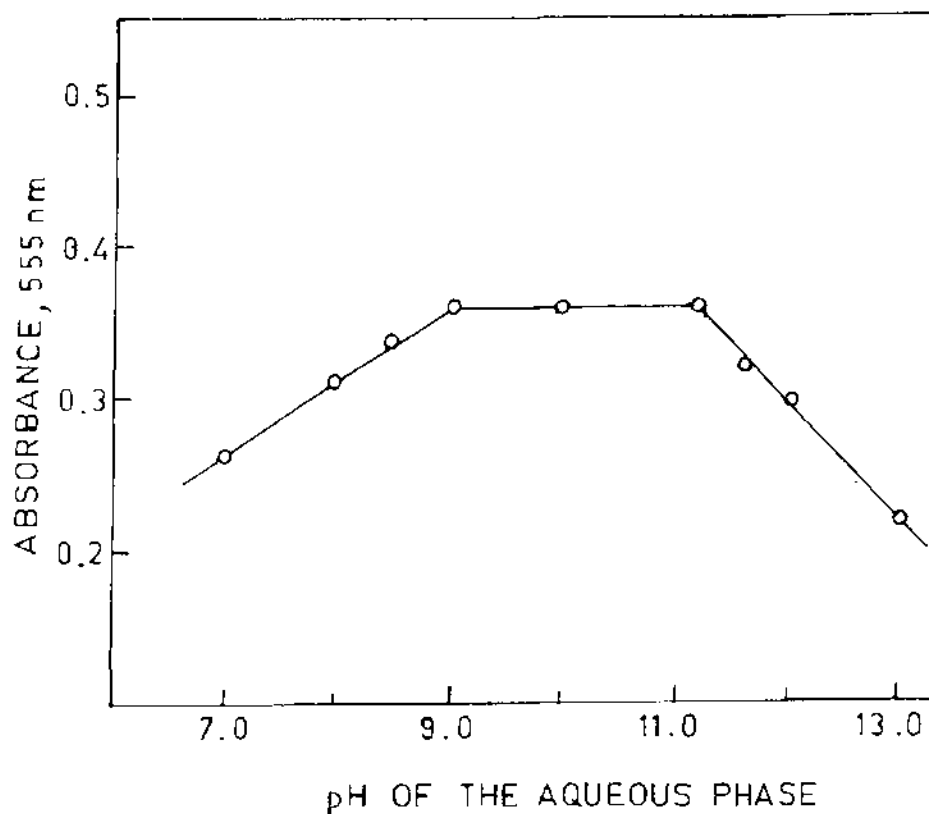


FIG. 5.7 EFFECT OF pH OF THE AQUEOUS PHASE ON THE COLOUR DEVELOPMENT OF Mn(II)-PAN COMPLEX IN WATER + METHANOL MIXTURE

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M}; C_{\text{PAN}} = 0.8 \times 10^{-4} \text{ M.}$$

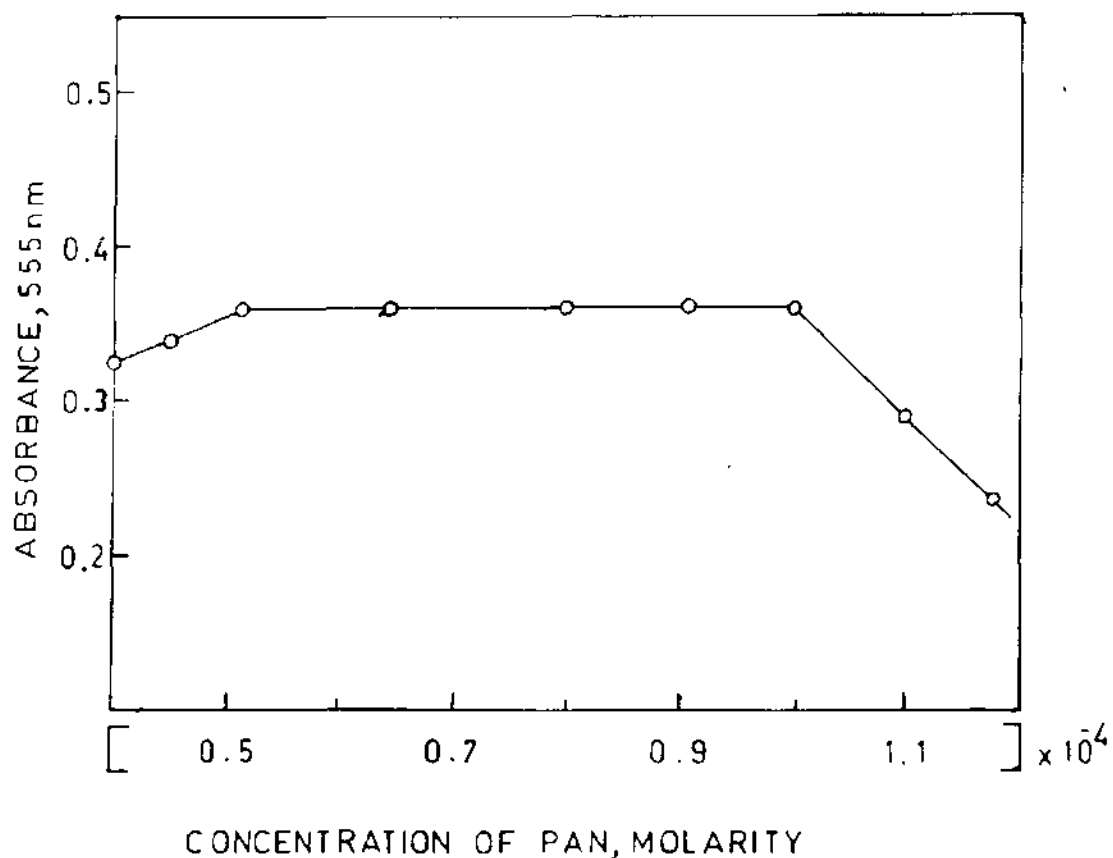


FIG. 5.8 EFFECT OF PAN CONCENTRATION ON THE FORMATION AND ABSORBANCE Mn(II)-PAN COMPLEX IN WATER + METHANOL MIXTURE

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M}; \text{pH} = 10.0 \pm 0.2.$$

BEER'S LAW, CORRELATION COEFFICIENT AND MOLAR ABSORPTIVITY

The Mn(II)-PAN system follows Beer's law upto 0.7 ppm (10.5 $\mu\text{g/ppm}$ aqueous medium) with a correlation coefficient⁶³ of 0.99. The optimum concentration range for the determination of manganese(II) is found to be between 0.2 - 0.7 ppm (3.0-10.5 $\mu\text{g/15 ml}$ aqueous solution), which is evaluated from calibration curve data (Table 5.9, Figure 5.9). The molar absorptivity of the red coloured complex is found to be $4.94 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 555 nm. According to Sandell's definition⁴ the sensitivity of the method is $0.001 \mu\text{g/cm}^2$ for 0.001 absorbance unit.

PRECISION OF THE METHOD AND DETECTION LIMIT

From the statistical data, the precision of the method was checked at 6.0 $\mu\text{g/10 ml}$ manganese(II) of aqueous phase. The value of mean absorbance and standard deviation were calculated to be 0.36 and ± 0.0052 , respectively for ten independent determinations. The relative standard deviation of the method was found to be $\pm 1.4\%$. At 95% probability, the confidence limit⁶³ of the system in terms of mean absorbance and molar absorptivity were found to be (0.36 ± 0.004) and $(4.94 \pm 0.05) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively (Table 5.10). The detection limit of the method is 0.02 $\mu\text{g/ml}$ in aqueous solution.

EFFECT OF DIVERSE IONS

The influence of foreign ions on the determination of manganese(II) was examined. A known amount of diverse ions

TABLE 5.9 CALIBRATION CURVE DATA AND CORRELATION COEFFICIENT FOR THE DETERMINATION OF MANGANESE(II) AS Mn(II)-PAN COMPLEX IN WATER + METHANOL MIXTURE

$$C_{\text{PAN}} = 0.8 \times 10^{-4} \text{ M}$$

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

| No. of obser- vation | Concentration of Mn(II) in aqueous methanol $X_i = \mu\text{g}/15 \text{ ml}$ | Absorbance at 555 nm Y_i | Correlation coefficient r |
|-------------------------|--|----------------------------------|-----------------------------------|
| | 1.0 | 0.06 | |
| | 3.0 | 0.18 | |
| | 5.0 | 0.30 | |
| 7 | 7.0 | 0.43 | 0.99 |
| | 9.0 | 0.54 | |
| | 10.0 | 0.60 | |
| | 10.5 | 0.63 | |

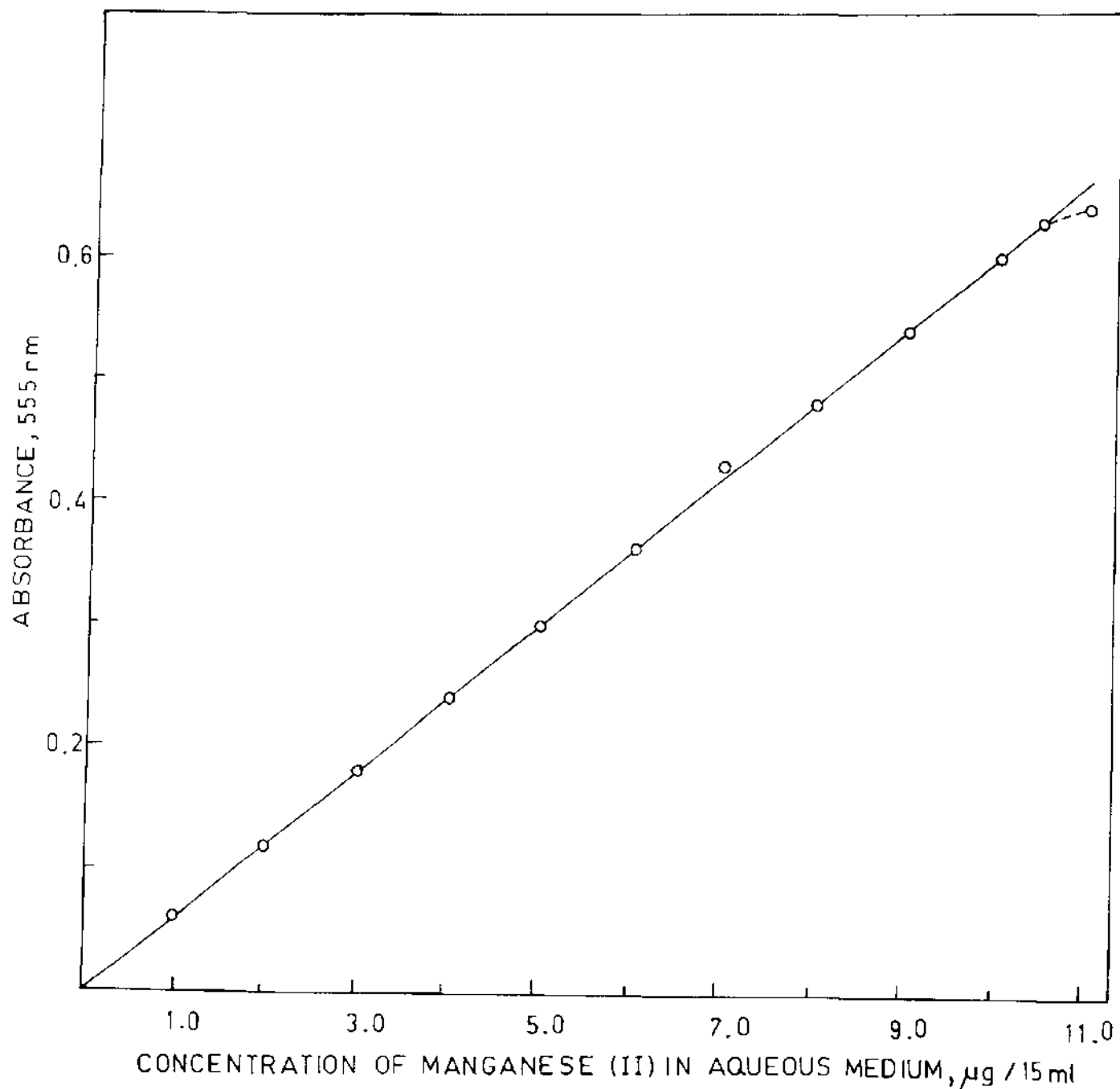


FIG.5.9 CALIBRATION CURVE FOR THE DETERMINATION OF MANGANESE(II) AS Mn(II) -PAN COMPLEX IN WATER + METHANOL MIXTURE

TABLE 5.10 DETERMINATION OF PRECISION OF THE METHOD

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M (6.0 } \mu\text{g/10 ml aqueous phase)}$$

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

$$C_{\text{PAN}} = 0.8 \times 10^{-4} \text{ M}$$

| No. of obser- vation | Absorbance at 555 nm | Mean absorbance | Standard deviation | Relative standard deviation | Value of 't' at 95% confi dence level | Confidence limit | $\left[r = \left(\bar{x} + \frac{t_s}{\sqrt{N}} \right) \right]$ |
|-------------------------|-------------------------|--------------------|-----------------------|-----------------------------------|---|-------------------------------------|--|
| N | | \bar{x} | $\pm s$ | $\pm, \%$ | | In terms of mean absor- bance | In terms of mol- ar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1}$ $\times 10^4$ |
| | 0.36 | | | | | | |
| | 0.37 | | | | | | |
| | 0.36 | | | | | | |
| | 0.36 | | | | | | |
| 10 | 0.37 | 0.36 | 0.0052 | 1.4 | 2.262 | (0.36 \pm 0.004) | (4.94 \pm 0.05) |
| | 0.36 | | | | | | |
| | 0.37 | | | | | | |
| | 0.36 | | | | | | |
| | 0.37 | | | | | | |
| | 0.36 | | | | | | |

were added in a fixed concentration of manganese(II) ion i.e. 6.0 μg Mn(II). Manganese(II) was determined in presence of diverse ions as described in above procedure. None of the common metal ions, except Zn(II) and Pb(II), interfere. Interference from Zn(II) and Pb(II) were masked by the addition of EDTA solution prior to the extraction. The tolerance limits of various ions are shown in Table 5.11.

TABLE 5.11 EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 6.0 μg MANGANESE(II)

| Ion | Added as | Tolerance limit [#] mg |
|---------|---|------------------------------------|
| Zn(II) | ZnSO ₄ · 7H ₂ O | 0.01* |
| Pb(II) | Pb(NO ₃) ₂ | 0.01* |
| Cu(II) | CuSO ₄ · 5H ₂ O | 0.05 |
| Ni(II) | NiSO ₄ · 6H ₂ O | 0.05 |
| Cd(II) | 3CdSO ₄ · 8H ₂ O | 0.05 |
| Fe(III) | FeCl ₃ · 6H ₂ O | 0.08 |
| As(V) | Na ₃ AsO ₄ · 12H ₂ O | 0.5 |
| V(V) | NH ₄ VO ₃ | 0.5 |
| Bi(III) | Bi ₂ (SO ₄) ₃ | 0.8 |
| Sb(III) | (SbO)KC ₄ H ₄ O ₆ · ½H ₂ O | 1.0 |
| Cr(III) | Cr ₂ (SO ₄) ₃ · Al ₂ (SO ₄) ₃ · 2H ₂ O | 1.0 |
| Ba(II) | BaCl ₂ | 1.5 |
| Al(III) | Al(NO ₃) ₃ · 6H ₂ O | 1.5 |
| Co(II) | CoSO ₄ · 6H ₂ O | 2.0 |
| Ca(II) | CaCl ₂ · H ₂ O | 2.0 |
| Iodide | NaI | 2.0 |
| Mo(VI) | (NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O | 2.5 |
| Mg(II) | MgSO ₄ · 7H ₂ O | 3.0 |

Contd..

TABLE 5.11 (Contd.)

| Ion | Added as | Tolerance limit [#] mg |
|-------------|---|------------------------------------|
| Se(IV) | Na_2SeO_3 | 3.0 |
| Phosphate | $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ | 3.0 |
| Bicarbonate | Na_2HCO_3 | 4.0 |
| Carbonate | Na_2CO_3 | 4.0 |
| Persulphate | $\text{Na}_2\text{S}_2\text{O}_8$ | 5.0 |
| Sulphate | K_2SO_4 | 5.0 |
| Nitrate | KNO_3 | 5.0 |
| Thiourea | - | 7.0 |
| Oxalate | $\text{Na}_2\text{C}_2\text{O}_4$ | 7.0 |
| Citrate | $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ | 10 |
| EDTA | $\text{Na}_2\text{-EDTA}$ | 12 |
| Tartrate | $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ | 12 |

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

* Masked by 1 ml of 1% (w/v) EDTA solution.

COMPOSITION AND REACTION MECHANISM

In order to trace out the composition of metal complex, curve-fitting method was applied. The results show that the ratio of metal to ligand (HDPBA/PAN) is found to be 1:2 in the metal complex.

PROCEDURE

[A] DETERMINATION OF THE RATIO OF HDPBA

The metal ion solution containing 12.0 μg of Mn(II) was extracted with HDPBA by previously described procedure. The above experiment was repeated with a various known concentration of HDPBA solution, in order to obtain a series of data (Table 5.12, figure 5.10). The distribution ratio of the metal was evaluated as discussed in Chapter II.

The graph was plotted between logarithmic value of distribution ratio (D) versus log molar concentration of the reagent. The slope of the curve was found to be 2.1, close to integer 2. The slope reveals that two molecule of HDPBA is necessary for each metal in the formation of Mn(II)-HDPBA complex.

[B] DETERMINATION OF THE RATIO OF PAN

The manganese(II) is stripped from Mn(II)-HDPBA complex containing 6.0 μg of Mn(II), to the aqueous solution, in acidic medium. A known concentration of PAN solution is added at pH 10.0 \pm 0.2 and the absorbance of the metal complex is

TABLE 5.12 CURVE-FITTING METHOD FOR THE DETERMINATION OF RATIO OF MANGANESE(II) AND HDPBA IN Mn(II)-HDPBA COMPLEX, FORMED IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M (12.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 9.0 \pm 0.2$$

| Concentration of HDPBA in organic phase, M $\times 10^{-3}$ | Log M | $D = \frac{A_{\text{eq}}}{A_{\text{max}} - A_{\text{eq}}}$ | Log D |
|--|-------|--|-------|
| 5.0 | -2.30 | 11.00 | 1.04 |
| 4.0 | -2.40 | 6.30 | 0.80 |
| 3.0 | -2.52 | 3.40 | 0.53 |
| 2.5 | -2.60 | 2.48 | 0.40 |

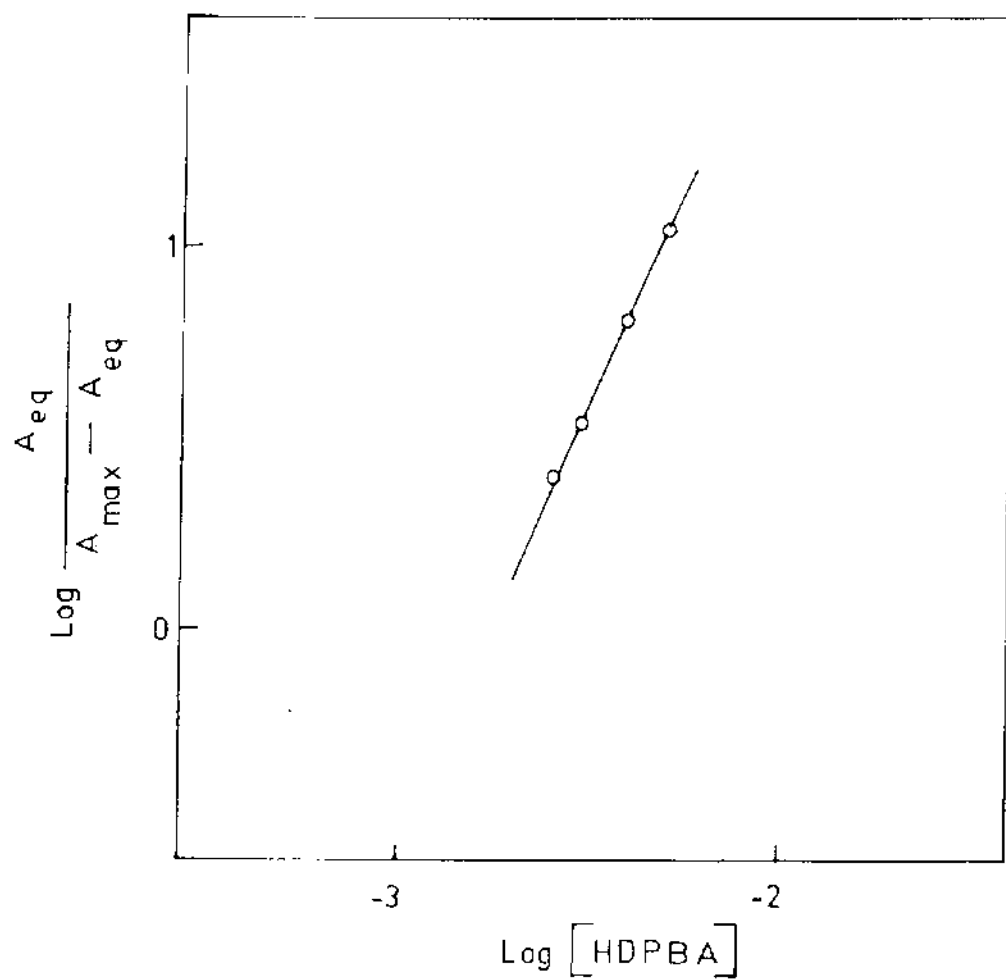


FIG. 5.10 CURVE-FITTING METHOD FOR THE DETERMINATION OF MANGANESE(II) TO HDPBA RATIO IN Mn(II)-HDPBA COMPLEX, FORMED IN CHLOROFORM

$$C_{\text{Mn(II)}} = 2.18 \times 10^{-5} \text{ M};$$

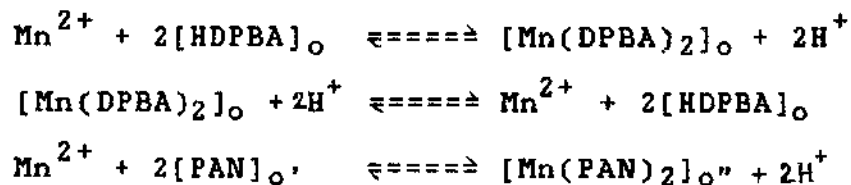
$$\text{pH} = 9.0 \pm 0.2;$$

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

measured against reagent blank at 555 nm. This procedure was repeated to obtain a series of data (Table 5.13, Figure 5.11). The distribution ratio was calculated as in the chapter II.

The graph was plotted between logarithmic value of distribution ratio versus log molar concentration of the reagent. The slope of the curve was found to be 2.0. The results indicate that two molecule of PAN was needed for each metal for the formation of Mn(II)-PAN complex. The similar type of complex formation are suggested by Betteridge et al.⁶⁴ and Goto et al.²²

The overall reaction mechanism can be written as,



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

TABLE 5.13 CURVE-FITTING METHOD FOR THE DETERMINATION OF RATIO OF MANGANESE(II) TO PAN IN Mn(II)-PAN COMPLEX, FORMED IN WATER + METHANOL MIXTURE

$$C_{\text{Mn(II)}} = 1.09 \times 10^{-5} \text{ M (6.0 } \mu\text{g/10 ml aqueous phase)}$$

$$\text{pH} = 9.0 \pm 0.2$$

| Concentration of PAN in aqueous methanol, M $\times 10^{-5}$ | Log M | D = $\frac{A_{\text{eq}}}{A_{\text{max}} - A_{\text{eq}}}$ | Log D |
|---|-------|--|-------|
| 4.5 | -4.35 | 13.40 | 1.13 |
| 4.0 | -4.40 | 9.28 | 0.97 |
| 3.0 | -4.52 | 5.54 | 0.74 |
| 2.0 | -4.70 | 2.60 | 0.40 |

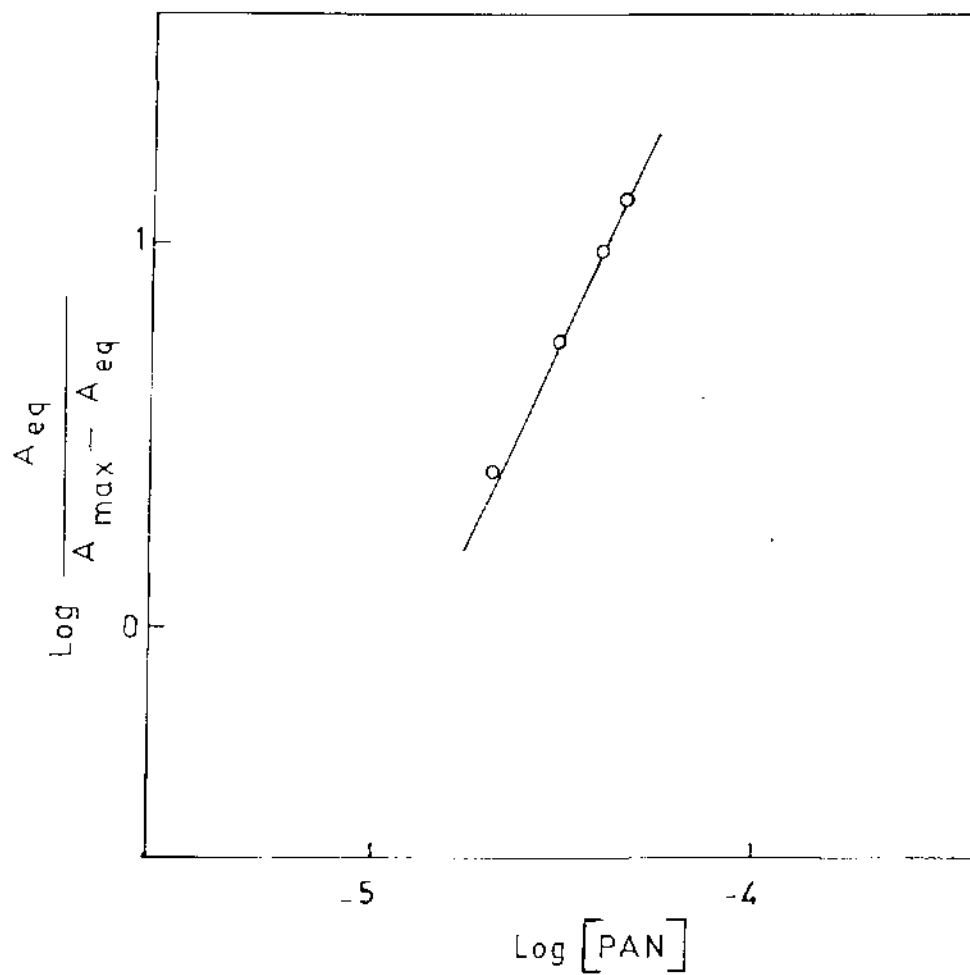


FIG. 5.11 CURVE-FITTING METHOD FOR THE DETERMINATION OF MANGANESE(II) TO PAN RATIO IN $Mn(II)$ -PAN COMPLEX, FORMED IN WATER + METHANOL MIXTURE

$$C_{Mn(II)} = 1.09 \times 10^{-5} \text{ M};$$

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

$$\lambda_{\text{max}} = 555 \text{ nm.}$$

APPLICATION OF THE METHOD

The method has been applied successfully for the determination of manganese(II) in environmental samples viz. industrial waste water, sea water, coal ash, coal dust and cement dust. The results are shown in Table 5.14. The preparation and digestion procedure of the samples are summarized below.

- [1] Water samples - A known volume of water samples (400 ml) was taken in a beaker and reduced by evaporation and adjusted to a volume of 10ml and the amount of manganese was determined as in the procedure described earlier.
- [2] Coal ash - A weighed amount of coal ash in a platinum dish was treated with 1 ml of perchloric acid and 10 ml of hydrochloric acid.⁶⁵ The mixture was then heated on a hot plate and evaporated almost to dryness. The residue were 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 early described procedure.
- [3] Coal dust and Cement dust - A weighed amount of samples was digested by acid treatment (aqua regia, HCl and H₂SO₄). The dried samples were dissolved in 0.5 M hydrochloric acid, and made upto the mark with distilled water in a 100-ml volumetric flask. An aliquot of the sample solution was taken and the metal content was determined as in the above described procedure.

TABLE 5.14 DETERMINATION OF MANGANESE(II) IN ENVIRONMENTAL SAMPLES

| Sample | Mn(II) found in ppm | | Relative standard deviation* ±, % |
|------------------------------|---------------------|------------|--------------------------------------|
| | Present method | AAS method | |
| Kesari metal ^a | 0.10 | 0.11 | 1.4 |
| Singhania steel ^b | 0.70 | 0.72 | 1.2 |
| M.P. metal ^c | 0.06 | 0.05 | 1.2 |
| Swastic wires ^d | 0.28 | 0.27 | 1.3 |
| Sea water ^e | 0.26 | 0.27 | 1.3 |
| Coal ash ^f | 521 | 523 | 1.3 |
| Coal dust ^g | 445 | 446 | 1.3 |
| Cement dust ^h | 394 | 396 | 1.4 |

a, b and c - Obtained from Urla Industrial Estate, Raipur(M.P.).

d - Obtained from Bhanpuri, Raipur(M.P.).

e - Obtained from Vishakhapatnum (A.P.).

f, g and h - Obtained from Mandhar Cement Factory, Raipur(M.P.).

* - Average of six determinations.

COMPARISON WITH OTHER METHODS

Many methods have been reported for the spectrophotometric determination of manganese. The analytical characteristics of some methods have been compared with the present method in Table 5.15. The comparison reveals that the present method is superior to other reported methods in terms of sensitivity, selectivity and reproducibility.

TABLE 5.15 COMPARATIVE STUDY OF SOME SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF MANGANESE

| Reagents | pH/Acidity | Solvent | λ_{max} nm | Molar absorp- tivity $\text{l mol}^{-1} \text{cm}^{-1}$ | Remarks | Refer- ence |
|---|------------|-------------------------------------|------------------------------|---|--|----------------|
| Potassium permanga- nate + Tetra-butylamm- onium chloride | 3.0-8.0 | Dichloro ethane | 545 525 | 2500 2600 | Poor sensitivity. | 10 |
| 1-(2-Pyridylazo)-2- naphthol + o/w-type microemulsifier | 9.5 | Water + n-butanol + n-heptane | 500 | 37900 | Heating require at 5-28°C, time consuming. | 30 |
| Thiothenoylfluoroac- etone + 1,10-Phenan- throline | 7.3±0.3 | Xylene | 375 | 35800 | Cu, Zn, Cd, and Co interfere. | 47 |
| 4-(2-Thiazolylazo) resorcinol | 8.8 | t-Butyl alcohol | 540 | 41760 | EDTA, Zn, Cd and Pb interfere and masked by cyanide. | 33 |
| 2-Hydroxy-1-naphthal- doxime | 10.0 | Chloroform | 390 | 12000 | pH is critical, sensi- tivity is low. | 53 |
| Xanthates | 6.5-9.0 | Chloroform | 457 | 5300 | Many transition metals including Fe and V interfere, interference of Al and Cu are masked by masking agents. | 49 |
| Salicylaldehyde Guanylhydrazone | 8.2 | - | 400 | 5214 | Cr, Fe, Ni, EDTA etc. interfere, poor sensi- tivity, pH is critical. | 50 |
| 1,10-Phenanthroline + Tetraiodofluorescein | 9.5 | Ethyl acetate | 544 | 105000 | Time consuming, pH is critical | 16 |
| Benzohydroxamic acid + Pyridine, and -picoline, collidine and piperidine | - | Amyl alcohol | 500 | 6062 | Sensitivity is low. | 46 |

Contd..

TABLE 5.15 (Contd.)

| Reagents | pH/Acidity | Solvent | λ_{max} nm | Molar absorp- tivity $l \text{ mol}^{-1} \text{ cm}^{-1}$ | Remarks | Refer- ence |
|--|--|---------------------|------------------------------|---|---|-------------------|
| 4,5-Dibromophenylfl- uorone + Cetyltrimethyl ammonium bromide | 9.0 | - | 590 | 137000 | Many metal ions inter- fere and removed by using buffer solution. | 18 |
| Permanganate | 2.0-3.5 M H_2SO_4 | Water | 522 | 1900 | Bi, Sn, Cr and Ce inter- fere. | 5 |
| 3-Phenyl-2-mercapto- propionic acid | 6.3-9.4 | 1-Pentanol | 625 | 7300 | Co, V, Al, Cr, Cd, Zn and Pb interfere. | 57 |
| 1,10-Phenanthroline + Thenoyltrifluoroacetone | 0.25-0.75 M H_2SO_4 | Xylene | 440 450 | 2500 3000 | Ce, Fe and chloride seriously interfere. | 58 |
| N-Hydroxy-N, N'-diphe- nylbenzamidine + 1-(2- Pyridylazo)-2-naphthol | 8.0-9.5 | Water + Methanol | 555 | 49400 | Zn and Pb interfere but can be masked by EDTA solution. | Present method |

CONCLUSION

A simple and sensitive extraction-spectrophotometric method for the determination of manganese(II) at trace levels has been described. In the present method, N-hydroxy-N,N'-diphenylbenzamidine(HDPBA) is introduced as an extracting reagent alongwith 1-(2-pyridylazo)-2-naphthol (PAN) to improve the selectivity as well as sensitivity of the method. The present method overcomes all the drawbacks of classical PAN methods and other reported methods. The method has been successfully applied for the determination of manganese(II) in environmental samples.

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