ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES

STUDIES ON N^1-HYDROXY-N^1,N^2-DIPHENYLBENZAMIDINE COMPLEXES BY SOLVENT EXTRACTION AND SPECTROPHOTOMETRY

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Dejene Ayele

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ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

STUDIES ON MANGANESE-N^1-HYDROXY-N^1,N^2-DIPHENYLBENZAMIDINE COMPLEXES BY SOLVENT EXTRACTION AND SPECTROPHOTOMETRY

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To my parents

and

Ato Tesgaye Mengistu, W/o Romanwork

Eshetu and their children

C O N T E N T S

A C K N O W L E D G E M E N T

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LIST OF TABLES

PAGE

LIST OF FIGURES

PAGE

A B S T R A C T

Studies on Manganese-N^1-Hydroxy-N^1,N^2-diphenylbenzamidine Complexes by Solvent Extraction and Spectrophotometry.

Advisor: Dr. B.S. Chandravanshi

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine was found to react with Mn(II) and Mn(VII) forming ethanol soluble deep-green complexes in the pH range 7.5 - 8.5 and 3.5 - 9.5 respectively. The complex formed in the MnO_4^-- HDPBA system has been found to be quantitatively extractable into amyl alcohol over a wide pH range. The spectra of the complexes formed in the Mn(II)-HDPBA and MnO_4^--HDPBA systems exhibited absorption maxima in the visible region at 625 nm and 614 nm with molar absorptivities of 4600 and 5350 l mol^{-1} cm^{-1} respectively. Composition of the complexes formed in the two systems have been found to be 1:3 and 1:4 (Mn:HDPBA), respectively. The effects of experimental variables have been studied and the photometric characteristic have been evaluated for all the three systems.

On the basis of these studies a simple, precise, fairly sensitive, and highly selective method has been developed for the determination of Mn(VII) by solvent extraction and spectrophotometry. The method has been applied successfully for the determination of manganese in steels, bronze, ferromanganese, manganin, and tea powder samples.

I N T R O D U C T I O N

1.1. Occurence and Applications of Manganese (1 - 4)

Manganese does not occur in nature in the free state, but it is widely distributed in the combined state. It is the twelveth most abundant element and constitutes about 0.085 % the earths crust. The most common manganese minerals are oxides, silicates and carbonates. Manganese is present in most igneous rock to the extent of about 0.1 %. The average river water is estimated to contain about 1 ppm of manganese as a result of the weathering of rocks, and manganese content of ocean water varies from 0.7 to 10 ppb. Manganese has been found in meteorites, ranging from traces upto about 6 %, and its presence in the sun and other stars has been established by spectroscopic observation. It has also been found in every kind of plant and animal tissue, in concentrations ranging from a few parts per billion to more than one part per hundred; in general it is more abundant in vegetable than in animal tissue.

The human body manganese content is estimated to be 12 - 20 mg and the normal requirement of the human diet has been estimated to be about 4 mg per day. The consumption of tea and coffee provides a large source of the metal. Seeds, nuts and cereals also have high manganese contents, but milk products and sea foods contain low.

Normal level of manganese in plants range from 20 to 500 ppm.

A deficiency of the element in all organisms studied, ranging from bacteria through plants to mammals inhibits growth, diminishes life expectancy and causes skeletal abnormalities. Some typical examples of manganese deficiency in animals are the skeletal disorder perosis or "slipped tendon disease" in chickens and the development of a genetic mutant in mice known as the "pallid mouse" in the of spring of manganese deficient animals. In man it has been suggested that "aprosoline disease" may well be a manganese deficiency. The liver appears to be a key tissue in manganese metabolism, where it acts as the co-factor for many liver enzymes such as hepatic mitochondrial superoxide dismutase and pyruvate mitochondrial superoxide dismutase and pyruvate carboxylase. An increase in serum manganese was found during liver metastases and hepatobiliary disease such as acute hepatitis, chronic hepatitis, post hepatitis cirrhosis, cirrhosis, and extra-hepatic biliary obstruction. A correlation between serum albumin and serum manganese concentrations in acute, chronic and post necrotic cirrhosis and between serum aminotransferase activities and serum manganese concentration was also found, and postulated that increased serum manganese levels could be used as an index of liver cell damage. Manganese deficiency in

higher plants causes mottled chlorosis (lack of chlorophyll) in which the leaves become pale or yellow while the veins remain green.

Although less common than with other elements, toxological effects caused by excessive exposure to manganese are known. Chronic manganese poisoning has chiefly been found in miners or in ore-crushing mills. The manganese enters the body via the lungs by inhalation of the dust, and chronic manganese poisoning usually results after one to three year's exposure to large amounts of dust. Manganese salts taken in to the body either by injection or orally are not so dangerous since most is excreted.

Manganese has got several industrial applications, and some of the manganese minerals of greatest industrial importance are pyrolusite (MnO_2), manganite ($Mn_2O_3.H_2O$), braunite ($3Mn_2O_3.MnSiO_3$); hausmannite (Mn_3O_4), rhodochrosite ($MnCO_3$), rhodonite ($MnSiO_3$) and bementite ($2MnSiO_3.H_2O$.

The use of manganese in glass making is probably almost as old as that art itself. Addition of small amounts of pyrolusite to the molton glass "washes out" the green or yellow tint due to iron compounds in the silica; greater amounts of the mineral produce colors in glass and in ceramic glazes ranging from pink through violet to black. Ferromanganese is used as an additive

to control the sulfur content of steel. Today the major industrial use of manganese is as an alloying and cleansing agent for steels, iron and non-ferrous metals.

Uses of manganese that are minor from the standpoint of quantity consumption, but important nevertheless, include its role in the manufacture of optical glass and light filters to achieve desired transmission and absorption characteristics and in carbon-arc electrodes to improve emission energy in certain spectral regions; its role as a catalyst in photosynthesis and photo-chemical polymerization; and its effectiveness in enhancing the lethal effect of ultraviolet irradiation to retard the growth of molds, yeasts and bacteria.

1.2. The Chemistry of Manganese (1,2,5,6)

From the analytical standpoint the important oxidation states of manganese are +2, +4 and +7. The other valence states, +1, +3, +5 and +6 are possible but in general they are more or less unstable. The chemistry of manganese in its common oxidation states is briefly reviewed below.

1.2.1. Manganese(II).

Manganese(II) is the most important, and under normal conditions, the most stable oxidation state. Manganous salts are mostly water soluble. In acid or neutral aqueous solution the manganese(II) ion exists as

the pale pink hexaaquo ion, $Mn(H_2O)_6^{2+}$, which is quite stable to oxidation. However, in basic solution the hydroxide, $Mn(OH)_2$, is precipitated, and this rapidly darkens in air due to oxidation, as shown by the base potentials :

$$MnO_2 \xrightarrow{-0.1V} Mn_2O_3 \xrightarrow{-0.2V} Mn(OH)_2.$$

The Sulfate, $MnSO_4$, is very stable and may be used for manganese analysis as it can be obtained on fuming down sulfuric acid solutions to dryness. The complexes of manganese(II) are thermodynamically less stable in comparison with analogous complex species of the other bivalent transition metals (ie. Fe, Co, Ni) which follow manganese in the periodic table. However, chelating ligands such as ethylenediamine, oxalate, or EDTA form complexes isolable from aqueous solutions.

Manganese(II) is oxidised to Mn(VII) using oxidizing agents such as potassium periodate, sodium bismuthate, lead dioxide or peroxodisulfate according to the following reactions.

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightleftharpoons 2MnO_4^- + 5IO_3^- + 6H^+$$

$$2Mn^{2+} + 5PbO_2 + 4H^+ \rightleftharpoons 2MnO_4^- + 5Pb^{2+} + 2H_2O$$

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightleftharpoons 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

$$2M^{2+} + 5NaBiO_3 + 14H^+ \longrightarrow 2MnO_4^- + 5Bi^{3+} + 5Na^+ + 7H_2O$$

The periodate reaction is quite rapid in a nitric-phosphoric acid solution at 100°c. The peroxodisulphate oxidation is effected in the presence of a catalyst, Ag^+ ion. In the absence of Ag^+, or if an excess of Mn^{2+} ions is present, brown $Mn(OH)_2$ is precipitated.

$$2MnO_4^- + 3Mn^{2+} + 7H_2O \longrightarrow 5MnO(OH)_2 + 4H^+$$

In contrast to the other reactions mentioned the bismuthate reaction proceeds in the cold, and excess of Mn^{2+} salts do not interfere.

Stepwise oxidation of Mn(II) by peroxodisulphate in phosphoric acid medium (7-9). The oxidation of Mn(II) by $S_2O_8^{2-}$ to Mn(VII) in phosphoric acid medium proceeds via a stable Mn(III) and Mn(IV) species. The reaction is on catalyzed by Ag^+ and exhibits first order dependence on $[S_2O_8^{2-}]$, $[Ag^+]$ and is independent of $[Mn(II)]$. The $[H^+]$ has no significant effect on the reaction. It is observed that the PO_4^{3-} ion stabilises the transient Mn(III) and Mn(IV) species by forming a stable and soluble phosphato complexes.

For the formation of Mn(IV) from Mn(II) the Stoichiometry is found to correspond one mole of peroxodisulphate (PDS) per mole of Mn(II) oxidised. This result

confirms a two electron transfer process, corresponding to the formation of Mn(IV). When the kinetic measurements were made with varying amounts of Mn(II) at fixed $[PDS]$ and $[Ag^+]$, the ascending portions of the absorbance-versus-time plots were linear and parallel to each other, further confirming the independence of the reaction rate of $[Mn(II)]$.

It is also interesting to note that there is a small but definite time lag before the Mn(IV) formed in the first stage of the reaction is further oxidised to Mn(VII). This is presumably because the Ag^{3+} formed in the rate-determining step attacks only the lower oxidation states, Mn(II) and Mn(III), in preference to Mn(IV) as long as they are present and further oxidation of manganese(IV) to Mn(VII) is possible only after these are completely converted into Mn(IV).

Both the formation of Mn(IV) and its further oxidation to Mn(VII) follows a zero order kinetic law with respect to Mn(II), while the orders with respect to $[PDS]$ and $[Ag^+]$ were each found to be unity.

Kinetic experiments carried out to establish the role played by PO_4^{3-} ion in this reaction at constant $[H^+]$ have shown that it has an accelerating effect on the first stage of oxidation, Mn(II) $\longrightarrow$ Mn(IV), while it has an inhibitory effect on the second stage of the oxidation, Mn(IV) $\longrightarrow$ Mn(VII).

Since the PO_4^{3-} ion complexes the Mn(IV) species, oxidation potential of Mn(IV)/Mn(II) couple is lowered while that of Mn(VII)/Mn(IV) couple is raised. This causes the observed difference between the rates of the two stages of oxidation in presence of PO_4^{3-} . To account for the above observations, the following scheme has been proposed.

Scheme.

$$S_2O_8^{2-} \underset{}{\overset{K}{\rightleftharpoons}} 2SO_4^{\cdot-} \qquad (1)$$

$$Ag^+ + 2SO_4^{\cdot-} \xrightarrow[K]{slow} Ag^{3+} + SO^{2-} \qquad (2)$$

$$Mn^{2+} + Ag^{3+} \xrightarrow{fast} \text{products}$$

The rate of the reaction is given by the expression $-d[S_2O_8^{2-}]/dt = k[Ag^+][SO_4^{\cdot-}]^2$. From the equilibrium (1), the equilibrium constant $K = [SO_4^{\cdot-}]^2 / [S_2O_8^{2-}]$. The rate expression then reduces to the following equation : $-d[S_2O_8^{2-}]/dt = kK[S_2O_8^{2-}][Ag^+] = K_{obs}[S_2O_8^{2-}][Ag^+]$ where $K_{obs} = kK$.

The activation parameters from the Arrhenius plots were calculated to be as shown :

$E_{act} = 52 \pm 4$ KJ mole^{-1},

$S^* = -57 \pm 2$JK^{-1} mole^{-1} for Mn(II)--→Mn(IV)

and $E_{act} = 56 \pm 5$KJ mole^{-1},

$S^* = -44 \pm 2$JK^{-1} mole^{-1} for Mn(IV)----→ Mn(VII)

1.2.2. Manganese(III).

The chemistry of manganese(III) is not extensive. The manganic ion can be obtained by electrolytic or persulfate oxidation of Mn(II) solutions or by reduction of MnO_4^-. It can not be obtained in high concentrations as it is reduced by water. It also has a strong tendency to hydrolyze and to disproportionate in weakly acidic solutions:

$$2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2(s) + 4H^+, \quad K \approx 10^9.$$

Manganese(III) is stable in the solid state (e.g. manganese(III) phosphate). In solution stabilisation may be achieved by coordination; the dark brown crystalline acetylacetone, $Mn(ac\ ac)_3$, is readily obtained by oxidation of basic solutions of manganese(II) by O_2 or Cl_2 in the presence of acetylacetone (5).

1.2.3. Manganese(IV) and (V).

The only really important compound of Mn(IV) is manganese dioxide, a grey to black solid found in nature as pyrolusite. It is inert to most acids except when heated, but it does not dissolve to give Mn(IV) in solution; instead, it functions as an oxidising agent, the exact manner of this depending on the acid. With HCl, chlorine is evolved:

$$MnO_2(s) + 4H^+ + 4Cl^- \longrightarrow MnCl_4 + 2H_2O$$

$$MnCl_4 \longrightarrow MnCl_2 + Cl_2$$

with fuming sulfuric acid, oxygen is evolved:

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnO_4 + 2H_2O + O_2 .$$

Manganese(V) is little known except in bright blue " hypomanganates" that are formed by reduction of permanganate with an excess of sulfite. A permanganite $KMnO_3$, is known only as a solid product of the alkali fusion of MnO_2.

1.2.4. Manganese(VI) and (VII).

Manganese(VI) is known only as the deep green manganate ion, MnO_4^{2-}. This is formed on oxidizing MnO_2 in fused KOH with KNO_3, or air. The manganate ion is stable only in very basic solutions. In acid, neutral or slightly basic solutions it readily disproportionates according to the equation:

$$3MnO_4^{2-} + 4H^+ \rightleftharpoons 2MnO_4^- + MnO_2(s) + 2H_2O, \quad K \approx 10^{58}.$$

Manganese(VII) is best known in the form of salts of the permanganate ion. Aqueous solutions of MnO_4^- may be prepared by oxidation of solutions of Mn(II) ion as described in section 1.1.1. The permanganate ion has an intense purple color, and crystalline salts appear almost black.

Solutions of permanganate are intrinsically unstable, decomposing slowly but observably in acid solution:

$$4MnO_4^- + 4H^+ \rightleftharpoons 3O_2(g) + 2H_2O + 4MnO_2(s).$$

In neutral or slightly alkaline solution in the dark, decomposition is immeasurably slow. It is catalysed by light so that standard permanganate solutions should be stored in dark bottles .

In slightly basic solution, permanganate is a powerful oxidant:

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2(s) + 4OH^-, \quad E^o = +1.23 \text{ V.}$$

In very strong base and with an excess of MnO_4^- , however, manganate ion is produced:

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-}, \qquad E^o = +0.56 \text{ V.}$$

In acid solution permanganate is reduced to Mn(II) by an excess of reducing agent:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O , \quad E^o = +1.51 \text{ V}$$

but because MnO_4^- oxidises Mn^{2+}:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+ ,$$

$$E^o = +0.46 \text{ V.}$$

The product in presence of an excess of permanganate is MnO_2. The addition of small amounts of $KMnO_4$ to concentrated H_2SO_4 gives a clear green solution believed to contain the planar ion MnO_3^+ :

$$KMnO_4 + 3H_2SO_4 \rightleftharpoons K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^-$$

With larger amounts of $KMnO_4$, the dangerous explosive oil, Mn_2O_7 , separates. This can be extracted in to CCl_4 or chlorofluorocarbons in which it is reasonably stable and safe.

1.3. Reagents used for Spectrophotometric Determination of Manganese.

Several organic reagents have been recommended in literature for the extraction and/or spectrophotometric determination of manganese. Of these reagents some of the recently used reagents which may find wide analytical applications are briefly reviewed below.

A number of N^1-hydroxy-N^1,N^2- diarylsubstituted-p-toluamidines have been employed for the spectrophotometric determination of micro quantities of manganese(10). The compounds develop ethanol soluble deep green manganese complex (λmax 620-635 nm with ε 5220-7550 l $mol^{-1}cm^{-1}$) in ammoniacal medium. However, the maximum intensities of the complexes are obtained only after standing for 1 h . Oxalate, EDTA, Cu(II), Ni(II), Co(II), Pd(II), and Fe(III) seriously interfere with the determination.

3-phenyl-2-mercaptopropionic acid has been used for an extraction-spectrophotometric determination of manganese(II) based on the formation of a 1:2 complex (11). The manganese complex is extracted into isoamyl alcohol in the pH range 6.3 - 9.4 and determined by measuring the absorbance of the extract at the wavelength of maximum absorbance, 625 nm (ε = 7.3×10^3 l $mol^{-1}cm^{-1}$). The determination procedure involves stepwise masking of

Pd(II), Cu(II), Ni(II), Fe(II), and Fe(III) with cyanide (after reduction with ascorbic acid), Ti(IV) with fluoride, Al(III), Cr(III), Cd(II), Zn(II), and Pb(II) with citrate or cyanide ions. Likewise, Co(II) and V(V) still cause serious interferences. Besides these, a large excess of the reagent (a minimum of 80-fold) and a relatively longer shaking time (about 10 min) is required for complete extraction of manganese. The color intensity of the complex is constant only for 2 h.

An extraction-spectrophotometric determination of permanganate with ethylene-bis(triphenylphosphonium) cation has been reported (12) . The method is based on the extraction of erhylene-bis(triphenylphosphonium)-permanganate ion pair into chloroform at pH 6. The absorbance of the colored extract is measured at 548 nm (ε = 2380 l $mol^{-1}cm^{-1}$). The ion-pair formed is stable for 1 min only, however, addition of potassium periodate to the aqueous permanganate solution gives colored extract which is stable for 30 min.

Thiothenoyltrifluoroacetone, together with 1,10-phenanthroline has been used for extraction-spectrophotometric determination of Mn(II) (13) . The method is based on extraction of Mn(II) at pH 7.3 from 1,10-phenanthroline solution with thiothenoyltrifluoroacetone into xylene. The extract is washed with borate buffer at pH 11.5

and the absorbance is measured at 375 nm (ϵ = 35,800 l $mol^{-1}cm^{-1}$) . Preliminary extraction at pH 7.3, of interfering metal ions such as Mn(II), Cd(II), Cu(II) or Co(II) with thiothenoyltrifluoroacetone (in the absence of 1, 10-phananthroline) is required.

K-butylxanthate has been used for the extraction-spectrophotometric determination of Mn(II). The method is based on the extraction of Mn(II) at pH 6.5 into chloroform with an excess of K-butylxanthate and measurement of the absorbance at 457 nm (ϵ = 5500 l $mol^{-1}cm^{-1}$)(14). Many transition metal ions including Fe(III) and V(V), interfere, and need prior extraction at pH 5.8 into $CHCl_3$ after addition of K-ethylxanthate in slight excess. Interference by Al(III) is prevented by addition of fluoride, and that of Cu(II) by extraction as the butylxanthate at pH 5.8.

A spectrophotometric method has been developed for the determination of Mn(II) based on the formation of colored mixed-ligand complexes of Mn(II) with 2,2'-bipyridyl and (2-nitrophenylazo)-, (4-nitrophenylazo)- or (2,4-dinitrophenylazo) catechol (15) . The complex is extracted into $CHCl_3$ from an aqueous phase at pH 10. The complex exhibits maximum absorption at 525 nm (ϵ = 58,000)*. Zn(II), Co(II), Ni(II), Cd(II), EDTA, and $P_2O_7^{4-}$ ions interfere in the determination.

* l $mol^{-1}cm^{-1}$

Salicylaldoxime has been used for the simultaneous spectrophotometric determination of manganese(II) and iron(III) in borate buffered medium at pH 9.2 by measuring the absorbance at 410 and 500 nm (the λ_{max} of the respective complexes)(16). Beer's law is obeyed in the concentration range 1 to 7 ug ml^{-1} of either metal ion. The method is not very selective. In the determination of 2.2 ug ml^{-1} each of Mn(II) and Fe(II), the tolerance limit for Cu(II), Co(II), Ni(II), Zn(II), Cr(III), V(IV) or Ti(IV) is only 0.6 ug ml^{-1}.

A spectrophotometric method for the determination of manganese with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol has been reported (17). The method is based on the formation of a 1:2 (M:L) colored complex in aqueous ethanol medium at pH 8.5 and measuring the absorbance at 575 nm (ϵ = 127,000)* vs a reagent blank. The method is not very selective in that Ag(I), Pb(II), Cd(II), Ni(II), Co(II), Cr(III), and V(V) interfere in the determination.

o-Hydroxyhydroquinonephthalein has been used for the spectrophotometric determination of manganese(II) in aqueous ethanol medium at pH 9 (18). The absorbance is measured at 535 nm after keeping the solution for 15 min at 20 to 25°C. The Sandell sensitivity of the method is 0.38 ng cm^{-2} and the coefficient of variation is 1.22 %.

Manganese(II) has been spectrophotometrically determined using 4-(2-thiazoylazo) resorcinol in aqueous

* 1 $mol^{-1}cm^{-1}$

solution at pH 8.8 (19). The absorbance is measured at 549 nm. The system obeys Beer's law upto 1.6 $\mu g\ ml^{-1}$. Fe(III), Co(II), Zn(II), Cd(II), Pb(II), and EDTA interfere seriously in the determination.

Bivalent Mn has been determined with N^1-hydroxy-N^1-m-tolyl-N^2-(2,3-xylyl)benzamidine hydrochloride at pH 9.6 in a 70 % ethanolic medium by measuring the absorbance at 610 nm (ϵ = 4400)* (20). Color development is complete in 1 h and with 25-fold excess of the reagent. Oxalate, Cu(II), Pd(II), Ni(II), Co(II), Fe(III), V(V), and EDTA interfer seriously in the determination.

The formation of a 1:2 (metal to ligand) colored complex at pH 8.7 to 10.0 of Mn(II) with 5'-chloro-2', 4-dihydroxypropiophenoneoxime has been used for the determination of manganese(II) (21). The absorbance is measured at 405 nm and the Sandell sensitivity is 8.8 ng cm^{-2}. Cu(II), Pd(II), Ni(II), Fe(II), and U(VI) ions interfere in the determination of manganese using this method.

1-(2-quinolylazo)-2,4,5,-tryhydroxybenzene has been applied for the spectrophotometric determination of manganese using different water miscible solvents (22) in such a way that the final solution is 50 % ($v/_v$) aqueous. The maximum absorption wavelength varies between 560 - 590 nm and the molar extinction coefficients between 2.0×10^4 l $mol^{-1}cm^{-1}$ -- 6.7×10^4 l $mol^{-1}cm^{-1}$. Full color

* l $Mol^{-1}cm^{-1}$

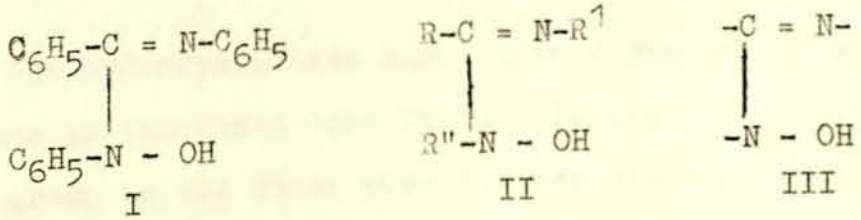
development is attained after 30 min at 25°c, and the absorbance remains constant upto 12 h. Temperature controll (± 2°C) is important in obtaining consistent results. The effect of foreign ions is not described at all.

Manganese(II) has been determined spectrophotometrically by using isophthalohydroxamic acid in aqueous ammoniacal medium (23). The absorbance of the Mn-isophthalohydroxamic acid (1:2) complex is measured at 490 nm (ϵ = 3760 l mol^{-1} cm^{-1}) after 30 min. Fe(III), Sn(II), Sb(III), Bi(III), Ru(III), and Rh(III) ions interfere in the determination.

In the present investigation N^1-hydroxy-N^1,N^2-diphenylbenzamidine, which has become a popular chelating agent in recent years, has been employed for the extraction-spectrophotometric determination of manganese. Hence its general properties and analytical applications are briefly reviewed below.

1.4. N^1-Hydroxy-N^1,N^2-Diarylbenzamidines as Analytical Reagents

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine, I, and its analogues, II, are typical monobasic and bidentate chelating agents having functional grouping, III,

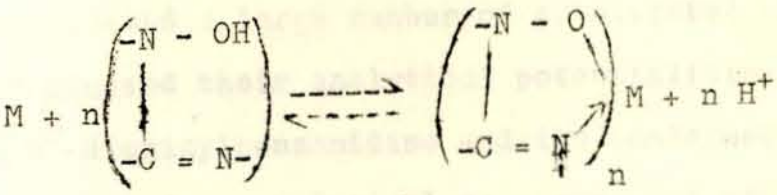


I II III

where R, R', and R" are phenyl or substituted phenyl groups.

N^1-Hydroxy-N^1,N^2-diarylbenzamidines are pale yellow crystalline solids and stable toward heat, light and can be stored indefinetely without deterioration. These compounds are insoluble in water but soluble in common organic solvents such as alcohol, acetone, cholroform, benzene, and toluene. Their solutions in organic solvents are light yellow and stable for several days at room temperature.

Hydroxyamidines react with metal ions to form five membered ring complexes. The metal chelates may be neutral or charged depending upon the coordination number and charge of metal ion. The complexation reaction of hydroxyamidines can be represented by the general complexation equilibrium,



the charge of the metal ion has been omitted for simplicity.

The hydroxyamidines have wider scope as analytical reagents in the sense that by substitution of a particular group in the three phenyl rings attached to the

functional grouping, their complexing properties can be modified. Hence, the sensitivity and selectivity for a particular method of determination can be improved. Some of the metal chelates of hydroxyamidines are water insoluble, thermally stable and directly weighable. Such metal chelates can be used for gravimetric determination of the metal ions. Most of the metal complexes of hydroxyamidines are intensily colored and highly stable. These reaction products can be used for simple spectrophotometric determination in aqueous systems or for the simultaneous extraction and spectrophotometric determination of metal ions.

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine(HDPBA), the parent compound, was introduced as analytical reagent for the first time in 1974 by Satyanarayana and Mishra (24) for the extraction and spectrophotometric determination of vanadium(V). Later on Mishra and coworkers synthesized a large number of substituted hydroxy-amidines and studied their analytical potentialities. N^1-Hydroxy-N^1,N^2-diphinylbenzamidine and its analogues have been widely used as analytical reagents, and studies on the applicability of these reagents have continued until very recently for the detection and determination of several metal ions in gravimetric analysis, solvent extraction and spectrophotometry.

N^1-Hydroxy-N^1,N^2-diarylbenzamidines have been used for the gravimetric determination of nickel (25) and copper (26 - 28), gravimetric (29 , 30) and extraction-spectrophotometric determination of molybdenum (31 , 32), spectrophotometric determination of tungsten (33), spectrophotometric determination in aqueous solution (34) and extraction-spectrophotometric determination of iron (35, 36-40), spectrophotometric determination of manganese(II) in aqueous ethanolic solution (41), extraction-spectrophotometric determination of vanadium(V) (42 - 50), spectrophotometric (51) and extraction-spectrophotometric determination of cobalt (52), and extraction-spectrophotometric determination of niobium(V) (53) and gold(III) (54).

1.5. Aim of the Present Study

In common with most of the positive metal ions, manganese possesses the property of forming complex species with many of the chelating agents, some of which that have been used for the spectrophotometric determination are described in section 1.3. Because chelation is such a common property of metal ions, the analytical use of complex-forming reagents is restricted by many potential interferences. Fortunately, however, there are so many chelating agents available, and so many possible combinations of conditions (pH, masking agent, oxidation state, etc.) that there is a good chance to find the right combination for the separation or determination of a given

metal in the presence of almost any other metals. Thus a reagent with better selectivity and sensitivity could be obtained by examining the various possible reagents for a particular metal ion under different conditions.

The literature survey reveals that there is a wide variation among the reported spectrophotometric methods for the determination of manganese with regard to selectivity, sensitivity, precision, speed and convenience. Hence there is a need to find a suitable reagent and/or proper conditions for the sensitive, selective, rapid, and precise spectrophotometric determination of manganese.

Although some N^1-hydroxy-N^1,N^2-diarylbenzamidines have been used for the spectrophotometric determination of Mn(II) in aqueous medium, the parent compound (HDPBA) has not been used. Besides this the nature of the reaction and the stoicheometry of the complex have not been established. Further more, several ions have been found to interfere seriously in the determination.

Hence the complex formation reactions of different manganese species with HDPBA have been studied spectrophotometrically in detail under different experimental conditions in the present investigation in order (i) to find out the manganese species (Mn(II), Mn(III), Mn(IV), Mn(VI), or Mn(VII) involved in the complex formation, (ii) to determine the stoicheometric compositions of

Mn-HDEBA complex species, and (iii) to improve the selectivity, precision, and speed of the analysis.

2. THEORETICAL BACKGROUND

2.1. Solvent Extraction (55 - 60)

Solvent extraction is partition of one or more components between two liquids of limited miscibility. Such liquid-liquid partition is caused by the different solubilities of a given substance in the two phases. This method of partition of a given substance from one phase to the other is extremely useful for very rapid and clean separation of trace and major components of both organic and inorganic substances. A further advantage of extraction is that the extract usually has some properties, i.e. absorption of light, fluorescence, radio activity, and volatility, on which the determination of the isolated constituent can be based. Some additional features of solvent extraction make the method attractive when applied to a particular separation. These features are:

(i) several successive extractions can be made inorder to diminish the unextracted solute to a negligible amount, even when the distribution constant of the solute is not large;

(ii) The process is applicable in two ways; interfering substances are extracted, leaving the desired constituent in the first solvent; or the desired constituent is extracted, leaving the impurities in the first solvent;

(iii) extraction methods may sometimes be used to avoid coprecipitation and/or postprecipitation phenomena that

would be present in a precipitation separation of the same constituents;

(iv) solutes present in very small concentration may be gathered by extraction into a small volume of a second solvent when the distribution constnat is large.

2.1.1. Solvent Extraction of Metal Chelates

If a metal ion is extracted from an aqueous solution into an organic solvent the metal ion must exist as an uncharged particle which can be either an electroneutral complex (chelate) or an ion-association species that can be transfered across the liquid-liquid boundary.

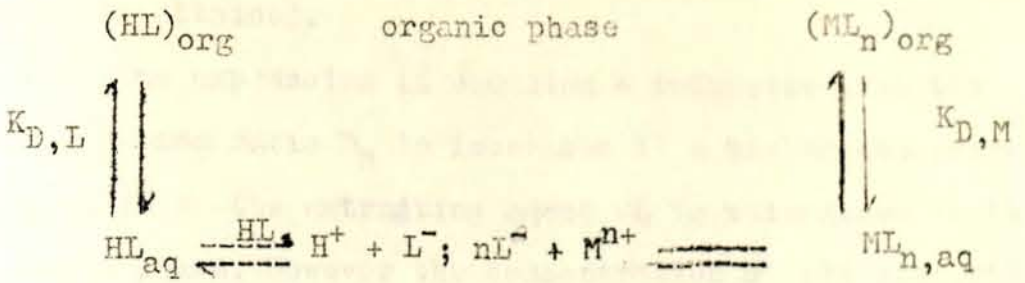
The extraction of a metal ion M with the extraction reagent HL, forming a chelate ML_n soluble in an organic solvent, is expressed by the equilibrium

$$M_{aq} + nHL_{org} \rightleftharpoons ML_{n,org} + nH^+_{aq} \qquad (1)$$

which is characterized by the extraction constant:

$$K_{ex} = \frac{[ML_n]_{org}[H^+]^n_{aq}}{[M]_{aq}[HL]^n_{org}} = D_M\left(\frac{[H^+]_{aq}}{[HL]_{org}}\right)^n \qquad (2)$$

The equilibrium involved in the extraction of metal chelates can be expressed by the following scheme:



Equation 2 can be written as

$$D_M = K_{ex}\left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n = \frac{K_{D,M}\beta_n}{K_{D,L}\beta_{HL}^n}\left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n \qquad (3)$$

Taking the logarithms, equation 3 can be written as

$$\log D_M = \log K_{ex} + n \log [HL]_{org} + npH \qquad (4)$$

If a certain metal ion has to be transfered into the organic phase, the value of the distribution ratio D_M for that metal should be as high as possible.

Equation 3 indicates that the distribution ratio D_M of the metal M should be directly proportional to the stability constant β_n of the complex ML_n and the n^{th} power of the dissociation constant β_{HL}^{-1} of the extracting reagent HL. The value of the distribution constant $K_{D,M}$ of the metal chelate ML_n should be as high as possible, and the value of the distribution constant $K_{D,L}$ of the extracting reagent HL should be low if high value of D_M

is to be attained.

The expression in equation 4 indicates that the distribution ratio D_M is increased if a higher concentrratration of the extracting agent HL is maintained in the organic phase. However the concentration of the extracting agent can not be increased arbitrarily because of the limited solubility and also because of the possibility of disturbing effects on the subsequent determination of the constituent being extracted. Equation 4 also shows that, with increasing pH the value of D_M becomes higher and the increase depends on the oxidation state of the metal ion being extracted. The value of D_M increases with pH up to a certain maximum value which corresponds, for the simple case being considered, to the value of the distribution constant $K_{D,M}$ of the chelate ML_n.

Other factors, such as temperature, ionic strength, and kinetics of the extraction can also influence D_M, in addition to the factors explicitly expressed by the quantities in equation 4.

A change in temperature, eventhough it is not possible to predict how it affects, generally change the value of an equilibrium constant. Ionic strength influences D_M by affecting the relative permitivity and the value of the extraction constant K_{ex}. There is no kinetic effect involved in the value of D_M, provided that the distribution ratio has been determined for an equilibrium state.

In practice, however, kinetic masking can be utilized if the rate of extraction of one species is much faster than that of another.

The completeness of transfer of a metal M in any extractable form into the organic phase is given by the degree of extraction E, which is usually expressed in percent:

$$E_M = \frac{100 C_{M,org} V_{org}}{C_{M,org} V_{org} + C_{M,aq} V_{aq}} = \frac{100 D_M}{D_M + \left(\frac{v_{aq}}{v_{org}}\right)} \qquad (5)$$

which is the fraction of the substance extracted from the aqueous phase (volume V_{aq}) into the organic solvent (volume V_{org}). As shown in equation 5 the degree of extraction depends both on the distribution ratio and the ratio of the volumes of the two phases.

From the analytical point of view the extraction can be considered as quantitative if 99.9 % of the metal ion is transferred into the organic phase. If volumes of the two phases are equal and only one extraction is performed, then for the extraction to be quantitative it is necessary that $D_M \geq 10^3$.

2.2. Spectrophotometry (55 - 59, 61 - 66)

In spectrophotometry, a monochromatic light is directed at a sample and the intensity of the radiation which is transmitted is measured. The radiation absorbed

by the sample is determined by comparing the intensity of the transmited light when no absorbing species is present to the transmited intensity when there is absorbing species. Provided that the optical pathlength l and the absorption coeffecient ϵ of the substance being determined at a given wavelength are known and the absorbance A is measured it is possible to use Beer's law in order to determine the unknown concentration.

$$C = \frac{A}{\epsilon l} \qquad (6)$$

The expression shows that there is a linear relationship between the absorbance A and concentration C of a given solution if the optical path length and the wavelength of the radiation are kept constant.

In order to develop a reliable spectrophotometric method for determination of a desired constituent of a colored system, several factors need to be investigated. The analytical wavelength selected is usually the one at which the difference in absorbance between the colored reaction product and the colorimetric reagent is greatest:

$$\lambda(\text{product})_{max} - \lambda(\text{reagent})_{max} \geq 100 \text{ nm}$$

The amount of reagent chosen for the standardized procedure should be so large that slight differences in the amount of unused reagent cause differences in absorbance that are no greater than the precision of making the measurement.

Ideally, the colored species should be stable with

time, so that a rigid time schedule need not be used in performing the analysis, and there should be a considerable range of pH over which the absorbance does not vary. When pH control is very critical , appropriate buffers of high capacity are usually required.

Conformity to Beer's law simplifies the calibration procedure as well as the calculations in multi-component analysis. However it is not essential for satisfactory analysis.

Foreign substances should neither prevent the desired color reaction nor give a closely similar color (absorption spectrum). Tests should always be made for other components likely to be present in the samples to be present in the samples to be analyzed.

In addition to the above mentioned factors, the reliability of a method also depends on the nature of the organic reagent used. Organic reagents used in spectrophotometric method should be sufficiently stable and resistant to aerial oxidation or to photometric decomposition.

2.2.1. Accuracy and Precision of Photometric Determination

The accuracy and precision of a photometric determination depends on the type of instrument used and can be evaluated from the Ringbom's plot in which percent transmittance T is plotted against the logarithm of concentration C resulting in a Sigmoid or S-shaped curve. The

Ringbom's plot has two very useful features: (a) The accuracy of the analysis at any concentration level can be evaluated by using the following relationship.

$$\frac{\Delta C/C}{\Delta T} = \frac{2.303}{\Delta T/\Delta \log C} \qquad (7)$$

where $\Delta C/C$ is the relative analysis error for a given photometric error ΔT. Ringbom has showed that the accuracy is greatest when the relation in equation 7 reach a minimum, i.e. at the point of the steepest slope ($\Delta T/\Delta \log C$).

(b) The concentration range within which the analysis error is minimum can be evaluated by constructing a tangent to the steepest portion of the curve. The slope is then translated to points of tangency to the curve which define the concentration limits within which the relative analysis error is minimum .

2.2.2. Sensitivity and Limit of Determination

The sinsitivity of a photometric analysis is a measure of the ability to detect a smallest concentration difference and is defined as the slope $^{dA}/_{dC}$ of the calibration curve $C = f(A)$ at the origin which can be expressed as

$$C = (A - A_o)(^{dA}/_{dC})^{-1} \qquad (8)$$

where C is the concentration, A is the absorbance of solution of the substance being determined, and A_o is the blank.

The steeper the slope of the calibration line, the higher is the sensitivity of the determination; it is thus proportional to the absorption coefficient of the species which is measured and to the path-length through the cuvette. The sensitivity of a photometric determination can thus be increased, as follows from the Beer's law, if the wavelength is chosen in the region of high avsorption maximum, and if a long enough cuvette is taken for the measurement.

The lowest concentration of a given substance which can be determined by a method is generally quoted in terms of limit of detection, defined as that quantity (or concentration) of a substance approaches zero.

Two of the common methods used to calculate the limit of determination are discussed below.

(1) Kaiser considers that the attainable limit of determination should be distinguishable from the fluctuation of the signal obtained for a blank determination and on a statistical basis he has derived the expression

$$C_{min} = (A_{min} - A_o)\left(\frac{da}{dC}\right)^{-1} = 3S_o\left(\frac{dA}{dC}\right)^{-1} = \frac{3S_o}{\epsilon l} \qquad (9)$$

where S_o is the standard deviation for the blank determination. (2) Sandell defines the limit of determination (he calls it the "sensitivity") as the weight in μg per 1 ml of solution, which corresponds to an absorbance

A = 0.001 measured in a cuvette of cross-sectional area of 1 cm^2 and l = 1 cm. Its dimensions are $\mu g\ cm^{-2}$

$$C_S = \frac{M}{\epsilon} \left[\mu g\ ml^{-1}\right] \qquad (10)$$

where M is the molar mass of the substance to be determined. The disadvantage of this method is that the spread of the blank determinations is not taken into account.

2.2.3. Spectrophotometric Methods for Determination of Composition of Metal Complexes

Among the several methods used for the determination of metal complexes (56, 58, 60, 62), the most commonly used are the continuous variations (64,65), the mole ratio (58,66), and the extraction methods (56).

2.2.3.1. Method of Continuous Variations

The Job's method of continuous variations is one of the most commonly used method for determining the composition of metal complexes in solution.

The formation of a metal complex ML_n can be represented by the complexation equilibrium

$$M + nL \rightleftharpoons ML_n \qquad (11)$$

in which M is a metallic ion and L may be either a molecule or an ion. The dissociation constant is given by

$$K = \frac{[M][L]^n}{[ML_n]} \qquad (12)$$

Suppose that species M and L react according to equation 11 and that solution of M and L both concentration m moles per liter are mixed in varying proportions. Let the mixtures be made by the addition of X liter of L to (1 - X) liter of M (X< 1), with no appreciable volume change on mixing. For any mixture the following equations apply

$$[M] = m(1 - X) - [ML_n] \tag{13}$$

$$[L] = mX - n[ML_n] \tag{14}$$

$$[M][L]^n = K[ML_n] \tag{15}$$

The condition for a maximum in the curve of ML_n plotted against X is that

$$\frac{d[ML_n]}{dX} = 0 \tag{16}$$

differentiation of equations 13, 14 and 15 and combination of the three resulting differential equations with equations 13 to 16 gives:

$$n = \frac{X}{1-X} \tag{17}$$

Determination of the value of X for which $[ML_n]$ is a maximum allows the calculation of n by equation 17.

Thus a series of solutions is prepared in which the sum of the molar concentrations of M and L is the same while their mole fractions very between 0 and1l. If the sbsorbance is measured at a wavelength, where the

complex ML_n absorbs but M and L do not absorb, the value of X at the point of maximum absorbance will correspond to maximum concentration of ML_n . Accordingly the absorbance of the solution is plotted against X, the mole fraction of the ligand in the solution and then n is calculated from the abscissa of the maximum of the curve by using equation 17.

2.2.3.2. Mole-Ratio Method

This method is based upon consideration of a complexation equilibrium in equation 11. If the complex ML_n is very little dissociated, a plot of absorbance against mole-ratio of component L to component M, with the concentration of M held constant and that of L varied, rises steeply from the origin as a straight line for mole ratios below that corresponding to the complex formed, then breaks sharply to a constant absorbance at the mole ratio of $L/_M$ in the complex. If the concentration of M is held constant and L is varied, the break in the curve indicates the mole ratio $M/_L$ in the complex ML_n.

2.2.3.3. Extraction Method

Consider the extraction equilibrium in equation 1 for which the D_M is given by equation 18

$$D_M = \frac{[ML_n]_{org}}{[M]_{aq}} = K_{ex}\left(\frac{[HL]_{org}}{[H^+]}\right)^n \qquad (18)$$

Since $[M]_{aq} = C_M - [ML_n]_{org}$

equation 18 can be written as

$$\log \frac{[ML_n]_{org}}{C_M - [ML_n]_{org}} = \text{Log } K_{ex} + n \log [HL]_{org} + npH \qquad (19)$$

where C_M is the total concentration of the metal ion. If the complex ML_n is the only species that is extracted into the organic phase that absorbs at the selected wavelength then from Beer's law $[ML_n] = A/\epsilon$ and $C_M = A_{max}/\epsilon$ (for l = 1 cm) where A is the equilibrium absorbance and A_{max} is the maximum absorbance with an excess of the ligand in the organic phase, equation 18 can thus be written as

$$\log \frac{A}{A_{max} - A} = \log K_{ex} + n \log [HL] + n\,PH \qquad (20)$$

Thus the slope of the curve obtained by plotting $\log \frac{A}{A_{max} - A}$ against $\log [HL]_{org}$ gives the number of ligands, n, in the complex.

3. EXPERIMENTAL

3.1. Equipments

A Beckman Model 24 UV-Vis spectrophotometer equipped with matched 1-cm quartz cuvettes and a Beckman Recorder were used for recording the absorption spectra and absorbance measurements. The pH values of the solutions were measured with a Beckman Chem-Mate pH meter. A Varian Tectron Model 575 Series atomic absorption spectrometer was used for atomic absorption determination of manganese.

3.2. Reagents and Solutions

Standard solution of Manganese(II). A stock solution of manganese(II) was prepared by dissolving 0.845 g of manganese(II) sulfate monohydrate (BDH, AnalaR) in distilled water, acidified with dilute sulfuric acid, and diluted to 500ml with distilled water. The manganese content of the solution was determined complexometrically using EDTA (67).

Standard Permanganate Solution. A stock solution of manganese(VII) was prepared by dissolving 1.5794 g of potassium permanganate (BDH, AnalaR) in 500 ml of distilled water, boiling the solution gently for 1 h, cooling, filtering through a sintered glass filter to remove any manganese (IV) oxide formed, and diluting exactly to 1 litre with distilled water (12).

EDTA Solution. A stock solution of 0.05 M ethylenediaminetetraacetic acid (EDTA) was prepared by dissolving the disodium salt in distilled water. The solution was standardized against magnesium chloride (BDH,AnalaR) using NH_3/NH_4Cl buffer at pH 10 and Eriochrome Black T (BBT) indicator.

Oxidizing Agents. A 5% (w/v) KIO_4 was prepared by dissolving 25 g KIO_4 in a mixture of 300 ml water and 100 ml water and 100 ml concentrated HNO_3 and heating to complete dissolution. The solution was cooled and diluted to 500 ml with distilled water and used for oxidation of Mn(II) (68).

A 1 % (w/v) solution of $K_2S_2O_8$ (BDH,AnalaR) and solid PbO_2 (Hoppkins & Williams) and $NaBiO_3$(BDH, AnalaR) were also used for oxidation of manganese(II) (69).

Reducing Agents. A 0.01 M solution of ascorbic acid (Hopkins and Williams) and $NH_2OH.HCl$, respectively, in distilled water were used for the reduction of higher oxidation states of manganese to manganese(II).

Solution of Electrolyte. A 2.0 M solution of potassium nitrate (BDH, AnalaR) in distilled water was used to adjust the ionic strength of the solution for extraction.

Solutions of Foreign Ions. Solutions of foreign ions were prepared by dissolving known amount of reagent grade salts in distilled water to give 10 mg of the ion per milliliter of solution. The solutions were acidified whenever

necessary to prevent hydrolysis. In general nitrate salts were used for the cations and sodium or ammonium salts were used for the anions.

Nitric Acid and Ammonia. Dilute nitric acid (Riede-de Haen) and ammonia (Riedel-de Haen) solutions were used for adjusting the pH of the solutions.

Reagent Solutions. N^1-Hydroxy-N^1,N^2-diphenylbenzamidine, HDPBA, was synthesized by the condensation of N-phenylbenzimidoyl chloride with N-phenylhydroxylamine at 0°C in ether (52), m.p 160-162°C, reported 163°C (24).

A 0.005 M solution of the reagent, HDPBA, in 96 % (v/v) ethanol was used for the spectrophotometric determination of manganese(II) and manganese(VII) in aqueous ethanol medium.

A 0.01 M solution of the reagent in amyl alcohol was used for the extraction of Mn(VII).

Solvents. Ethanol (96 %,v/v) (Riedel-de Haen) and other solvents were used as received without further purification. Amyl alcohol (Riedel-de Haen) was distilled once before use. Once used, it was recovered by double distillation and used again.

Drying Agent. Anhydrous sodium sulfate (Riedel-de Haen) was used for drying the colored extract.

3.3. Preparation of Sample Solutions

3.3.1. Tea Powder Accurately known weight of tea powder,

3 g, (Red label, Insta Impex Co(K) Ltd. Mombassa, Kenya) was added to 300 ml boiling water, boiled for 5 to 20 min as required, and filtered through a Buchner funnel. The clear extract was transfered to a 250 ml Kjeldhal flask and evaporated to dryness. The residue was decomposed with 10 ml of a mixture of nitric, sulfuric and perchloric acids in the ratio of 3:1:1 (70) by heating over the bunsen burner for about 2 h. The heating was continued after addition of about 10 ml of dilute sulfuric acid until the volume was reduced to about 5 ml. The residue was cooled and then reboiled with 25 ml of distilled water. To this solution 10 ml of 5 % (w/v) KIO_4 was added and heated to boiling to oxidize any manganese species to manganese (VII). The solution was cooled, transfered to a 50 ml volumetric flask and diluted to the mark with water. Suitable aliquots of this solution were taken for the analysis.

3.3.2. Steel, Bronze, Manganin and Ferromanganese Samples (52, 71)

Artificial samples of steel, bronze, manganin, and ferromanganese were prepared by mixing the aqueous solutions of the respective metal ions in suitable proportions. The solutions were treated with KIO_4 to oxidize manganese (II) to manganese(VII) and diluted to known volumes respectively. These solutions were used for the analysis.

3.4. Procedures

3.4.1. Standardization of Manganese Solutions. A 10 ml aliquot of the manganese(II) or manganese(VII) solution was transfered into a 250 ml conical flask. About 0.5 g of ascorbic acid and 5 ml of NH_3/NH_4Cl buffer of pH 10 were added and the solution was diluted to 50 ml with distilled water. The solution was titrated with 0.05 M EDTA solution after adding 5 drops of 0.5 % EBT indicator solution until the initial reddish color of the solution turned blue with the final drop of EDTA.

3.4.2. Qualitative Test for Oxidation State of Manganese. Aliquots of manganese(II) solution (2 ml of 0.002 M each) were transfered into 5 different beakers (50 ml each). To each of this was added, none, 1 ml of 0.1 M solution of ascorbic acid, 1 ml of 0.1 M solution of $NH_2OH.HCl$, 1 ml of 30 % (v/v) H_2O_2, and 1 ml of 0.05 M $K_2S_2O_8$, respectively. A 10 ml aliquot of 0.005 M reagent solution in ethanol was added to each beaker. The pH of each solution was varied between 3 and 10, and the solution was diluted to 25 ml with suitable amounts of ethanol and water to give 60 % (v/v) ethanol in the final solution. The color change of each solution was monitored visually and spectrophotometrically at different time intervals.

3.4.3. Determination of Mn(II) from Aqueous Ethanol Medium An aliquot of the solution containing 25 - 250 µg of

manganese(II) was transfered into a 50 ml beaker and 10 ml of 0.005 M solution of HDPDA in ethanol was added to it. The pH of the solution was adjusted to 7 - 8 using dilute solutions of HNO_3 and NH_3 and the solution was allowed to stand for 6 h with occasional shaking. The solution was quantitatively transfered to a 25 ml volumetric flask and diluted to the mark with sufficient amount of ethanol and water to give 60 % (v/v) ethanol solution in the final solution. The absorbance of the colored solution was measured at 625 nm against the reagent blank.

For calibration, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50 ml of the standard solution (500 µg ml^{-1} Mn(II)) were used through the procedure.

3.4.4. Determination of Mn(II) from Aqueous Ethanol Medium in Presence of $K_2S_2O_8$. An aliquot of the solution containing 25 - 250 µg of manganese(II) was transfered into a 50 ml beaker and 1 ml of 1 % $K_2S_2O_8$ solution was added to it. A 10 ml aliquot of 0.005 M solution of the reagent in ethanol was added to the solution and the pH was adjusted to 7 - 8 using dilute solutions of nitric acid and ammonia. The solution was quantitatively transfered into a 25 ml volumetric flask and allowed to stand for 30 min with occasional shaking. The solution was diluted to volume with sufficient amount of ethanol and distilled water to give 60 % (v/v) ethanol in the final solution. The absorbance of the colored solution was measured at 625 nm against the reagent blank

For calibration 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, ml of the standard solution (500ug ml^{-1} Mn(II)) was used through the procedure.

3.4.5. Determination of Mn(VII) From Aqueous Ethanol Medium

An aliquot of the solution containing 25 - 250 ug of Mn(VII) was transfered into a 50 ml beaker. A 10 ml aliquot of 0.005 M reagent solution in ethanol was added to the solution and the pH was adjusted to 7 - 8 using dilute solutions of HNO_3 and NH_3. The solution was quantitatively transfered into a 25 ml volumatric flask and diluted to the mark with the required amount of ethanol and water to give 60 % (v/v) ethanol in the final solution. The absorbance of the colored solution was measured at 614 nm against the reagent blank.

For calibration 0.05, 0.10, 0.20, 0.30, 0.40, 0.50 ml of the standard solution (500 ug ml^{-1} Mn(VII) was used through the procedure.

3.4.6. Determination of Mn(VII) by Solvent Extraction

An aliquit of the solution containing 25 - 250 ug of manganese(VII) was transfered into a 50 - ml beaker and diluted to 10 ml with water. The pH of the solution was adjusted to 6 - 8 using dilute solutions of HNO_3 and NH_3 and the solution was quantitatively transfered into a 100-ml separating funnel. A 10 ml aliquot of 0.01 M HDPBA in amyl alcohol was added to the funnel and the mixture was shaken vigorously for two minutes. The funnel was allowed to stand (for about 2 - 3 minutes) until the two phase separated completely. The aqueous phase was separated and the organic phase was collected in a 50 - ml beaker containing about 2 g of anhydrous sodium sulfate. The aqueous phase was again transfered into the funnel and washed with about 5 ml of amyl alcohol. The washing was mixed with the colored extract and transfered into a 25 ml volumetric flask. The beaker was washed continuously with amyl alcohol until no green color was left with the sodium sulfate. The washings were added to the flask and the extract was diluted to the mark with amyl-alcohol. The absorbance of the colored solution was measured at 614 nm against the reagent blank.

For calibration, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50 ml of the standard solution (500 $\mu g\ ml^{-1}$ Mn(VII)) were used through the procedure.

3.4.7. Studying the Effect of Variables

The effect of a particular variable was studied by measuring the absorbance of the solution of each system following the general procedures described above, keeping all experimental variables constant, except the one under study.

In aqueous ethanol systems the completeness of the complex formation was examined by measuring the absorbances of the solutions at a particular condition of a variable parameter and at its optimum condition following the general procedure. The reaction was considered to be incomplete when the absorbance was found to be less than maximum and constant value obtained at the optimum conditions of each system.

The quantitative extraction of manganese from the aqueous permanganate solution was examined by checking the presence or absence of manganese in the aqueous phase left after extraction at any particular condition. The extraction was considered to be complete when manganese was not detected in the aqueous phase.

3.4.8. Tests for Complete Extraction of Manganese

The aqueous phase left after extraction was reduced

to about 1-2 ml by evaporation and 2 drops of 0.1 M $NH_2OH.HCl$ was added to it to reduce any manganese species to Mn(II). The solution was transfere into a test tube and 2 drops each of NH_3/NH_4Cl buffer of pH 10 and 0.5 % EBT was added to it. The appearance of light blue color indicated the absence of manganese in the aqueous phase, whereas the appearance of wine red color indicated the presence of manganese in the aqueous phase.

The presence of manganese in the organic phase, i.e. in the clored extract, was also tested. The residue left after the distillation of amyl alcohol from the colored extract was decomposed by heating with a mixture of 1 ml of HNO_3, H_2SO_4 and $HClO_4$ in the ratios of 3:1:1. The residue was cooled and dissolved in 1 ml of 3 N H_2SO_4. The presence of manganese in the solution was confirmed by its oxidation to permanganate with 5 drops of KIO_4 solution.

3.4.9. Detrmination of the Composition of the Complexes

The Method of Continuous Variations. A series of solutions was prepared for each system in which the mole fractions of manganese to HDPBA were varied between 0 and 1 to give a constant total consentration of 8.0×10^{-4} M. The pH of the solution in the aqueous ethanol systems was adjusted to 8 ± 0.2 and the pH of the aqueous phase in the extraction system was adjusted to 6 ± 0.2. Then proceeded as described in sections 3.4.3., 3.4.5, and 3.4.6,

respectively. The absorbances were plotted against the mole fractions of the ligand, and the maximum of the curve gave the mole fraction of the ligand in the complex.

Extraction Method. A series of solutions was prepared in which the concentration of Mn(VII) (1.6×10^{-4} M) and the pH(6 ± 0.1) were kept constant and concentration of HDPBA was varied over a wide range (1 : 1 to 1 : 50; M : L). The complex was extracted by the procedure described in section 3.4.6, and the absorbance of the colored extract was measured at 614 nm against the reagent blank. The quantity $\log \frac{A}{A_{max} - A}$ was plotted against the $\log [HDPBA]$. The slope of the curve gave the number of ligands in the complex.

3.4.10 Study of the Effect of Foreign Ions

The effect of foreign ions on the determination of manganese(VII) by the extraction system was studied by adding a known amount of a particular ion to an aqueous solution containing 100 ug of Mn(VII). Then extraction and determination of the manganese were made according to the procedure described in section 3.4.6.

The effect of iron(III) was studied by adding known amounts of fluoride to mask it.

3.4.11. Oxidation of Mn(II) with KIO_4

A 5 ml aliquot of 0.01 M solution of Mn(II) was

transfered into a 250 ml conical flask and 10 ml of 5 % (w/v) KIO_4 was added to the solutions. The solution was diluted to 25 ml with water and heated to boiling. The purple permanganate solution obtained was cooled and diluted to 100 ml with distilled water. Suitable aliquots of this solution was taken for extraction and determination of Mn(VII).

3.4.12. Determination of Mn(VII) in Sample by Solvent Extraction

An aliquot of the sample solution containing 25 - 250 ug of Mn(VII) was transfered into a 50-ml beaker and 5 ml of 5 % (w/v) sodium fluoride was added to it. solution was diluted to 10 ml and then proceeded as described in section 3.4.6.

3.4.13. Determination of Mn(VII) by AAS

The manganese content of the sample solution containing 5-25 $\mu g\ ml^{-1}$ of Mn(VII) was also determined by AAS at its 279.5 nm resonce line with air-acetylene flame ststem.

For calibration, 5, 10, 15,20, and 25 ug ml^{-1} Mn(VII) were used through the procedure.

4. RESULTS AND DISCUSSION

Mn(II)-HDPBA system and MnO_4^- - HDPBA(Mn(VII)-HDPBA) system mentioned throughout the result and discussion refers to the complex species formed by the reaction of Mn(II) with HDPBA and MnO_4^- with HDPBA, respectively.

4.1. Reaction Conditions and Absorption Spectra

Mn(II)-HDPBA Aqueous Ethanol System. Mn(II) was found to react with HDPBA in aqueous ethanol medium to give a deep green complex in the P^H range 6.5-8.5 on exposure to atmospheric air for about 6 h.

When the reaction was conducted in the presence of $NH_2OH.HCl$ or ascorbic acid the Mn(II)-HDPBA aqueous ethanol system was found to give no color formation. Whereas in the presence of $K_2S_2O_8$ or H_2O_2 the green Mn(II)-HDPBA complex was obtained rapidly.

These results, i.e., absence of complex formation in the presence of reducing agents and the rapid color deveopment in the presence of oxidizing agents, indicate that the manganese species involved in the complex formation is not Mn(II) but some higher oxidation state manganese species resulting from air, H_2O_2 or $K_2S_2O_8$ oxidation.

It was also found that Mn(II) was not extractable with the HDPBA solution in organic solvents such as amyl alcohol and 1-hexanol.

The absorption spectra of Mn(II)-HDPBA complex has been recorded both in the presence and absence of $K_2S_2O_8$ in aqueous ethanol medium. The absorption spectra were found to be similar under both conditions with wavelength of absorption maximum invariably at 625 nm(Fig.1). However there was a significant difference in the band intensities. The molar absorptivity was found to be 4600 l mol^{-1} cm^{-1} in the presence of $K_2S_2O_8$ whereas in the absence of $K_2S_2O_8$ the absorbance increases with time.

These results indicate that the complex species formed both in the absence and presence of $K_2S_2O_8$ are identical involving manganese species with some higher oxidation state other than +2 in the complex formation, and the oxidation of Mn(II) is not complete in the absence of $K_2S_2O_8$ (i.e. with air).

The results obtained also indicate that the manganese species involved in the complex formation is most likely to be Mn(III) as evidenced by the oxidation of Mn(II) to Mn(III) by $K_2S_2O_8$ (70). Similarly the formation of $Mn(acac)_3$ by oxidation of basic solution of Mn(II) by O_2 or Cl_2 in the presence of acetylacetone has been reported (5).

Mn(VII)-HDPBA Aqueous Ethanol and Extraction Systems. Mn(VII) was found to react with HDPBA in aqueous ethanol medium in the p^H range 3.5-9.5 to give a deep green complex immediately. The spectrum of the complex has been recorded and showed an intense absorption band at 614 nm with molar absorption coefficient 5350 l mol^{-1} cm^{-1} (Fig. 2).

Several water immiscible solvents such as n-butanol, 1-hexanol, amyl alcohol, chloroform, benzene, toluene, and xylene were tried as solvents for extraction. The green complex was found to be not extractable into benzene, toluene, and xylene. The complex was found to be readily extractable into n-butanol, 1-hexanol, amyl alcohol, and chloroform.

The absorption spectrum of the deep green extract in each solvent has been recorded and found to be similar in all the solvent with minor variation in intensity of the absorption band. Of the solvents, amyl alcohol and 1-hexanol gave a better sensitivity with almost identical absorption spectra, and hence the detailed study has been conducted with amyl alcohol.

The maximum of the absorption band was found to coincide with that of Mn(VII)-HDPBA aqueous ethanol system both in intensity and position (max = 614 nm, = 5350 l mol^{-1} cm^{-1}) (Fig. 2). These results indicate the formation of identical complex species in the two Mn(VII)-HDPBA aqueous ethanol and Mn(VII)-HDPBA extraction) systems wi which is different from the complex formed in the Mn(II)-HDPBA system.

The spectrum for the reagent blank (HDPBA in 60 % ($^{v}/_{v}$) ethanol or in amyl alcohol has been recorded and it was found that the reagent did not show significant absorption above 450 nm upto 700 nm (Fig. 1 & 2). However all absorbance measurements have been made against reagent blank to ensure maximum accuracy.

4.2. Effects of Experimental Variables

Effect of p^H. The optimum p^H range for the maximum and constant absorbance in the Mn(II)-HDPBA aqueous ethanol system has been found to be 7.5-8.5 (Table 1 and Fig. 3). Absorbance of the complex was found to decrease with decreasing and increasing p^H behind the optimum range. The decrease in absorbance at lower p^H values may be due to the incomplete oxidation of Mn(II) to Mn(III) which retards the formation of the complex. The decrease in absorbance at higher p^H values could be due to the formation of the white manganeous hydroxide precipitate which results in an incomplete complex formation of the metal.

The optimum p^H range for the maximum color development in the Mn(VII)-HDPBA aqueous ethanol system was found to be 3.5-9.5 (Table 2 & Fig. 4). Below p^H 3.5 and above p^H 9.5 the solution becomes brown and exhibited a different absorption spectra, probably due to protonation of the ligand and some radox reaction of Mn(VII), respectively.

The optimum p^H range of the aqueous phase for the complete extraction of Mn(VII)-HDPBA was found to be 3.5-9.5(Table 2 & Fig. 4). At lower p^H values extraction of Mn(VII) decreases due to the incomplete complexation because of protonation of the ligand. At higher p^H values extraction of Mn(VII) decreases, probably due to the formation of manganese dioxide or some other side reactions.

Effect of Amount of HDPBA. A minimum of 9-fold molar excess of the reagent, HDPBA, was found to be necessary for complete color develppment in the Mn(II)-HDPBA aqueous ethanol system. A large excess of the reagent (upto 100-fold molar excess) was found to have no adverse effect (Table 3).

For complete color development in the Mn(VII)-HDPBA aqueous ethanol system and for the complete extraction of the metal from the aqueous phase in the Mn(VII)-HDPBA extracation system a minimum of 8-fold molar excess of the reagent was found to be necessary. A large excess upto 100-fold molar excess of the ligand has been found to have no adverse effect on the color development and extraction efficiency of the two systems, respectively (Table 4).

Though the reagent blank do not exhibited significant absorption at the wavelenghhs of maximum absorpation all absorbance measurements have been made against the reagent blank to ensure maximum accuracy.

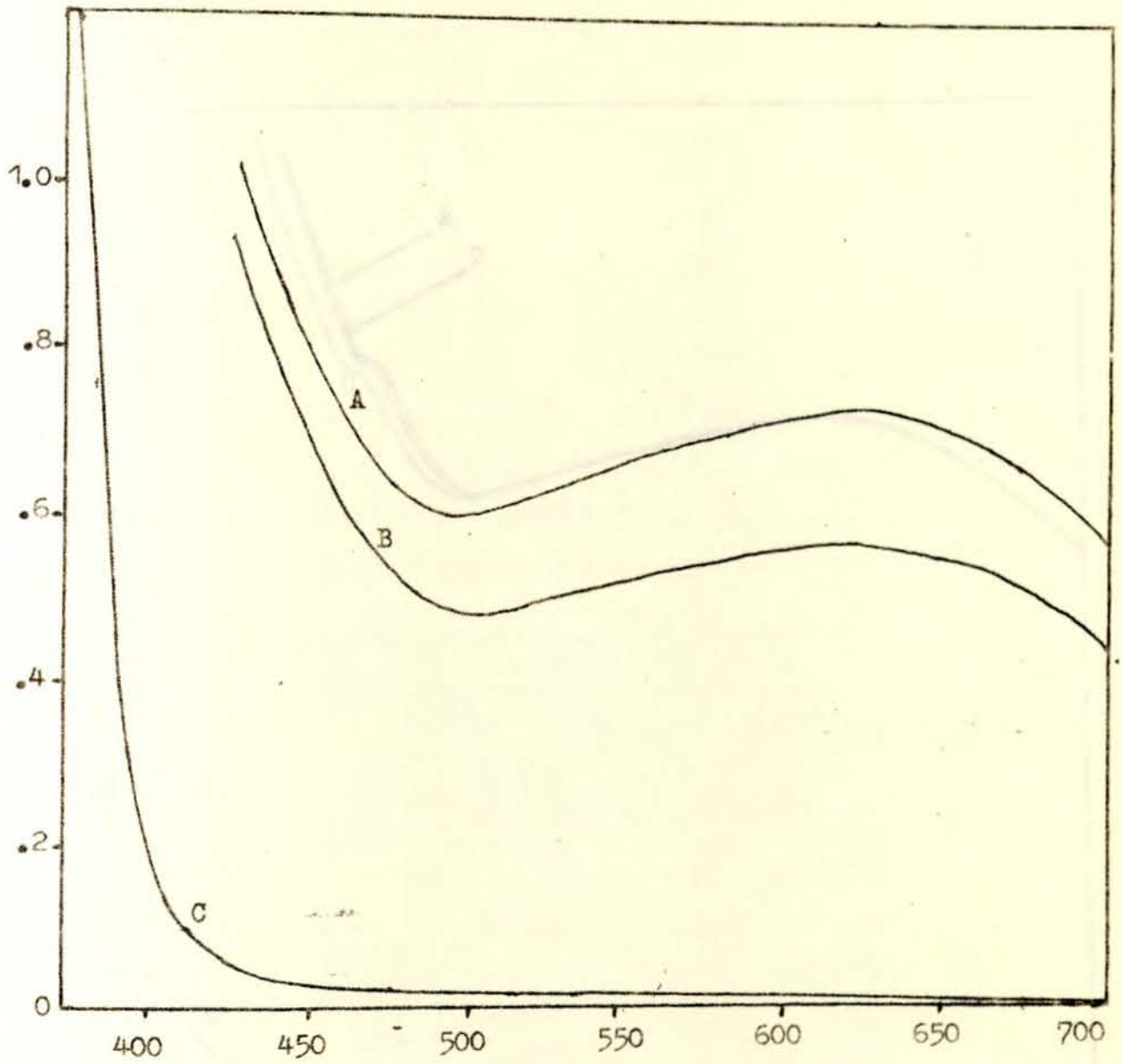


Fig.1 Absorption spectra of (A) 1.6 x 10^{-4} M Mn(II)-HDPBA complex in presence of $K_2S_2O_8$ (B) 1.6 x 10^{-4} M Mn(II)-HDPBA complex without $K_2S_2O_8$ (C) 2 x 10^{-3} M HDPBA, all in 60% ($^{v}/v$) ethanol.

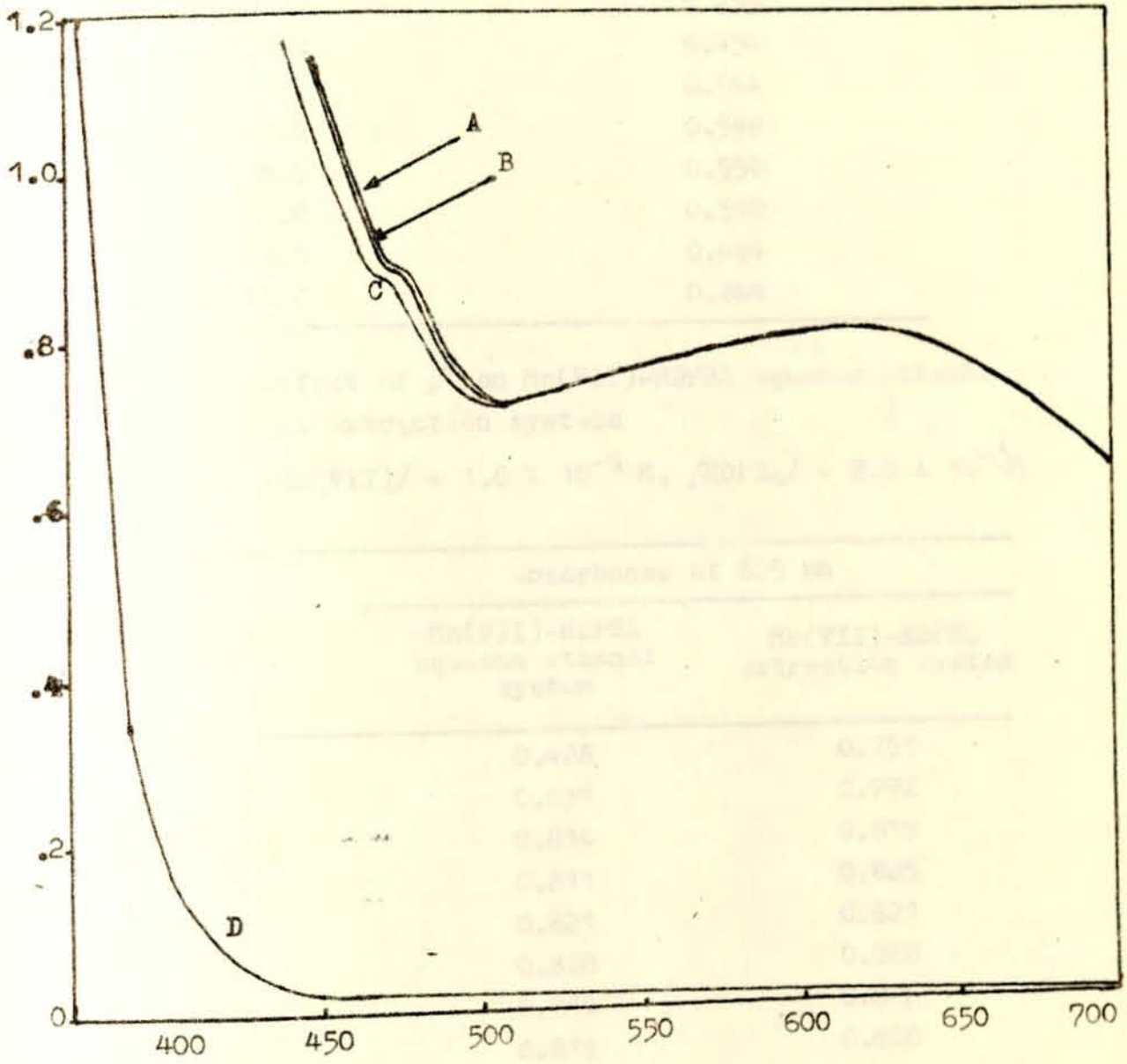


Fig.2 Absorption spectra of (A) 1.6 x 10^{-4}M Mn(VII)-HDPBA in 60% ($^{v}/v$) ethanol (B) 1.6 x 10^{-4}M Mn(VII)-HDPBA extraction (C) 1.6 x 10^{-4}M Mn(VII)-HDPBA extraction in presence of KIO_4 (D) 2 x 10^{-3}M HDPBA extraction.

Table 1. Effect of pH on Mn(II)-HDPBA aqueous ethanol system
$[Mn(II)] = 1.6 \times 10^{-4}$ M, $[HDPBA] = 2.8 \times 10^{-3}$ M

pH	Absorbance at 625 nm (t = 6 h)
6.0	0.083
6.5	0.255
7.0	0.454
7.5	0.544
8.0	0.548
8.5	0.550
9.0	0.510
9.5	0.424
10.0	0.264

Bable 2. Effect of pH on Mn(VII)-HDPBA aqueous ethanol and extraction systems
$[Mn(VII)] = 1.6 \times 10^{-4}$ M, $[HDPBA] = 2.8 \times 10^{-3}$ M

pH	Absorbance at 625 nm	
	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
2	0.428	0.759
3	0.631	0.792
3.5	0.814	0.819
4	0.811	0.825
5	0.821	0.821
6	0.828	0.828
7	0.814	0.825
8	0.815	0.828
8.5	0.814	0.824
9	0.816	0.821
9.5	0.812	0.820
10	0.754	0.782
11	0.733	0.769

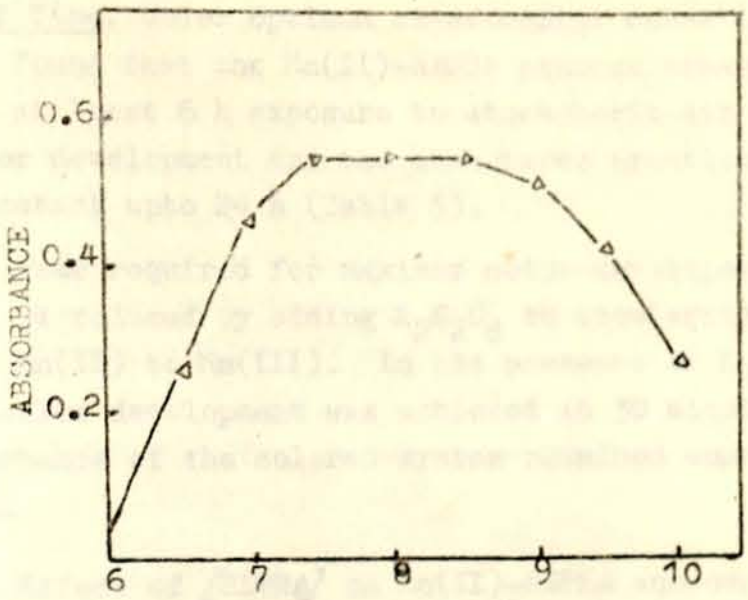


Fig.3 pH effect on Mn(II)-HDPBA aqueous ethanol system

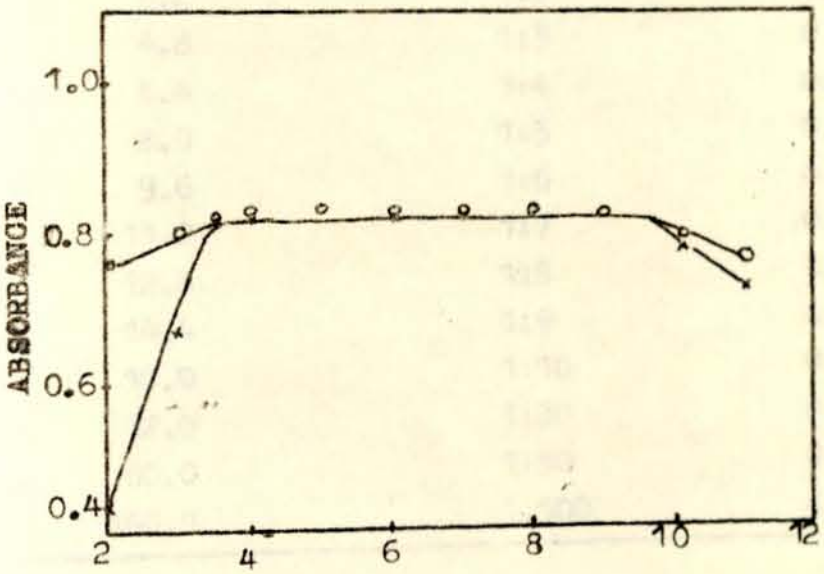


Fig.4 pH effect on (A) Mn(VII)-HDPBA aqueous ethanol and (B) Mn(VII)-HDPBA

Effect of Time. Under optimum experimental condition, it has been found that the Mn(II)-HDPBA aqueous ethanol system requires at least 6 h exposure to atmospheric air for maximum color development and the absorbance practically remains constant upto 24 h (Table 5).

The time required for maximum color development was found to be reduced by adding $K_2S_2O_8$ to accelerate exid - ation of Mn(II) to Mn(III). In the presence of $K_2S_2O_8$ maximum color development was achieved in 30 minutes and the absorbance of the colored system remained constant for 24 h.

Table 3. Effect of [HDPBA] on Mn(II)-HDPBA aqueous ethanol system [Mn(II)] = 1.6 x 10^{-4}M, pH = 8

[HDPBA] x 10^4M	[Mn(III)]:[HDPBA]	Absorbance at 625 nm
1.6	1:1	0.093
3.2	1:2	0.104
4.8	1:3	0.157
6.4	1:4	0.276
8.0	1:5	0.351
9.6	1:6	0.496
11.2	1:7	0.549
12.8	1:8	0.558
14.4	1:9	0.564
16.0	1:10	0.565
32.0	1:20	0.567
80.0	1:50	0.565
160.0	1.100	0.562

The optimum molar ratio range of Mn: $K_2S_2O_8$ for the rapid color development was found to be 1:4 - 1 : 15. At lower molar ratios oxidation was not complete where as at higher molar ratios precipitation occurs.

Maximum color development in the Mn(VII)-HDPBA aqueous ethanol system was achieved instantaneously under optimum conditions and the Mn(VII)-HDPBA complex was completely extracted into amyl alcohol within 2 minutes. The absorbance values of the colored complex in aqueous ethanol medium and the colored extract remained constant for 4 days at room temperature and then started declining gradually due to the decomposition of the complexes (Table 6).

Table 4. Effect of HDPBA on Mn(VII)-HDPBA aqueous ethanol and extraction systems
[Mn(VII)] = 1.6 x 10^{-4} M, pH = 8

[HDPBA] x 10^{4}M	[Mn(VII)]:[HDPBA]	Absorbance at 614 nm	
		Aqueous ethanol system	Extraction system
1.6	1:1	0.124	0.110
3.2	1:2	0.166	0.173
4.8	1:3	0.2988	0.268
6.4	1:4	0.499	0.411
8.0	1:5	0.586	0.565
9.6	1:6	0.764	0.767
11.2	1:7	0.802	0.798
12.8	1:8	0.827	0.828
16.0	1,10	0.821	0.825
32.0	1,20	0.831	0.824
80.0	1,50	0.824	0.831
160.0	1,100	0.832	0.835

Volume Ratio, Temperature and Ionic Strength. For the complete dissolution of the complex and to have a clear solution in the Mn(II)-HDPBA and Mn(VII)-HDPBA aqueous ethanol systems a minimum of 60% (v/v) ethanol was found to be necessary. Below 60% of ethanol the solution becomes turbid, whereas above 60%, upto 90%, of ethanol in the solution has no adverse effect on the absorbance of the complexes (Table 7).

In the Mn(VII)-HDPBA extraction system it has been found that the volume of the aqueous phase can be varied from 10 to 50 ml with respect to a fixed volume, 10 ml, of the organic phase (i.e. V_{aq} : V_{org} can be varied from 1:1 to 5:1) without any variation in the absorbance

Table 5. Effect of time on the color development and stability of the complex in the Mn(II)-HDPBA aqueous ethanol system in the presence and absence of $K_2S_2O_8$
/Mn(II)/ = 1.6 X 10^{-4}M, /HDPBA/ = 2X10^{-3}M
/$K_2S_2O_8$/ = 2 X 10^{-3}M, p^H = 8

Time, h,	Absorbance at 625 nm[a]	Absorbance at 625 nm[b]
½	0.382	0.730
1	0.463	0.734
2	0.487	0.739
3	0.546	0.735
4	0.554	0.735
5	0.580	0.733
6	0.585	0.736
8	0.587	0.732
24	0.592	0.729

a = Without $K_2S_2O_8$. b = With $K_2S_2O_8$.

Table 6. Effect of time on the stability of the complex in the Mn(VII)-HDPBA aqueous ethanol and extraction systems [Mn(VII)] = 1.6 X 10^{-4} M, [HDPBA]= 2 X 10^{-3} M

Time h	Absorbance at 614 nm	
	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
0	0.818	0.821
½	0.815	0.824
2	0.824	0.822
4	0.826	0.819
6	0.820	0.819
12	0.817	0.822
24	0.813	0.820
48	0.814	0.819
72	0.819	0.815
96	0.804	0.802
120	0.790	0.785

Table 7. Effect of the amount of ethanol in the solution, on Mn(II)-HDPBA and Mn(VII)-HDPBA aqueous ethanol systems [Mn(II)] or [Mn(VII)] = 1.6 X 10^{-4}M, [HDPBA] = 2.8 X 10^{-3}M

Ethanol % (v/v)	Mn(II)-HDPBA system Absorbance at 625 nm	Mn(VII)-HDPBA system Absorbance at 614 nm
40	*	*
50	*	*
60	0.578	0.831
80	0.575	0.832
90	0.576	0.830

* Turbid solution.

or extraction efficiency (Table 8.). At higher volume ratios there was gradual decrease in the degree of extraction of the complex. Hence repetitive extractions were found to be necessary for the complete extraction of Mn(VII) from larger volumes of the aqueous phase.

No significant changes in the absorbance values and the reaction time of the Mn(II)-HDPBA system was observed when the reaction was carried out at higher temperature upto 60°C. Variation in temperature between 20 and 40°C did not produce any measurable change in the absorbance of the Mn(VII)-HDPBA aqueous ethanol colored system or on the extraction efficiency of the Mn(VII)-HDPBA colored system (Table 9).

The wavelength of the absorption maxiumum and the absorbance of the Mn(VII)-HDPBA extraction system did not change when the ionic strength of the aqueous phase was varied between 0 to 2 M with respect to KNO_3 (Table 10).

The optimum conditions for the complex formation in the Mn(II)-HDPBA and Mn(VII)-HDPBA aqueous ethanol system and for the complete extraction of Mn(VII) into amyl alcohol with HDPBA are summarized in Table 11.

Table 8. Effect of aqueous to organic phase volume ratio on the Mn(VII)-HDPBA extraction
/Mn(VII)/ = 1.6 X 10^{-4} M, /HDPBA/ = 2 X 10^{-3} M,
Volume of aqueous phase = 10 ml

Volume of aqueous phase (ml)	Vaq/Vorg	Absorbance at 614 nm
10	1:1	0.826
25	2.5:1	0.820
50	5:1	0.817
100	10:1	0.765

4.3. Test for complete Extraction of Manganese

To confirm the completeness of extraction of manganese species into the organic phase under optimum conditions tests have been performed for the presence or absence of manganese in the aqueous phase left after extraction and i in the organic phase containing the colored extract by the p procedure described in section 3.4.8.

Under optimum conditions the presence of manganese could not be detected in the aqueous phase left after extraction, i.e., the extraction of manganese from the aqueous phase into the organic phase was found to be complete. This was further confirmed by the presence of manganese in the colored extract. The presence of manganese was detected in the aqueous phase left after extraction when less than 80fold molar excess of the reagent was used for extra extraction, when the pH of the aqueous phase was below 3 or when the volume of the aqueous phase was larger then 50 50 ml.

4.4 Composition of the Complexes

The composition of the complexes in the Mn(II)-HDPBA and Mn(VII)-HDPBA aqueous ethanol systems was determined by the method of continuous variations, and that of Mn(VII)-HDPBA complex extracted

Table 9. Effect of temperature on complex formation in Mn(II)-HDPBA and Mn(VII)-HDPBA aqueous ethanol systems and on the degree of extraction of Mn(VII)-HDPBA system
/Mn(II)/ or /Mn(VII)/ = 1.6 X 10^{-4} M, /HDPBA/ = 2.8 X 10^{-3} M

Temperature °C	Absorbance at 625 nm	Absorbance at 614 nm	
	Mn(II)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
20	0.629	0.824	0.831
40	0.632	0.826	0.828
60	0.630	-	-

Table 10. Effect of ionic strength of the aqueous phase on the Mn(VII)-HDPBA extraction system
/Mn(VII)/ = 8 X 10^{-5} M, /HDPBA/ = 2 X 10^{-3} M

/KNO_3/	Absorbance at 614 nm
0,0	0.429
0.1	0.436
0.5	0.433
1.0	0.425
2.0	0.429

into amyl alcohol was determined by the continuous variations and extraction methods.

The maximum absorbance in the continuous variations method was observed at the mole fraction of 0.75 of the ligand in the Mn(II)-HDPBA aqueous ethanol system. Whereas the maximum absorbance was found at the mole fraction of 0.80 of the ligand in both the

Table 11. Optimum conditions for complex formation and/or extraction of manganese with HDPBA

Parameter	Mn(II)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
pH	7.5-8.5	3.5-9.5	3.5-9.5
Amount of HDPBA	9-fold molar excess	8-fold molar excess	8-fold molar excess
Amount of $K_2S_2O_8$	1:4-1:15	-	-
Reaction extraction time	30 min*	immediate	2 min
Stability of the complex	24 h	96 h	96 h
Solvent ratio	60-90% (v/v)ethanol	60-90% (v/v)ethanol	1:1-5:1 (V_{aq} :V_{org})
Reaction/ extraction temperature	20-40°C	20-40°C	20-40°C
Ionic strength of aqueous phase	-	-	0-2 M KNO_3

* 6 h in the absence of $K_2S_2O_8$

Mn(VII)-HDPBA aqueous ethanol and extraction systems.

These results indicated that the ratio of Mn to HDPBA is 1:3 in the Mn(II)-HDPBA aqueous ethanol system and the ratio of Mn to HDPBA is 1:4 in both the Mn(VII)-HDPBA aqueous ethanol and extraction systems. The results are given in Table 12 and 13 and the curves are shown on Figures 5 to 7.

To determine the ratio of Mn to HDPBA by the extraction method, the quantity $\log \frac{A}{A_{max}-A}$ was plotted against the absorbance for a particular concentration of HDPBA and A_{max} is the absorbance in the presence of constant and

excess of HDPBA. The curve gave a slope of 3.9 which indicated that the ratio of the Mn to HDPBA in the complex is 1:4. The results are given in Table 14 and the curve is shown in Fig. 8.

Thus the composition of the complexes has been found to be 1:3 (Mn:HDPBA) in the Mn(II)-HDPBA aqueous ethanol system and 1:4 (Mn:HDPBA) in both the Mn(VII)-HDPBA aqueous ethanol and extraction systems.

The results obtained from the three systems indicate that the reaction products of the Mn(VII)-HDPBA aqueous ethanol and extraction system are exactly identical and are different from the reaction product of the Mn(II)-HDPBA aqueous ethanol system as revealed from their differences in the spectral properties and compositions. However the oxidation state of manganese species in the complex formed in the Mn(VII)-HDPBA aqueous ethanol and extraction systems has not been established.

4.5. Photometric Characteristics

The photometric characteristics: The molar absorptivities, photomtric sensitivities, the limits of determination, the concentration ranges obeyed by Beer's law, and the optimum concentration ranges for the photometric determination obtained from Ringbom's plot have been evaluted for the three methods involving Mn(II)-HDPBA aqueous ethanol system in presence of $K_2S_2O_8$ and Mn(VII)-HDPBA aqueous ethanol and extraction systems. The data are summarized in Table 15. The data for the calibration curves are given in Table 16 and the curves are shown in figures 9 and 10.

10. The results obtained show that the sensitivity of the method based on Mn(VII)-HDPBA systems are better than that of the Mn(II)-HDPBA system. In general the proposed methods have good sensitivities and can be applied for the determination of trace amounts of manganese.

The precision of the methods was evaluated by performing six independent analyses made on samples each containing 110 µg of Mn(II) or Mn(VII) per 25 ml in each of the three systems. The results indicate that the precision of the Mn(II)-HDPBA method is somewhat poor, whereas, the Mn(VII)-HDPBA methods are precise and give reproducible results. The results are summerized in Table 17.

Table 12. Results of continous variations method for Mn(II)-HDPBA aqueous ethanol system
C_T = [Mn(II)] + [HDPBA] = 8.0 X 10^{-4}M, p^H = 8

Mole fraction of Mn(II)	Mole fraction of HDPBA	Absorbance at 625 nm
0.0	1.00	0.003
0.1	0.90	0.199
0.2	0.80	0.379
0.25	0.75	0.503
0.30	0.70	0.476
0.33	0.67	0.458
0.40	0.60	0.418
0.50	0.50	0.358
0.60	0.40	0.285
0.70	0.30	0.222
0.80	0.20	0.112
0.90	0.10	0.069
1.00	0.0	0.002

As can be seen from Table 15 the Mn(VII)-HDPBA systems have better sensitivity as compaired to the Mn(II)-HDPBA systems. Of the two Mn(VII)-HDPBA systems further studies have been carried out with Mn(VII)-HDPBA extraction system due to the fact that extraction offers better selectivity over the one-phase homogeneous reaction systems.

Table 13. Results of continuous variations method for Mn(VII)-HDPBA aqueous ethanol and extraction system

C_T = [Mn(VII)] + [HDPBA] = 8.0 X 10^{-4} M, p^H = 8

Mole fraction of Mn(VII)	Mole fraction of HDPBA	Absorbance at 614 nm	
		aqueous ethanol system	extraction system
0.0	1.0	0.004	0.026
0.1	0.9	0.409	0.405
0.2	0.8	0.592	0.525
0.25	0.75	0.525	0.462
0.30	0.70	0.430	0.404
0.33	0.67	0.380	0.364
0.40	0.60	0.300	0.321
0.50	0.50	0.207	0.224
0.60	0.40	0.145	0.167
0.70	0.30	0.102	0.121
0.80	0.20	0.065	0.084
0.90	0.10	0.020	0.052
1.0	0.0	0.001	0.002

Table 14. Results of extraction method for the determination of Mn to HDPBA ratio in the Mn(VII)-HDPBA complex

[Mn(VII)] = 1.6 X 10^{-4}M, p^H = 6

[HDPBA] X 10^4M	log[HDPBA]	Absorbance at 614 nm	$\frac{A}{A_{max}-A}$	$\log\frac{A}{A_{max}-A}$
3.2	-3.49	0.105	0.145	-0.84
4.8	-3.32	0.292	0.549	-0.26
6.4	-3.19	0.534	1.819	0.26
8.0	-3.09	0.675	4.467	0.65
9.6	-3.02	0.739	8.511	0.93
11.2	-3.95	0.774	14.791	1.17
12.8	-3.89	0.790	21.878	1.40

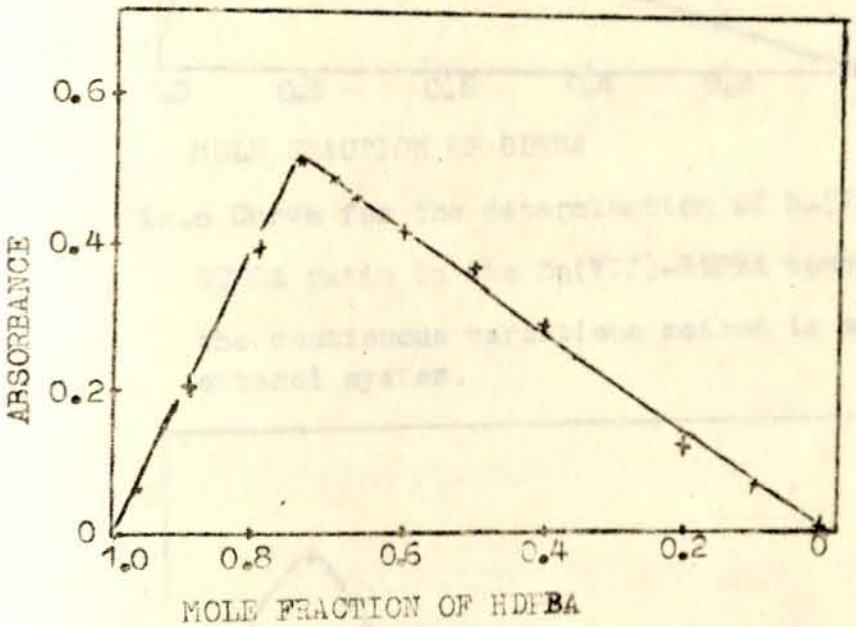


Fig.5 Curve for the determination of Mn(II) HDFBA ratio in the Mn(II)-HDFBA compl the continuous variations method.

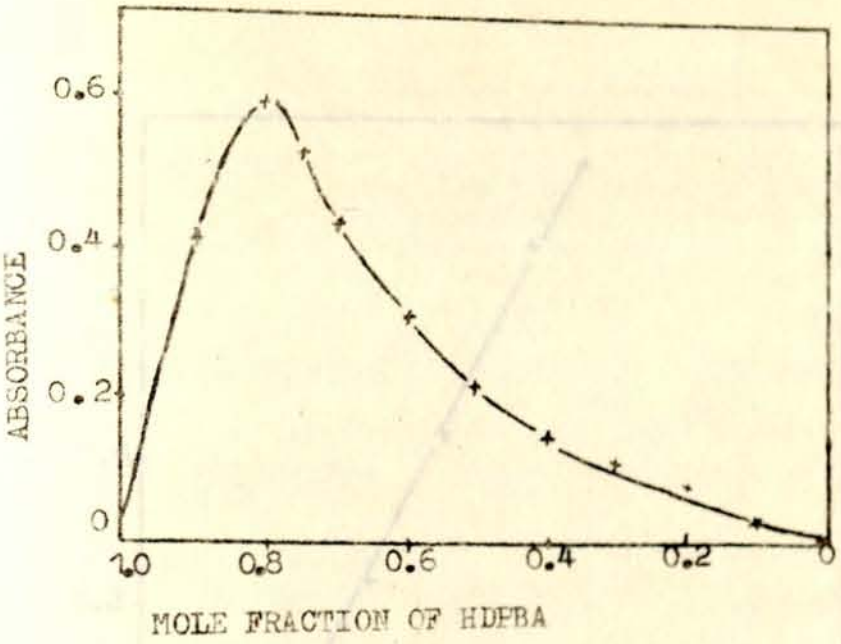


Fig.6 Curve for the determination of Mn(VII
HDPBA ratio in the Mn(VII)-HDPBA comple
the continuous variations method in aqu
ethanol system.

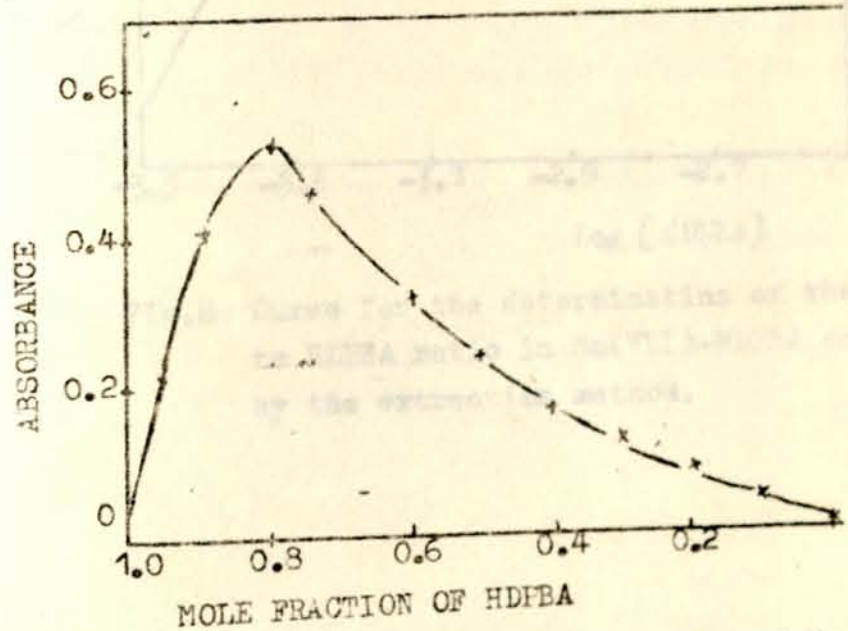


Fig.7 Curve for the determination of Mn
HDPBA ratio in the Mn(VII)-HDPBA com
continuous variations method in extr

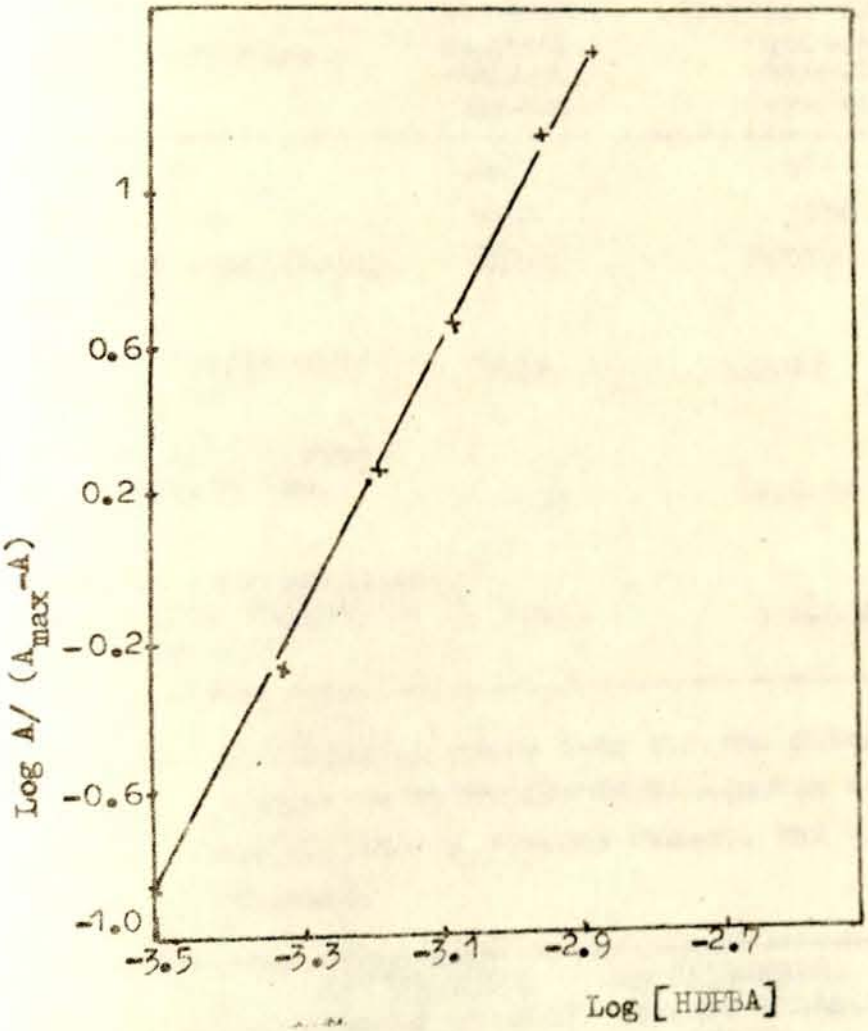


Fig.8 Curve for the determination of the Mn to HDPBA ratio in Mn(VII)-HDPBA comple by the extraction method.

Table 15. Photometric characteristics of the Mn-HDPBA complexes

Characteristics	Mn(II)-HDPBA aqueous - ethanol system	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
λmax, nm	625	614	614
, l mol^{-1} cm^{-1}	4600	5350	5350
Sandell sensitivity, $\mu g\ cm^{-2}$	0.012	0.010	0.010
Limit of determination $\mu g\ ml^{-1}$	0.02	0.02	0.03
Concentration range from Beer's law, $\mu g\ ml^{-1}$	1.1-13.2	0.5-11	0.5-11
Optimum concentration range from Ringbom's plot, $\mu g\ ml^{-1}$	2-10	1.4-8.8	1.4-8.8

Table 16. Calibration curve data for the determination of manganese by Mn(II)-HDPBA aqueous ethanol and Mn(VII)-HDPBA aqueous ethanol and extraction systems.

Concentration of manganese µg/25 ml	Mn(II)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA aqueous ethanol system	Mn(VII)-HDPBA extraction system
	Absorbance at 625 nm	Absorbance at 614 nm	Absorbance at 614 nm
13.74	-	0.052	0.053
27.47	0.089	0.104	0.107
54.94	0.178	0.213	0.214
109.88	0.361	0.424	0.427
164.82	0.533	0.637	0.642
219.76	0.714	0.847	0.856
274.70	0.902	1.065	1.070
329.64	1.051	-	-

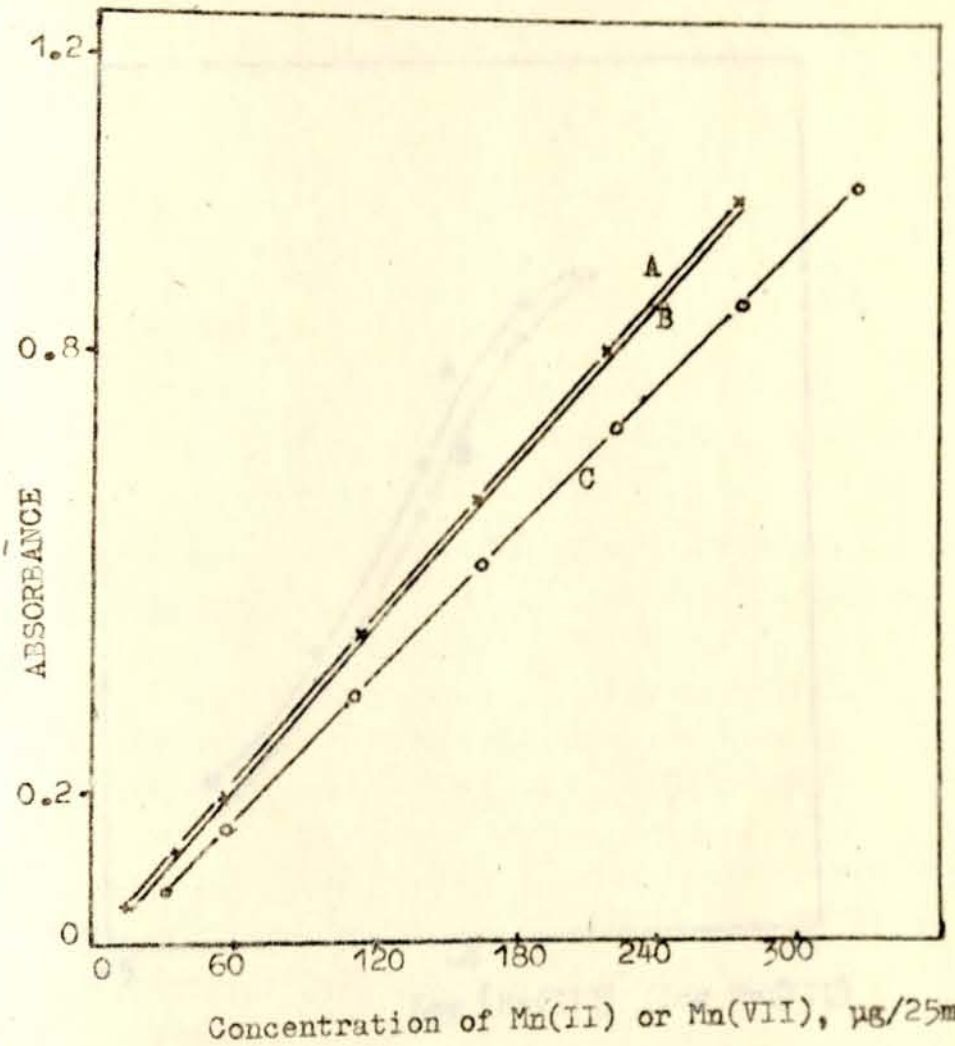


Fig.9 Calibration curve for the determination of manganese (A) Mn(VII)-HDPBA extraction (B) Mn(VI HDPBA aqueous ethanol and (C) Mn(II)-HDPHA aque ethanol systems.

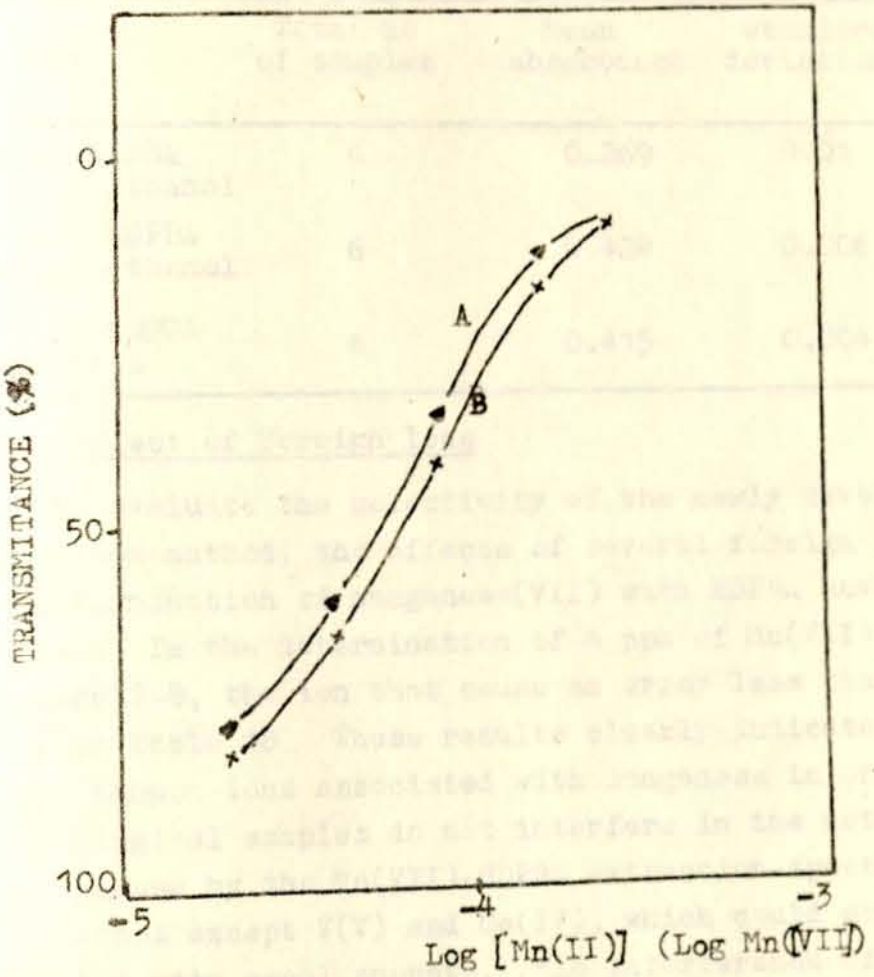


Fig.10 Ringbom's plot for the determination of (A) Mn(VII) and (B) Mn(II)

Table 17. Evaluation of precision of the methods
[Mn(II)] or [Mn(VII)] = 8 X 10^{-5} M
[HDPBA] = 2 X 10^{-3} M, p^H = 8

Method	Total no of samples	Mean absorbance	Standard deviation	Relative Standard deviation(%)
Mn(II)-HDPBA aqueous ethanol	6	0.269	0.01	4.4
Mn(VII)-HDPBA aqueous ethanol	6	0.424	0.006	1.6
Mn(VII)-HDPBA extraction	6	0.415	0.004	0.9

4.6. Effect of Foreign Ions

To evaluate the selectivity of the newly developed extraction method, the effects of several foreign ions on the determination of manganese(VII) with HDPBA have been studied. In the determination of 4 ppm of Mn(VII) in the p^H range 7-9, the ion that cause an error less than 2% are given in Table 18. These results clearly indicate that most of the common ions associated with manganese in ores, alloys, and biological samples do not interfere in the determination of manganese by the Mn(VII)-HDPBA extraction-spectrophotometric method except V(V) and Ce(IV), which could still be tolerated upto equal amounts. The interference of Fe(III) upto 15-fold excess with respect to manganese was overcome by masking it with fluoride.

4.7. Application

To investigate the analytical applicability of the newly developed extraction-spectrophotometric method for the determination of manganese, it has been applied to the analysis of steel, bronze, ferromanganese, manganin and tea-powder samples. Since manganese exists in lower oxidation states in most of its compounds the application has been preceeded by selecting a suitable oxidizing agent for the quantitative oxidation of Mn(II) to Mn(VII).

Table 18. Tolerance limit of foreign ions in the determination of Mn(VII) by Mn(VII)-HDPBA extraction system

Concentration of Mn(VII) = 4ppM , p'_H = 7-8

Ion	Tolerance limit, ppm
[a] Fe^{3+}	2 (60)[b]
[a] VO_3^-, Ce^{4+} (each)	4
Co^{2+}	30
Cu^{2+}, Hg^{2+}, Ni^{2+} (each)	40
[a] $Cr_2O_7^{2-}$	60
Th^{4+}, Zr^{4+}, UO_2^{2+}, Cr^{3+} (each)	160
Sn^{4+}, Ba^{2+} (each)	180
AsO_4^{3-}	260
La^{3+}	270
EDTA, Be^{2+}, Pb^{2+} (each)	320
Cd^{2+}	600
Mg^{2+}	700
Na^+, K^+, Ca^{2+}, Sr^{2+}, Al^{3+}, Zn^{2+}, NH_4^+, NO_3^-, MoO_4^{2-}, SO_4^{2-}, WO_4^-, $S_2O_8^{2-}$, IO_4^-, acetate, tartarate, phthalate, citrate (each)	800[c]
ClO_4^-, PO_4^{3-}, Cl^-, Li^+ oxalate, borate (each)	2000[c]
F^-	4000[c]

a. Causes positive interference when present in amounts greater than the tolerance limit.
b. Masked by 4000 ppm of fluoride ions.
c. Studied upto the indicated amount only.

Oxidation of Mn(II) to Mn(VII). Different oxidizing agents such as PbO_2, $K_2S_2O_8$, $NaBiO_3$, and KIO_4, were examined for the quantitative oxidation of Mn(II) to Mn(VII).

PbO_2 and $K_2S_2O_8$ were found to be unsuitable for the quantitative oxidation of Mn(II) to Mn(VII) because these oxidizing agents lead to incomplete oxidation of Mn(II). Consequently the excess Mn(II) reduces the MnO_4^- formed to Mn(VI), and $MnO(OH)_2$ ppt is formed during the adjustement of pH to 7-8 prior to extraction.

$NaBiO_3$ was found to be effective for the oxidation of Mn(II) to Mn(VII) in strongly acidic medium. However when pH was adjusted to 7-8, the execss $NaBiO_3$, and $Bi(OH)_3$ were precipitated. Thus $NaBiO_3$ was found to be unsuitable for the oxidation of Mn(II) to Mn(VII) and its subsequent determination by the proposed method.

KIO_4 was found to be the most efficient for the quantitative oxidation of Mn(II) to Mn(VII) and therefore it was selected for further studies on the application of the proposed method.

Effect of the Amount of KIO_4. The effect of the amount of KIO_4 on the oxidation of Mn(II) and its subsequent extraction has been studied.

The oxidation was performed with varying amount of KIO_4 while keeping the concentration of Mn(II) constant. It has been found that minimum of 1:15 (Mn:KIO_4) molar ratio was needed for complete oxidation of Mn(II) to MnO_4^- and excess KIO_4 upto 60-fold molar excess gave a similar result. Above 60-fold molar excess, precipitate formation occured during pH adjustement and below 15-fold molar excess oxidation was not complete (Table 19).

It was also found that when extraction was performed the acidic medium (pH 4-7) using the optimum amount of KIO_4, color of the complex changed from green to brown and resulted in a shift of λ_{max} of the complex. However when the Mn(VII) resulting from oxidation of Mn(II) with KIO_4 was extracted at pH 7-8 results obtained were identical with that of standard MnO_4^- (Fig. 2). Therefore the extraction of MnO_4^- from sample solutions was carried out in the pH range 7-8.

To verify the quantitative oxidation of Mn(II) with KIO_4 and its subsequent extraction three samples of permanganate: (i) standard permanganate solution, (ii) standard permanganate solution mixed with periodate solution, and (iii) permanganate solution obtained from the oxidation of Mn(II) with KIO_4, were analyzed and the results obtained were found to be identical (Table 20). These results indicate that excess periodate and its reduction product (iodate) have no adverse effect on the extraction and determination of permanganate with HDPBA.

Table 19. Effect of amount of KIO_4 on oxidation of Mn(II) to Mn(VII) and its determination iwth HDPBA

$[Mn(II)] = 1.5 \times 10^{-4}$M, $[HDPBA] = 2 \times 10^{-3}$M, pH=8

KIO_4 used for oxidation X 10^4 M	$[Mn(II)] : [KIO_4]$	Absorbance at 614 nm
18.8	1:12:5	0.614
22.5	1:15	0.812
30.0	1:20	0.818
60.0	1:40	0.810
82.5	1:55	0.822
97.5	1:65	*

* Could not be extracted because of precipitate formation in the aqueous phase.

Analysis of Alloys Samples. Applicability of the method developed has been evaluated by determining the amount of manganese present in artificially prepared samples whose compositions are given below.

(a) Manganese: 85% Cu, 3% Ni, 1% Fe, and 11% Mn.

(b) Manganese bronze: 4.5% Mn, 0.005% p, 68% Cu, 0.05% Sn, 0.10% Pb, 1.00% Ni, 4% Fe, 7.5% Al, 0.10% Si and 14.7%n.

(c) Ferromanganese: 70% Mn, 7.25% C, 1.25% Si, 0.35% P, and 21.15% Fe.

Table 20. Verification of the quantitative oxidation of Mn(II) with KIO_4 and its subseqent extraction with HDPBA
$[HDPBA] = 4 \times 10^{-3}$ M, $[Mn] : [kIO_4] = 1:20$, pH=8

Concentration of Mn(VII) or Mn(II) X 10^5M	Absorbance at 614 nm		
	Mn(II) oxidized with IO_4	MnO_4^- with added KIO_4	MnO_4^- without KIO_4
1.89	0.093	0.091	0.092
3.78	0.197	0.191	0.199
7.56	0.405	0.400	0.401
11.34	0.606	0.599	0.604
15.12	0.813	0.803	0.807
18.90	1.011	1.041	1.011

(d) Manganese Steel: 12% Mn and 88% Fe.

(e) Alloys Steel Sample No. 241/1: 19.61% W, 5.03% Cr, 0.52% Mo, 1.57%V, 5.67% V, 5.67% Co, 0.85% C, 0.33% Si, 0.075% Ni, 0.10% Cu, 65.87% Fe, and 0.295% Mn.

Of these samples the alloys steel sample No. 241/1 was analyzed by the standari adlition technique since the ratio of Fe to Mn(226:1) was above the masking limit (15:1). The results of the analysis are summerized in T Table 21.

Analysis of Tea Extracts. The proposed method has also b been applied to the analysis of water extract of a commercial tea sample for its manganese content. The manganese content of the tea extract was also determined by AAS as a standard method to compare the results obtained by the newly developed method. The results are summerized in Table 22.

These results indicate that about 90% of manganese from tea powder is being extracted into water within 5 minutes and prolonged and successive boiling increases the extraction of manganese only slightly. The results obtained a also indicate that every cup of tea, i.e. prepared by boiling 3 g of tea powder in 300 ml of water contains about 0.96 mg of manganese.

In gereral, the experimental results are in good agreement with the actual values and/or with the results obtained by AAS method. Hence, the newly developed method is precise and reliable and can be applied for the determination of manganese in diverse samples.

4.8. Comparison with Other Spectrophotometric Methods

A comparative study of the proposed methods for the determination of manganese with the recently reported spectrophotometric methods in regard to sensitivity and selectivity interms of molar absorption coefficient and interference, are summerized in Table 23.

Table 21. Determination of manganese in synthetic alloys samples

No.	Sample	Mn added (%)	Mn found* (%)	RSD (%)	Relative error (%)
1	Manganin	11.00	10.94	0.90	0.58
2	Manganese bronze	4.50	4.49	0.62	0.24
3	Ferromanganese	70.00	70.45	0.65	0.64
4	Manganese Steel	12.00	11.94	0.70	0.50
5	Alloys steel sample No. 241/1	0.295	0.29	0.55	1.7

* Average of triplicate analyses.

Table 22. Determination of manganese in tea extract . (3% of tea powder exteacted with 300 ml boiling water)

Extraction condition	*Mn found, µg/g tea	
	Proposed method	AAS method
Single extraction for 5 minutes	320	325
First extraction for 20 minutes	340	346
Second extraction for 20 minutes	19	19
Third extraction for 20 minutes	9	9
Precision, RSD(%)	0.7	3

* Average of triplicate analyses.

Table 23 shows that the proposed extraction-spectrophotometric method for the determination of manganese is fairly sensitive and highly selective as compared to most of the methods. Thus the proposed method can be selected as a method for the determination of manganese in diverse samples.

Table 23. The sensitivities and selectivities of recently recommended spectrophotometric methods for manganese determination

Reagent	λ_{max}, nm, $l\ mol^{-1}\ cm^{-1}$	pH	Interfering ions	Reference
2-(5-bromo-2 pyridylazo)-5-diethylaminophenol	575 127,000	8,5	Cu(II),Co(II), Ni(II),Zn(II), Cr(III,V(IV), Ti(IV)	17
Thiothenoyltrifluoroacetone	375 35,800	7.3	Zn(II),Cd(II), Cu(II),Co(II)	13
4-(2-thiazoylazo) resorcinol	540 2-12[a]	8.8	EDTA, Co(II),Zn(II) Cd(II),Pb	19
N^1-Hydroxy-N^1-m-tolyl-N2-(23-xylyl) benzamidine hydrochloride	610 4400	9.4-10.1	EDTA, oxalate Cu(II),Pd(II) Ni(II),V(V),Co (II), Fe(III)	20
$2,2^1$-Bipyridyl with nitrophenylazocatechols	525 58,000	10	Zn(II),Co(II), Ni(II),Cd(II), EDTA,$P_2O_7^{4-}$	15
Isophthalohydroxmic acid	490 3,760	b	Fe(III),Sn(II) Sb(III),Bi(III), Ru(III),Rh(III)	23

Table 23 contd.

Reagent	λmax, nm, $l\ mol^{-1}\ cm^{-1}$	pH	Interfering ions	Reference
1-(2-Quinolylazo) -2,4,5-trihydroxy-benzene	575 67,000	9.2	b	22
N^1-Hydroxy-N^1,N^2-diaryl substituted-p-toluamicines	620-635 5220-7550	8.5-10	xalate, EDTA, Cu(II), Ni(II), Cu(II), Nd(II), Fe(II)	10
Ethylene-bis (triphenyl-phosphomium) cation	548 2380	6	Cyanide, EDTA thiosulphate and reducing agents	12
Salicylaldoxime	410 1-7[a]	9.2	Cu(II), Co(II), Ni(II), Zn(II), Cr(III), V(IV), Ti(IV).	16
K-butylxanthate	457 2-10[a]	6.5-9	b	14
N^1-Hydroxy-N^1,N^2-diphenylbenzamidine extraction method	614 5350	3.5-9.5	Fe(III)[c], V(V) &[d] Ce(IV)	Proposed method

a Linear range, $\mu g\ ml^{-1}$, [b]Not given. [c]Masked by fluoride.

[d]can be tolerated upto amounts equal to manganese.

5. CONCLUTION

N^1-Hydroxy-N^1,N^2-diphenylbenzamidine (HDPBA) has been found to react with both Mn(II) and Mn(VII) under different conditions forming different complex species.

A new method based on the complex formation of Mn(VII) with HDPBA have been developed for the determination of manganese by solvent extraction and spectrophotometry. The method is simple, precise, accurate, and free from the rigid control of experimental variables. The method is also fairly sensitive and highly selective and could be applied for the determination of trace amount of manganese in diverse samples.

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D E C L A R A T I O N

I, the undersigned, declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

Dejene Ayele

Signature _____

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