C H A P T E R-IV

PHOTOMETRIC DETERMINATION OF MANGANESE (II) WITH 2CHLOROQUINOLINE 3 - CARBALDEHYDE THIOSEMICARBAZONE

INTRODUCTION

Manganese appears to have been used by the ancient Egyptians and Romans for bleaching glass, for their glass often contains the equivalent of up to 2 per cent manganese oxide. J.H. Pott (1740) proved that pyrolusite proper does not contain iron, and furnishes a number of salts quite different from those obtained with iron oxides. C.W. Scheele (1774) made an important investigation on manganese, and T. Bergman (1774) suspected that some metal lay concealed in the mineral earth which he reduced with charcoal, so obtaining a metal regulus. A purer sample was isolated by J.F.John in 1807.

The metal Manganese does not occur free in nature. Manganese is largely used in the form of spiegeleisen and ferromanganese, and this is made by reducing a mixture of oxides of manganese and iron with carbon in a blast furnace. The pure metal is made by distilling a sample obtained by the aluminothermic or electrolytic methods.

The literature survey since the introduction of organic colourimetric reagents indicates a very striking lack of reports on estimation of Manganese. It may not be surprising if one states that a realy reliable method using organic complexing agent is yet to be developed. Oxidation of Manganese to Mn(VII) state and subsequent measurement of the charge transfer band at 575 nm is the only available method for the determination of manganese. However, recently some methods are reported to determine manganese in Mn(II) or Mn(III) states, of which 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone is one suitable photometric reagent for the determination of Manganese in Mn(II) state.

Manganese is essentially used in steel manufacture for deoxidation and the control of sulphur content. Manganese is vital to plant and animal life and is essential for reproduction in animals. Manganese is used in Ferroalloys like Ferro-Manganese containing 74-82 %, Spiegeleisen 16 to 20 % Silicomanganese 65-70 % and austenitic stainless steels 8 to 10 % manganese. Practically all commercial alloys of aluminium and magnesium contain manganese to improve corrosion resistance and mechanical properties. The presence of manganese in titanium improves the strength and workability of this light metal. An extremely high ability to damp variation is possessed by binary copper manganese alloys. Organic compounds of manganese are used in paints and varnishes as driers to promote the absorption of oxygen which causes paint to set. Manganese sulphate is used alone and admixed with fertilizers to supply trace quantity of manganese in agriculture.

Morgan and Stuman[1] have reviewed the spectrophotometric methods for the determination of Manganese in 1965. Some more spectrophotometric methods for manganese have been reported afterwards. Of the reported methods so far, some are summarised here. Due to numerous interferences reagents : benzohydroxamic acid[2], 2-theonyltrifluoroacetone[3], 4-(2-pyridylazo) resorcinol[4], gluconic acid[5], thiothenyltri Fluroacetone[6], cacotheline[7], and 4-phenyl-3-thiosemicarbazone of biacetylmonoxime[8] are not selective. Due to less kinetic stability complex formation is slow in case of leucomalachite green[9], acetaldoxime[10], tetraphenyl arsonium chloride[11] and Salicylic acid or acetylsalicylic acid[12]. Due to low thermodynamic stability in case of bismuthate[13], telluric acid[14], calcichrome[15], brucine[16] and cacotheline[17] complex is formed at elevated temperature.

4.1 Review of the Methods for the determination of Mn(II)

Reagent	pH	λmax	Molar extinction coefficient, Sandell sensitivity, Beer's law.	Interference	Reference
1	2	3	4	5	6
Formaldoxime	-	-	ϵ = 11,200 Beer's law is obeyed upto 0.1 to 30 μg Mn/ml.	Cu,Ni,Co interfere.	20
Acetaldoxime	-	520	-	Mg interferes but no interference by Cu, Ni,Co, V and Fe.	21
Xylenol orange	6.6 to 6.8	580	Beer's law is obeyed over the range 3-70 μg/25 ml.	-	22
1(-2 pyridylazo)-2-Naphthol	9.2	562	-	Zn, Pb, Co do not cause appreciable error.	23
Calcichrome	8 to 12	308 and 525	-	Many metals interfere.	24
5-hydroxy-6-(3-{1-methyl-2-piperidyl}2-pyridylazo) naphthalene-1-sulphonic acid (MAAN-5-1,5).	7 to 10	600	Sandell sensitivity is 0.0016 μg Cm^{-2}. Beer's law is obeyed for 5 to 50 μg.	-	25

1	2	3	4	5	6
{5-amino-2-[3-(1-methyl-2-piperidyl)-2-pyridylazo] phenol}	9.75	520	ϵ = 75, 740 Beer's law is obeyed for 0.08 to 0.1 µg per ml.	Cu, Ni, Co, Zn, Cd, Ti and In strongly interfere but Al, Sb, Ga, W can be tolerated.	26
M-gluconic acid	12.6	440	-	Cu(II), Co(II) and Ce(IV), interfere.	27
Alizarin complexan	-	570	-	-	28
Methyl thymol blue Xylenol orange 4-(2-pyridylazo)-resorcinol Salicylfluorone	- - - -	582 582 490 540	Beer's law is obeyed for 1.9 to 9.7 µg per litre.	-	29
acetyl salicylic acid	-	385	Beer's law obeyed for 0.005 to 0.0125 µg/ml.	Various ions interfere.	30
5,7 dichloro-8-hydroxyquinoline-Rhodamine 6 G	-	540	ϵ = 70,000	-	31
Salicylaldehyde isonicotynoylhydrazone	-	390-400	ϵ = 15,000 to 25,000 Beer's law is obeyed for 0.5 to 3 ppm	-	32

1	2	3	4	5	6
Salicylaldehyde benzoylhydrazone	-	390-400	ϵ = 15,000 to 25,000 Beer's law is obeyed for 0.5 to 3 ppm	-	33
Xylenol	6.85	580	Beer's law is obeyed over the range 0-0.16 ppm for complex (1:2) (M:L) and 0.16-0.43 ppm for complex (1:1).	-	34
disodium 1,2-diamino propane tetra-acetate	-	490	Beer's law is obeyed for 7 mg.	-	35
4-(2-pyridylazo) resorcinol	10.0	510	ϵ = 45,000 Beer's law is obeyed for upto 0.8 $\mu g\ ml^{-1}$ Sandell sensitivity is 0.0012 $\mu g\ Cm^{-2}$	Fe, Cu and V interfere.	36
3,6-bis-(4-carboxy phenylazo) Chromotropic acid.	-	720	ϵ = 150,000	Pyridine and Hydrazine interfere.	37
4-(2-pyridylazo) resorcinol	10.0	500	- Beer's law is obeyed for 0.1 to 1.3 $\mu g\ ml^{-1}$	-	38

1	2	3	4	5	6
1-(2-thiazolyazo)-2-Naphthol	9.2 to 9.8	565 to 585 nm	ϵ = 38,000	Fe, Co, Ni interfere.	39
8-hydroxy-7-phenyl-azoquinoline-5-sulphonic acid.	6.6 to 7.7	430	ϵ = 16,100	-	40
8-hydroxy-7-(2-thiazolylazo) quinoline	5.8 to 6.7	510	ϵ = 39,000	-	41
3,6-bis-(4-carboxyphenylazo) chromotropic acid	-	720	ϵ = 170,000	-	42
Dicyclopentadienyl-dithienylnibonium (in acetone)	-	546	-	-	43
Binazine (tatrazoline - hydrochloride)	10	420	Beer's law is obeyed for 0.2 to 15 $\mu g\ ml^{-1}$	Cu(II), Fe(III), Co(II) and Ni(II) interfere.	44
Periodate	-	525	Beer's law is obeyed for 0.2 to 20 $\mu g\ ml^{-1}$	Fe(III),Co(II),Cr(VI) can be tolerated.	45

1	2	3	4	5	6
N-m-tolyl-N'-2,5 xylyl-P-toluiamidine	9	620-635	Sandell sensitivity is 0.007 - 0.01 μg Cm^{-2}. Optimum analytical range 1.6 to 10 ppm.	-	46
N-hydroxy-N-phenyl-N'-benzyl-benzamide hydrochloride	8.4-9.3	590	ϵ = 5330 Beer's law is obeyed for upto 10 μg ml^{-1}	Ni, Co, Fe(III), Cu(II), Pd(II), V(V), interfere.	47
A) dithiozone B) 1-10 phenanthroline	-	507	ϵ = 46,000 Sandell sensitivity is 1.1 ng Cm^{-2}	-	48
Pyrophosphate in presence of($Na_4 P_2 O_7$)	5.3 to 8	480	ϵ = 105	-	49
Thiothenoyltrifluoro acetate	-	660	-	-	50
2'-Hydroxy-4',5'-dimethylacetophenone	5-6	560	-	-	51
3'-bromo-2'-hydroxy-5'-methylacetophenone	4-5	560	-	-	52

1	2	3	4	5	6
2'-hydroxy-3'-5'-dimethylacetophenone oxime	9.0 to 10.0	405	ϵ = 1300 Beer's law obeyed for 1-12 ppm	-	53
Salicylaldoxime	9.5	430	-	Fe interferes.	54
2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol	-	575	ϵ = 127,000	-	55
N^1-hydroxy-N^1-m-tolyl-N^2-(2,3-xylyl) benzamidemide hydrochloride.	9.4 to 10.1	610	ϵ = 4400 Sandell sensitivity is 12 ng Cm^{-2}	Co(II), Fe(III), VO_3^- interfere seriously.	56
Salicyldoxime	9.2	410	Beer's law is obeyed for 1 to 7 $\mu g\ ml^{-1}$	-	57
(d-5,10,15,20 tetrakis-(4-carboxyphenyl) porphine).	alkaline	469	ϵ = 97,900 Beer's law is obeyed for 25-560 $\mu g\ ml^{-1}$	-	58
1-(1,2,4-triazol-3-ylazo)$_2$-Naphthol	8	515	Beer's law is obeyed for 0 to 2.5 ppm	-	59
(1,1,1-trifluoro-4-mercapto-4-(2-thienyl) but-3-en-2-one) and 1,10 Phenanthroline	-	375	ϵ = 35,800	Cd,Zn,Cu(II),Co(II) interferes.	60

1	2	3	4	5	6
4-(2-thiazoylazo) resorcinol	8.8	540	-	Co(II),Zn,Cd and Pb(II) interfere seriously.	61
2-3 diphenylsuccinimide monoxime	-	490	Beer's law obeyed for upto 14 ppm	-	62
K-butyl Xanthalate	-	457	$\epsilon = 5500$	V(V) and Fe(III) interfere.	63
2',3',6',7'-tetrahydroxyspiro-{isobenzofuran-1(3H),9(9H) Xanthen}-3-one.	9	535	Sandell sensitivity 0.38 ng Cm^{-2}	-	64
Alizarin complexan	5.5	555	Beer's law obeyed upto 59.3 ppm	-	65
2-Oximinodimedone dithiosemicarbazone	9	435	$\epsilon = 5.9 \times 10^3$	-	66
-do-	0 to 2	380	$\epsilon = 1.0 \times 10^4$		
-do-	$HClo_4$ (.4 to 1 M)	490	$\epsilon = 5.6 \times 10^3$		
α, β, γ, δ-tetrakis (4-trimethylammonium phenyl) porphyrin (TAPP)	-	464	$\epsilon = 1.13 \times 10^5$	Cr(III),Cu(II),Co(II) interfere at high concentration.	67

1	2	3	4	5	6
4-(5)-imidazoleadoxime (IMALOX)	Alkaline	350	$\epsilon = 7.85 \times 10^3$ Beer's law obeyed for 0.8-8.0 µg/ml	Few ions interfere & can be masked with CN^-, NTA, tartarate.	68
Isophthaldihydroxamic acid.	-	490	$\epsilon = 3760$ Optimum range for determination 3-9 ppm.	Fe,Sn,Sb,Bi,Ru and Rb greater than 5 ppm interfere.	69
O-phenanthroline(1) chrome Azurol S(II) and cetyltrimethylammonium bromide(III).	10.2 to 11.3	635	$\epsilon = 8.0 \times 10^4$	Rare earths interfere.	70
α, β, γ, δ - tetrakis (4-sulphophenyl) porphine.	7.8 to 11.0	442	$\epsilon = 3.2 \times 10^5$ Beer's law obeyed for 0-0.125 µg Mn/L	Various ions interfere.	71
dipicolinedihydroxamic acid.	-	500	$\epsilon = 4.1 \times 10^3$ Beer's law obeyed for 0.5 to 5 ppm.	-	72

For some specific applications some of the reported reagents like MAAN-S-1,5[18], 4-(2-pyridylazo) resorcinol[19a] and 1-2 (thiozolylazo)-2-naphthol[19b] posses merit with respect to sensitivity, selectivity and thermodynamic stability.

The detailed study of reported photometric method for manganese determination is given in table 4.1.

The reagent QAT is proposed in this section for trace determination of manganese.

The present work accounts for spectrophotometric determination of Manganese (II) by -2-Chloroquinoline -3-carbaldehyde thiosemicarbazone (QAT). Manganese (II) forms yellow coloured complex with 2 - Chloroquinoline -3-carbaldehyde thiosemicarbazone (QAT). For Manganese optimum pH is 7.5 and λmax is 375 nm. Beer's law is obeyed upto 6 ppm of Manganese (II). The effect of pH, reagent concentration, and diverse ions have been studied. The molar absorptivity and Sandell sensitivity are 2.471×10^4 L $mole^{-1}$ cm^{-1} and 0.024 ng cm^{-2} respectively at 375 nm. The dissociation constant of complex Mn (II) - QAT is 1.479×10^{-5}. For Mn (II), Cu (II), Ni (II), Co (II), pyridine, hydrazine, Rare earths interefere.

EXPERIMENTAL

Standard Manganese Solution :

Standard Manganese solution 1 mg/ml was prepared from Manganese sulphate monohydrate and the solution was standardized volumetrically[73]. Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

Reagent Solution :

0.052 gm QAT was dissolved in DMF and diluted to 100 ml. The molarity of the solution is 1.96×10^{-4}M. The solution is found to be stable for more than a week.

Recommended Procedure :

To an aliquot of solution containing upto 5 ppm of Manganese, add 1.2 ml of the 1.96×10^{-4} M reagent solution and a buffer of solution 7.5. This is diluted to 10 ml with DMF and water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

Spectral Characteristics :

Figure 4.1 shows the absorption spectrum of the Manganese(II) - QAT complex containing 3.196×10^{-4} M of

Manganese (II) and 1.96 x 10^{-4} M reagent at pH 7.5 using reagent blank. Absorption measurements were made in the spectral region 345 nm to 410 nm and recorded in table 4.2. From the graph, it was found that 375 nm will be suitable wavelength for the Mn determination. The molar absorptivity of the complex is 2.417 x 10^{4} L $mole^{-1}$ cm^{-1} at 375 nm.

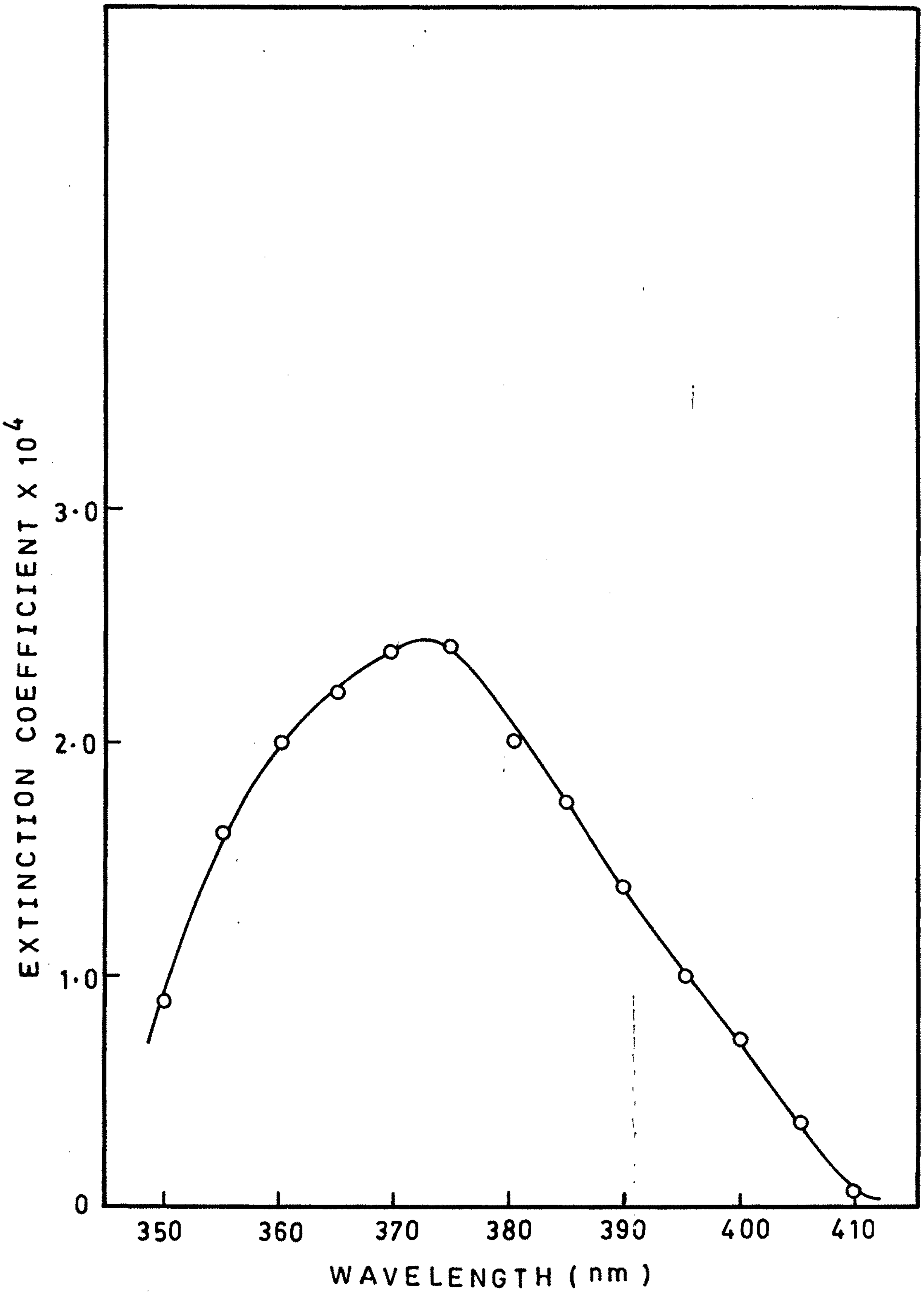
Table 4.2 : Molar Extinction Coefficients of Mn(II)-QAT Complex

QAT = 1.96 x 10^{-4}M, Mn(II) = 3.196 x 10^{-4}M

pH = 7.5

λ nm	Molar Ext. Coefficient of the complex x 10^{4} L $Mole^{-1}$ cm^{-1}
345	-
350	0.9063
355	1.648
360	2.060
365	2.253
370	2.417
375	2.417
380	2.087
385	1.758
390	1.429
395	1.098
400	0.7691
405	0.3846
410	0.1098

FIG. 4·1 – ABSORPTION SPECTRUM OF Mn(II) – QAT COMPLEX.



Effect of Time on absorbance :

In order to study effect of time on the absorbance of Mn(II)-QAT complex containing 3.196 x 10^{-4}M Mn(II)-QAT at pH 7.5, the absorbance measurements were recorded at different time-intervals at 375 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 24 hours.

Effect of Reagent Concentration :

Solutions containing the same amount of Mn(II) (3.196 x 10^{-4}M) but different amounts of reagent varying from 0.1 to 1.4 ml of 1.96 x 10^{-4}M reagent solutions were prepared. The pH 7.0 was added and the solution was made upto 10 ml with the DMF : water (3:2). Absorbance measurements were recorded at 375 nm against simultaneously prepared reagent blank. The data given in table 4.3, fig. 4.2 shows that 3.196 x 10^{-4}M Manganese solution required minimum 1.2 ml of 1.96 x 10^{-4}M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in absorbance. However, 1.2 ml of 1.96 x 10^{-4}M reagent solution was employed for further studies to ensure maximum colour intensity of the Manganese complex.

Table 4.3 : Effect of Reagent Concentration on the absorbance of Mn(II)-QAT Complex

Mn(II) = 3.196×10^{-4}M

QAT = 1.96×10^{-4}M

pH = 7.5

Reagent ml	Absorbance at 375 nm
.2	.04
.4	.08
.6	.16
.8	.25
1.0	.34
1.2	.420
1.4	.422

Effect of pH :

A series of solutions containing (3.196×10^{-4}M) Mn(II) and 1.96×10^{-4}M reagent solution but varying in pH from 2 to 10 were prepared and the absorption measurements were recorded at 375 nm. The results are summerised in the table 4.4. It was observed that maximum absorbance was obtained i at the pH 7.5. The absorbance of the solutions decrease at higher or lower pH values than this as shown in the figure 4.3. Hence pH 7.5 is maintained in further studies.

Table 4.4 : Effect of pH on the absorbance of Mn(II)-QAT Complex

$Mn(II) = 3.196 \times 10^{-4} M$, $QAT = 1.96 \times 10^{-4} M$

pH	Absorbance at 375 nm
4	.04
5	.06
6	.20
7	.35
7.5	.42
8	.39
9	.33
10	.26

Validity of Beer's Law and Sensitivity :

The solutions (final volume 10 ml) containing different amounts of Mn and the same amount of the reagent (Concentration $1.96 \times 10^{-4} M$) 1 ml; with the pH maintained at 7.5 were used for the study. The absorption measurements were recorded against reagent blank at 375 nm (Table 4.5, Fig.4.4). Beer's law is obeyed upto 6 ppm of Mn(II). The Sandell sensitivity[74] of the reaction is 0.024 ng/cm^2 of Mn(II). The Ringbom's plot (Fig.4.5) indicates that the optimum range is 3 to 7 ppm of Manganese(II).

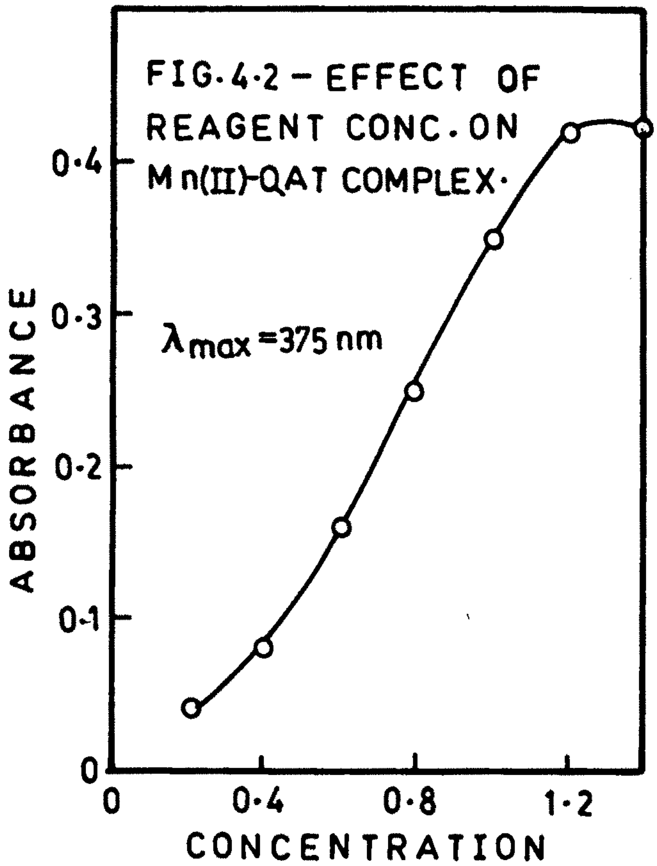


FIG.4·2 – EFFECT OF REAGENT CONC. ON Mn(II)-QAT COMPLEX.

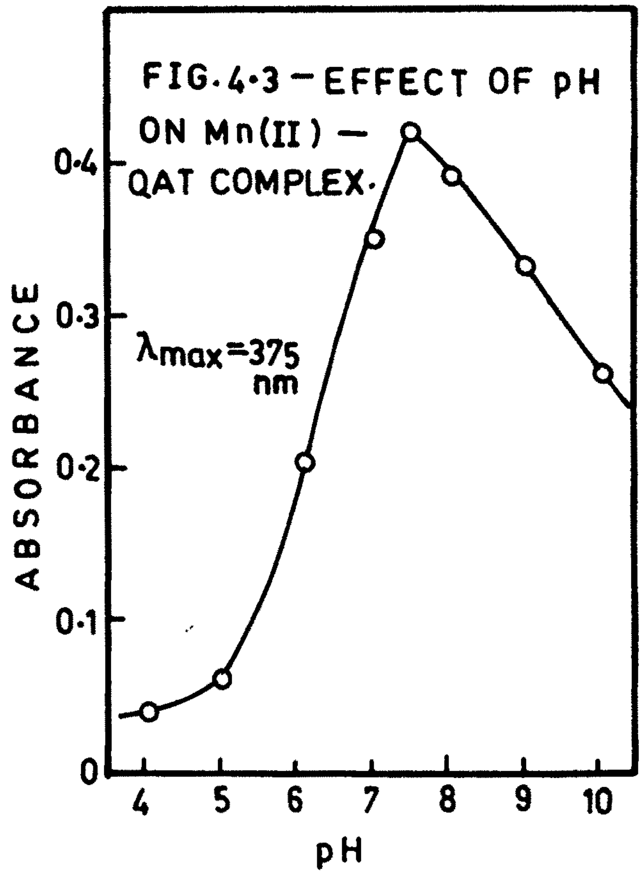


FIG.4·3 – EFFECT OF pH ON Mn(II) – QAT COMPLEX.

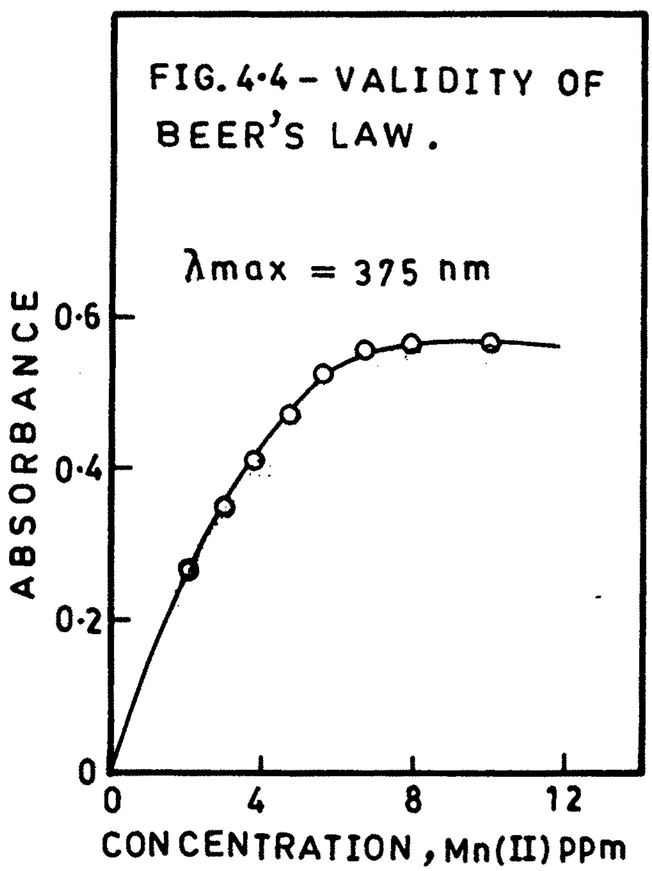


FIG. 4·4 – VALIDITY OF BEER'S LAW.

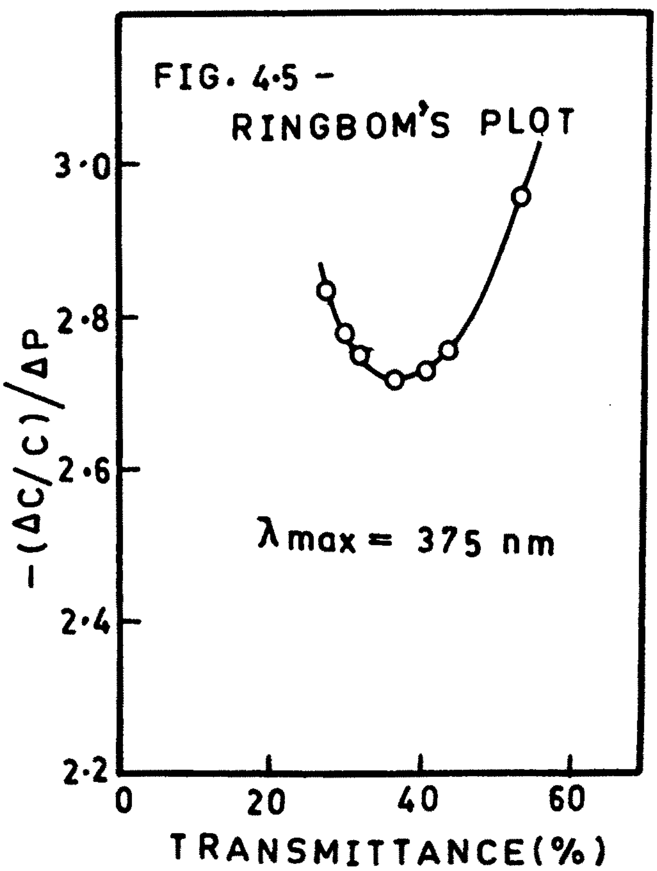


FIG. 4·5 – RINGBOM'S PLOT

Table 4.5 : Verification of Validity of Beer's Law for Mn(II)-QAT Complex

QAT = 1.96 x 10^{-4} M; pH = 7.5

Mn taken ppm	Absorbance at 375 nm
2	.27
3	.35
4	.39
5	.44
6	.50
7	.52
8	.540
10	.548

Composition of the Complex :

The combining ratio of metal to reagent was ascertained by Job's method of continuous variations[75] and Mole ratio method[76]. For Job's method of the continuous variation, a series of solution were prepared by mixing equimolar solutions of Mn(II) and reagent (1.96 x 10^{-4}). The pH of the solution was adjusted to 7.5. The absorbance of the solutions after diluting to 10 ml in volumetric flask were recorded at 375 nm against simultaneously prepared reagent blank (Fig. 4.6, Table 4.6). The plot indicates the existance of 1:2 complex with respect to metal and reagent represented as ML_2.

Table 4.6 : Determination of the formula of the Mn(II)-QAT Complex by Job's Method of Continuous Variation

Mn(II) = QAT = 1.96 x 10^{-4}M, pH = 7.5

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 375 nm
0.1	.9	.1	.21
0.2	.8	.2	.35
0.3	.7	.3	.60
0.4	.6	.4	.54
0.5	.5	.5	.43
0.6	.4	.6	.35
0.7	.3	.7	.29
0.8	.2	.8	.20
0.9	.1	.9	.15

The dissociation constant of the complex K, is calculated from the mole ratio plot by using the following equation :

$$K = \frac{\alpha c(n \alpha c)}{c (1-\alpha)}$$

Where $n = 2$,

c = molarity of the solution of the complex

α = degree of dissociation defined by

$$\alpha = \frac{Am - As}{Am}$$

A_m is the maximum absorption obtained from horizontal portion of the curve and A_s is the absorbance at stoichiometric molar ratio of reagent to Manganese in the complex. The value of k comes out to be 1.479×10^{-5}.

Mole Ratio Method :

For Mole ratio method, solutions containing the same final metal concentration (1.96×10^{-4}M) and different amount of reagent were prepared keeping pH at 7.5. Absorbance of the solutions were measured at 375 nm against reagent blank. The curve showed break at the metal to ligand ratio 1:2, confirming the results obtained by application of Job's method of continuous variations. (Fig. 4.7, Table 4.7).

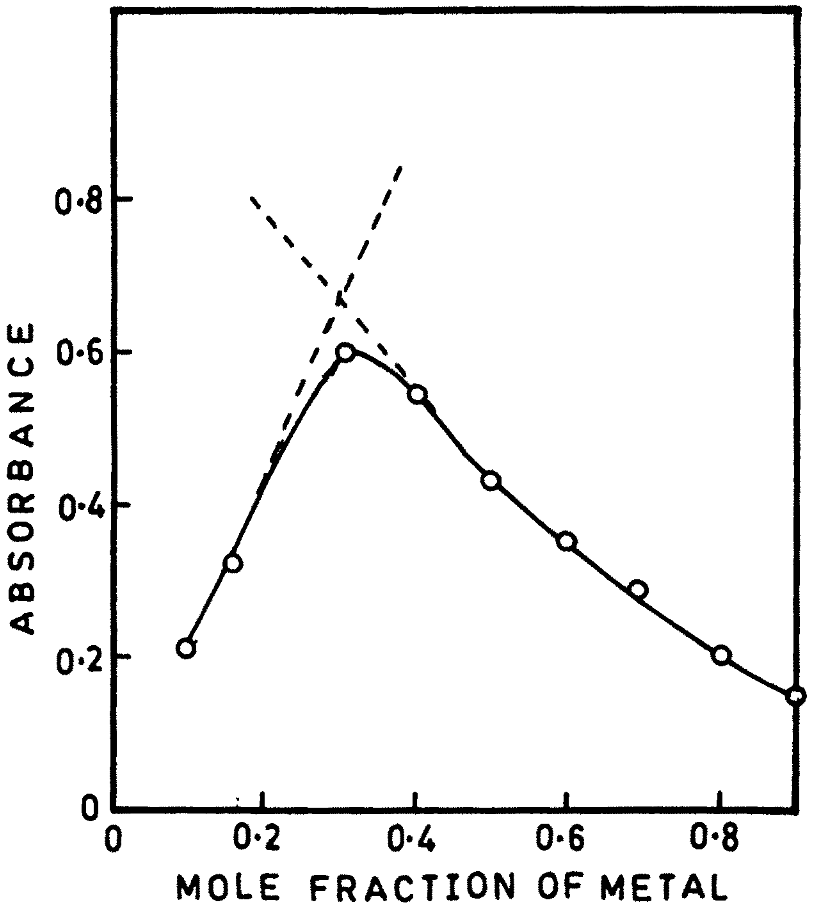


FIG. 4·6 — JOB'S PLOT FOR Mn(II)-QAT COMPLEX.

λ_{max} = 375 nm

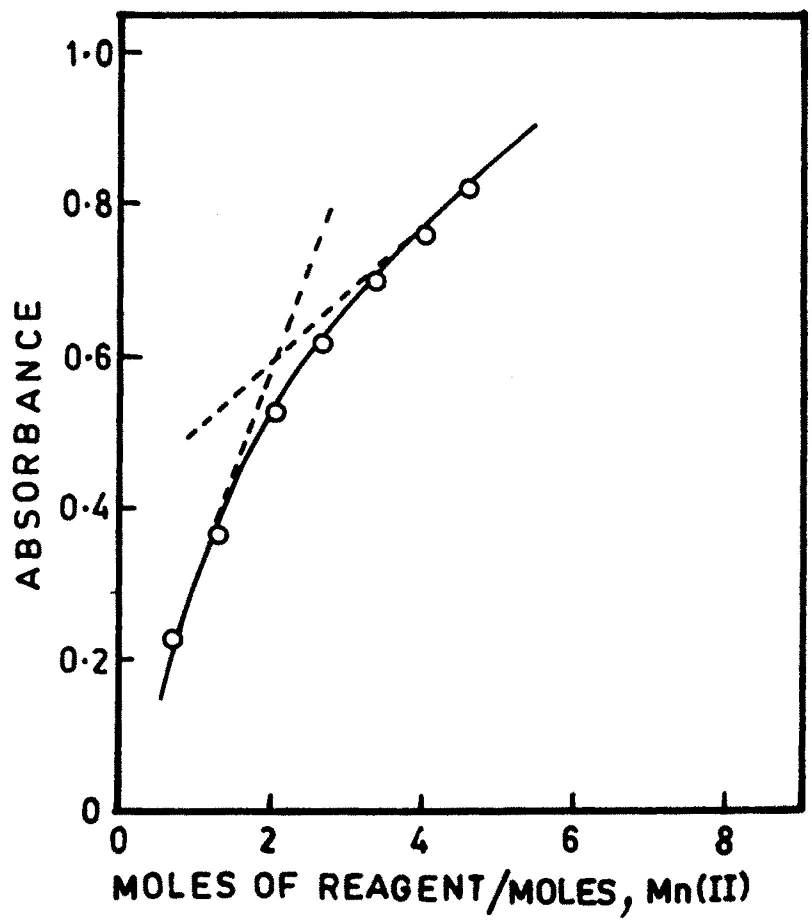


FIG. 4·7 — MOLE RATIO PLOT FOR Mn(II)-QAT COMPLEX.

λ_{max} = 375 nm

Table 4.7 : Determination of the formula of $Mn(II)$-QAT Complex by Mole Ratio Method

$Mn(II) = QAT = 1.96 \times 10^{-4} M$, pH=7.5

Metal ion ml	Reagent ml	Reagent to metal ratio	Absorbance at 375 nm
.3	.2	0.66	.22
.3	.4	1.33	.36
.3	.6	2.0	.53
.3	.8	2.66	.62
.3	1.0	3.33	.70
.3	1.2	4.00	.76
.3	1.4	4.66	.82

Effect of diverse ions :

The effect of diverse ions was studied using 2 ppm of Mn and 1.96×10^{-4} M reagent in a final volume of 10 ml at pH 7.5. The results indicated that Zn(II), Pd(II), Ni(II) and anions like cynide interfere strongly. The tolerance limit for various foreign ions tested has been shown in the table.

Effect of diverse ions :

Mn(II) = 2 ppm, QAT = 1.96×10^{-4}M, pH=7.5

Metal ion	Tolerance limit µg
V(V)	100
Ni(II)	None
Zn(II)	None
Mo(VI)	200
W(VI)	200
Pd(II)	None
Co(II)	200
Oxalate	1000
Pt(IV)	20
CN^-	None
F^-	1000
EDTA	None

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