

C H A P T E R - I I I

DETERMINATION OF MANGANESE

### 3.1 INTRODUCTION

The literature survey indicates a very striking lack of reports on estimation of manganese. Really a reliable method using organic complexing agent is yet to be developed. However, recently some methods are reported to determine manganese in Mn(II) or Mn(III) states. Salicylaldehyde guanylhydrazone is one suitable photometric reagent for the determination of manganese in Mn(II) state.

Manganese is used in metallurgical industries.<sup>1</sup> Manganese containing rocks (brown stone) are on ancient use in pottery and glass making.<sup>2</sup> Manganese is also used for manufacture of superhard alloy composite blades.<sup>3</sup> Manganese is essentially used in steel manufacture for deoxidation and the control of sulfur content. High strength tough steel plates are manufactured from manganese.<sup>4</sup> Stainless steel used for razor,<sup>5</sup> contains 1-4% Mn. Manganese is vital to plant and animal life and is essential for reproduction in animals. Manganese is used in ferroalloys like ferromanganese containing 74-82%, spiegeleisen 1.6 to 20%, silicomanganese 65-70% and austenitic stainless steel 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 vibrations 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 paints to set. Manganese sulphate is used alone and admixed with fertilizers to supply trace quantity of manganese in agriculture.

Manganese is determined complexometrically in ores with thiomalic acid indicator.<sup>6</sup> Semimicro quantity of Mn is determined in drinking water by using formaldoxime.<sup>7</sup> Manganese is determined with  $\beta$ -diketones<sup>8</sup> by HPLC method. By gas chromatography Mn(II) and Mn(III) are determined with trifluoroacetylacetone.<sup>9</sup>

Morgan and Stumm<sup>10</sup> have reviewed the spectrophotometric methods for the determination of manganese in 1965. Some more spectrophotometric methods have been reported afterwards. Manganese(II) is determined by extractive photometric methods with xanthates,<sup>11</sup> 1-(2-thiazolyazo)-2-naphthol,<sup>12</sup> thiothenoyltrifluoroacetone<sup>13</sup> and salicylaldoxime,<sup>14</sup> Mn(II) is also determined by chemiluminescence reaction.<sup>15</sup>

Due to numerous interferences, reagents, like benzo-hydroxamic acid,<sup>16</sup> 2-thenoyltrifluoroacetone,<sup>17</sup> 4-(2-pyridylazo)resorcinol,<sup>18</sup> gluconic acid,<sup>19</sup> cacotheline<sup>18</sup> and 4-phenyl-3-thiosemicarbazone of biacetyl monoxime<sup>20</sup> are not selective.

Due to less kinetic stability complex formation is slow in case of leucomalachite green,<sup>21</sup> acetaldoxime,<sup>22</sup> tetraphenyl arsonium chloride<sup>23</sup> and salicylic acid or acetylsalicylic acid.<sup>24</sup> Due to low thermodynamic stability in case of bis/muthate,<sup>25</sup> telluric acid,<sup>26</sup> calcichrome,<sup>27</sup> brucine<sup>28</sup> and cacotheline<sup>18</sup> complex is formed at elevated temperature.

For some specific applications, some of the reported reagents like MANN-S-l-S,<sup>29</sup> salicylfluorone,<sup>30</sup> xylenol orange,<sup>31</sup> O-hydroxyhydroquinone phthalein and zephiramine,<sup>32</sup> 2,3-diphenyl succinimide monoxime,<sup>33</sup> 8-hydroxyquinoline,<sup>34</sup> 3-ethyl-2-thiohydantoin<sup>35</sup>, O-toluidine and triethanolamine<sup>36</sup> etc. possess merit with respect to sensitivity, selectivity and thermodynamic stability.

The reagent SAG which is proposed in this chapter for trace determination of manganese(II) forms intense yellow complex instantaneously.

## 3.2 EXPERIMENTAL

### 3.2.1 Standard Solutions :

#### Standard Solution of Manganese :

A stock solution of manganese 1 mg/ml (0.01822 M) was prepared by dissolving manganese sulphate monohydrate in distilled water containing a few drops of sulphuric acid. It was standardized volumetrically.<sup>37</sup> Lower concentration

solutions were prepared by diluting stock solution with distilled water.

Reagent Solution :

A stock solution of the reagent was prepared by dissolving 178 mg of it in 100 ml distilled water (1.78 mg/ml i.e.  $1.0 \times 10^{-2}$  M).

Buffer Solution :

Buffer solution of pH 11.98 was prepared by mixing appropriate amounts of borax and NaOH.

All the other reagents used were of analytical grade.

3.2.2 Recommended Procedure :

An aliquot of the solution containing 10  $\mu$ g of manganese(II) was taken in 10 ml volumetric flask. To it was added 1.0 ml of the reagent (SAG) solution of concentration  $1.0 \times 10^{-3}$  M. The pH of the solution was adjusted to 8.20 with buffer solution and was diluted upto the mark with distilled water. The absorbance of the manganese(II)-SAG complex was measured at 400 nm against reagent blank. The concentration of manganese in an unknown solution was determined from a calibration curve obtained under identical conditions.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Spectral Characteristics :

The absorption spectrum of Mn(II)-SAG complex containing  $1.822 \times 10^{-4}$  M manganese(II) and  $1.0 \times 10^{-3}$  M reagent (SAG) was recorded at pH 8.20 against reagent blank. The complex has absorption maximum at 400 nm and molar extinction coefficient of the complex is  $5.214 \times 10^3$  l mole<sup>-1</sup>cm<sup>-1</sup> at 400 nm. The molar extinction coefficient of the reagent at 400 nm is zero l mole<sup>-1</sup>cm<sup>-1</sup> (Fig.3.1). The observations for the spectra are given in table 3.1.

#### 3.3.2 Effect of pH :

A series of solutions of different pH from 2.0 to 12.0 were prepared as per the recommended procedure. It was found that complex shows maximum and constant absorbance from 7.7 to 8.7. (Table 3.2, Fig. 3.2) and therefore, the study of manganese(II)-SAG complex was carried out at pH 8.20.

Table 3.1 : Molar extinction coefficients of the Mn(II)-SAG complex and the reagent(SAG)

Wavelength $\lambda$ , nm	Molar extinction coefficients, $\epsilon$	
	Mn(II)-SAG complex $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	Reagent, SAG $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$
370	0.1098	0.002
380	0.3568	0.001
390	0.4940	-
395	0.5150	-
400	0.5214	-
405	0.5100	-
410	0.4940	-
420	0.3842	-
430	0.2744	-
440	0.1647	-
450	0.1098	-
460	0.0823	-
470	0.0795	-
480	0.0662	-
490	0.0632	-
500	0.0555	-
510	0.0502	-
520	0.0482	-
530	0.0456	-
540	0.0420	-
550	0.0385	-
560	0.0340	-
570	0.0305	-
580	0.0297	-
590	0.0280	-
600	0.0265	-
610	0.0255	-

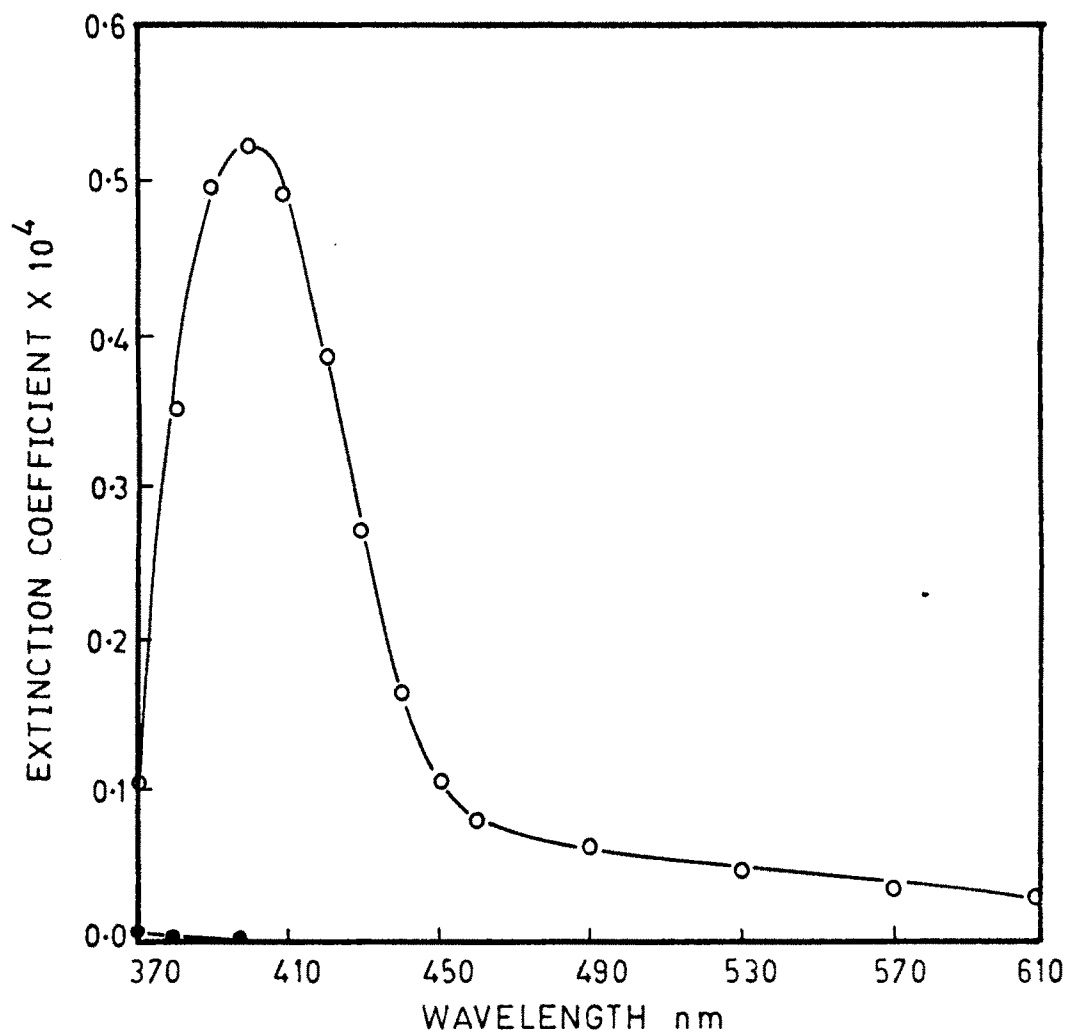


FIG.3-1 ○—○ ABSORPTION SPECTRUM OF MANGANESE(II) -SAG COMPLEX.  
●—● ABSORPTION SPECTRUM OF REAGENT (SAG)

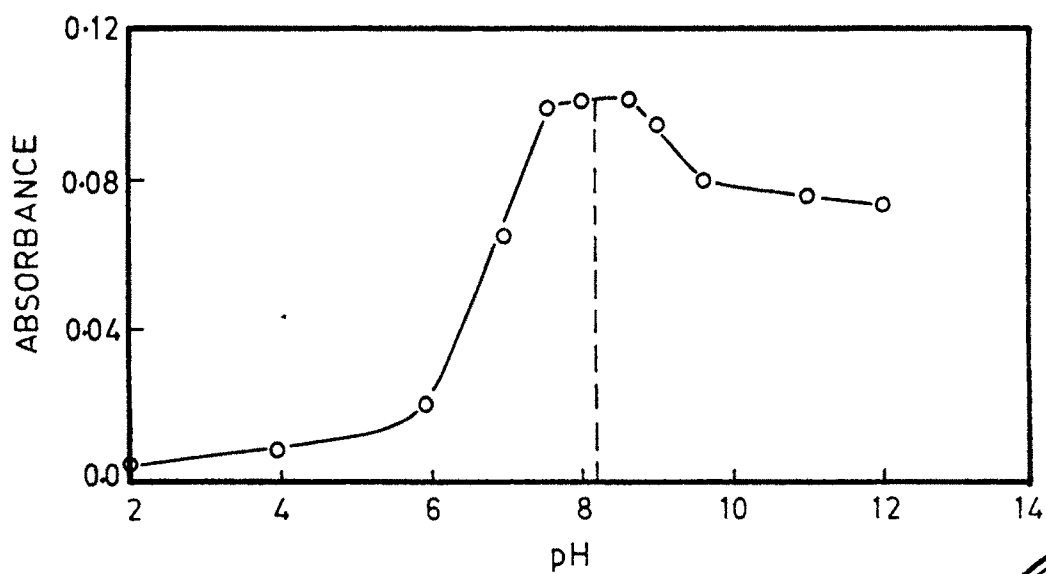


FIG. 3-2 EFFECT OF pH

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Table 3.2 : Effect of pH

pH	Absorbance at 400 nm
2.0	0.007
4.0	0.010
6.0	0.020
7.0	0.065
7.7	0.105
8.0	0.105
8.7	0.105
9.0	0.095
9.7	0.080
11.0	0.076
12.0	0.070

### 3.3.3 Effect of reagent concentration :

A series of solutions containing constant concentration of manganese (1.0 ppm) and different amount of SAG ranging in concentrations from  $2.0 \times 10^{-5}$  M to  $1.6 \times 10^{-4}$  M were prepared. Complex was developed as per recommended procedure and its absorbance was measured. Results in table 3.3 show that six fold molar excess of the reagent was sufficient for full colour development of 1.0 ppm of manganese.

Table 3.3 : Effect of reagent concentration

$$[\text{Mn(II)}] = 1.0 \text{ ppm}; \quad [\text{SAG}] = 1.0 \times 10^{-3} \text{ M}$$

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ml of SAG	Absorbance at 400 nm
0.2	0.030
0.4	0.055
0.6	0.070
0.8	0.080
1.0	0.095
1.2	0.095
1.4	0.095
1.6	0.095

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#### 3.3.4 Stability :

The complex formation is instantaneous and colour of the complex was stable for several hours. Complex formation was independent of temperature.

#### 3.3.5 Validity of Beer's Law :

The measurement of the absorbance of Mn(II)-SAG complex at pH 8.20 containing varying amounts of manganese showed that Beer's law is valid upto 14 ppm of Mn(II) (Fig.3.3).

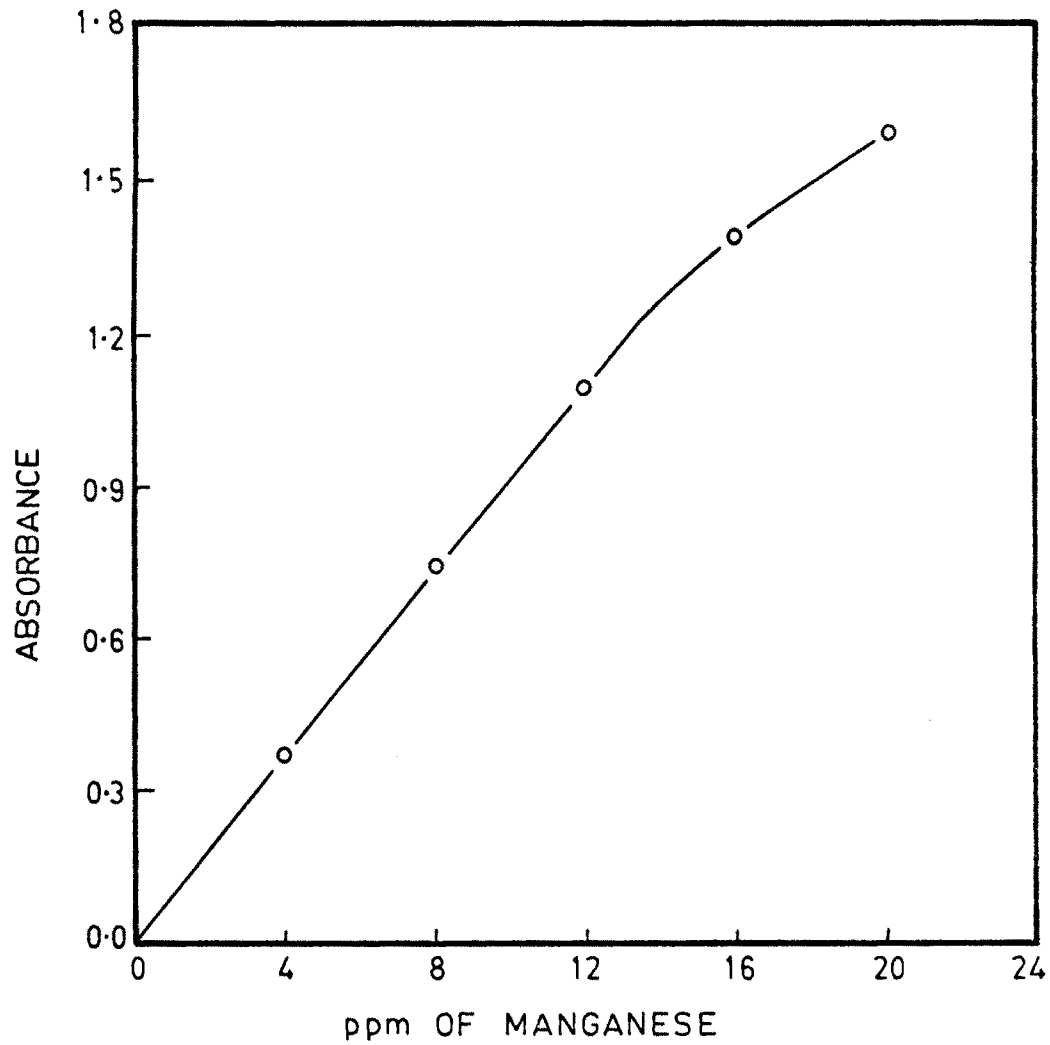


FIG.3.3 VALIDITY OF BEER'S LAW

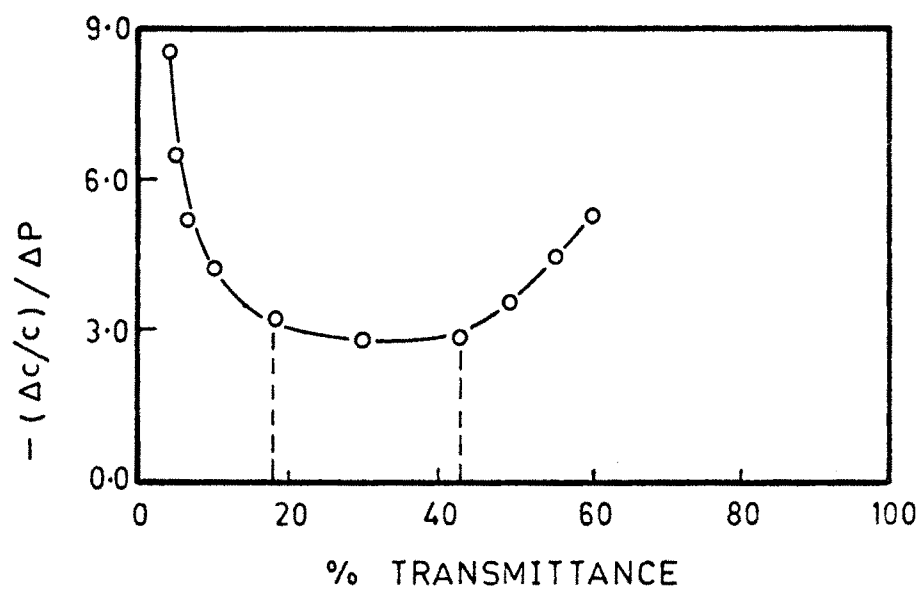


FIG.3.4 RINGBOM PLOT

The optimum concentration range for the determination of manganese was studied from the Ringbom plot<sup>38</sup> and found to be 4 to 8 ppm at the conditions chosen for the experiment (Fig. 3.4).

### 3.3.6 Composition of the complex :

The composition of the Mn(II)-SAG complex was ascertained by Job's method of continuous variation<sup>39</sup> (Table 3.4), mole ratio method<sup>40</sup> (Table 3.5) and slope ratio method.<sup>41</sup> Complex was developed by using equimolar solutions of manganese and the reagent (SAG). Job's plot (Fig.3.5) indicated the formation of 1:2 complex of Mn(II):SAG and this composition was confirmed by the mole ratio (Fig.3.6) and slope ratio method.

Table 3.4 : Job's continuous variation method

$$[\text{Mn(II)}] = [\text{SAG}] = 1.822 \times 10^{-4} \text{M}$$

Manganese (II) ml	Reagent (SAG) ml	Molar ratio M : L	Absorbances at $\lambda$		
			400 nm	420 nm	430 nm
0.0	1.8	-	-	-	-
0.2	1.6	1 : 8	0.017	0.010	0.005
0.4	1.4	2 : 7	0.035	0.025	0.015
0.6	1.2	1 : 2	0.055	0.040	0.030
0.8	1.0	4 : 5	0.050	0.037	0.027
1.0	0.8	5 : 4	0.042	0.031	0.020
1.2	0.6	2 : 1	0.030	0.021	0.013
1.4	0.4	7 : 2	0.020	0.012	0.007
1.6	0.2	8 : 1	0.010	0.005	0.002
1.8	0.0	-	-	-	-



Table 3.5 : Molar ratio method

$$[\text{Mn(II)}] = [\text{SAG}] = 1.822 \times 10^{-4} \text{ M}$$

Manganese (II) ml	Reagent (SAG) ml	Molar ratio M : L	Absorbances at $\lambda$	
			400 nm	420 nm
0.0	2.0	-	-	-
0.2	2.0	1 : 10	0.025	0.020
0.4	2.0	1 : 5	0.045	0.030
0.6	2.0	3 : 10	0.060	0.042
0.66	2.0	1 : 3	0.075	0.055
0.8	2.0	2 : 5	0.082	0.060
1.0	2.0	1 : 2	0.100	0.075
1.2	2.0	3 : 5	0.110	0.080
1.33	2.0	2 : 3	0.120	0.085
1.4	2.0	7 : 10	0.122	0.090
1.6	2.0	4 : 5	0.125	0.095
1.8	2.0	9 : 10	0.130	0.100
2.0	2.0	1 : 1	0.130	0.100

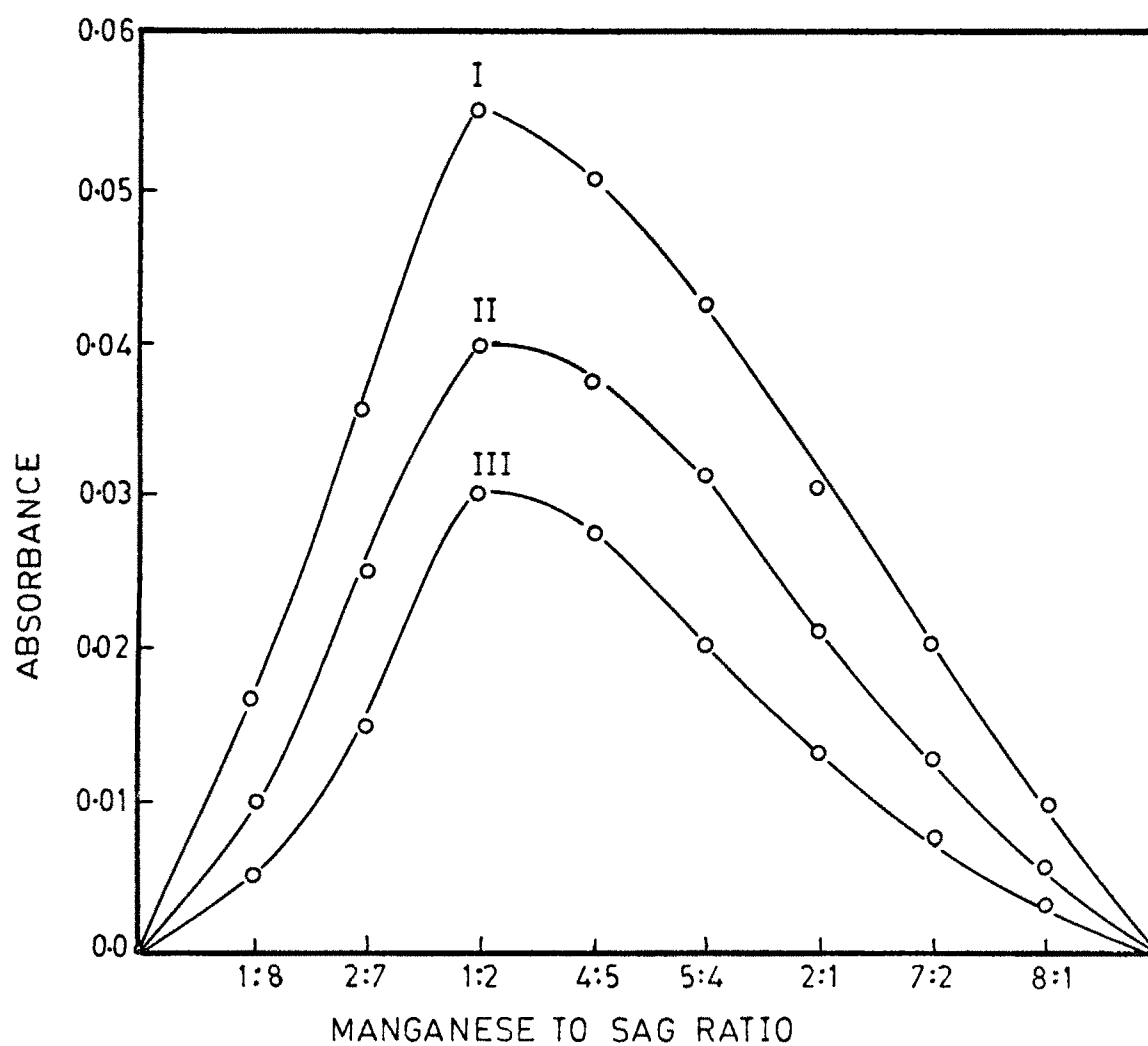


FIG.3.5 JOB'S CONTINUOUS VARIATION METHOD

I— 400 nm , II— 420 nm , III— 430 nm

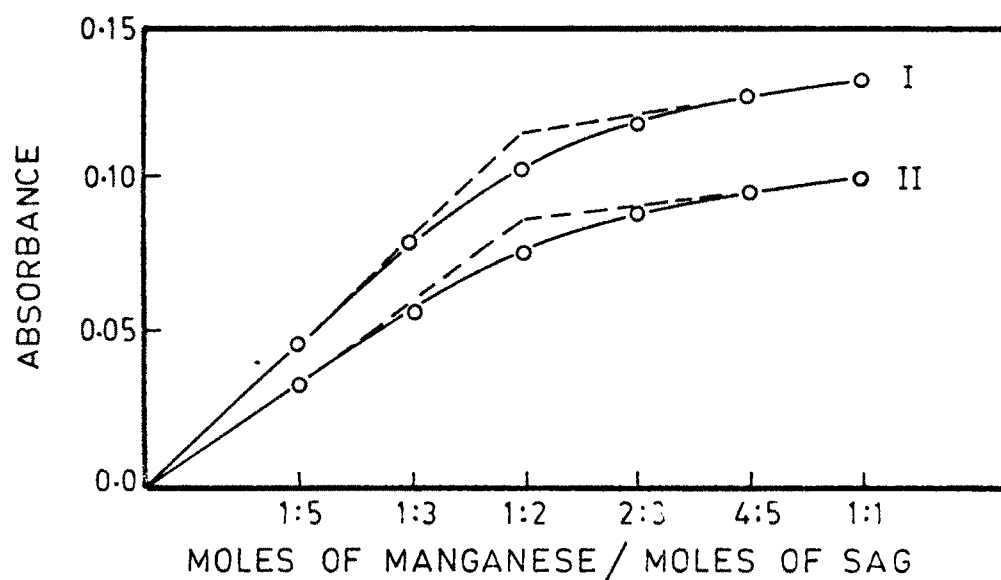
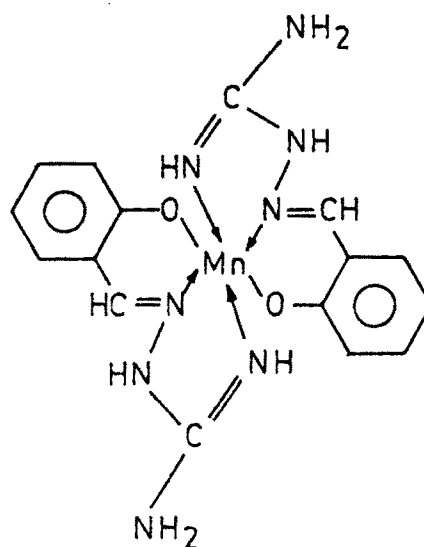


FIG.3.6 MOLE RATIO METHOD .

I— 400 nm , II— 420 nm .

The probable structure for Mn(II)-SAG may be shown as



### 3.3.7 Sensitivity :

The reagent or manganese complex do not show any effect due to light.

The photometric sensitivity of the method was calculated by the method of Sandell<sup>42</sup> and found to be 0.07842  $\mu\text{g}/\text{cm}^2$  at pH 8.20. Molar extinction coefficient of the system at 400 nm is  $5.214 \times 10^3 \text{ l mole}^{-1}\text{cm}^{-1}$ .

### 3.3.8 Degree of dissociation and instability constant :

The degree of dissociation was calculated by the method of Harvey and Manning.<sup>41</sup> The value of degree of dissociation ( $\alpha$ ) was found to be 0.1304.



The apparent instability constant<sup>43</sup> was found to be  $3.358 \times 10^{-12}$  for Mn(II)-SAG complex. The change in free energy<sup>44</sup> of the system is - 15.647 K cal/mole.

### 3.3.9 Reproducibility of the method :

The reproducibility of the method was tested by determining different amounts of manganese as per recommended procedure. The results are tabulated in table 3.6, which show that the method is reproducible. The standard deviations of the method calculated for six observations and the coefficient of variation are also given in table 3.6.

Table 3.6 : Reproducibility of the method

Mn(II) ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation, %
3.0	0.27	0.0035	1.296
6.0	0.54	0.006	1.111
9.0	0.82	0.009	1.097

### 3.3.10 Effect of diverse ions :

To study the effect of diverse ions of manganese(II)-SAG complex, various cations and anions were added to the solution containing 1.0 ppm of Mn(II). Colour was developed at pH 8.2

and measured at 400 nm. The results indicate that Cr(VI), Fe(II), Ni(II), Co(II), Ag(I) and EDTA<sup>-4</sup> interfere seriously. While the tolerance limits of oxalate and thiourea anions are 1300 ppm and 1100 ppm respectively. For various foreign ions, the tolerance limits are given in table 3.7.

Table 3.7 : Effect of diverse ions

$$[\text{Mn(II)}] = 1.0 \text{ ppm} ; [\text{SAG}] = 1.0 \times 10^{-3} \text{ M.}$$

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations</u>		
Cr(III)	CrCl <sub>3</sub> · 6H <sub>2</sub> O	0.1
V (IV)	VOSO <sub>4</sub> · H <sub>2</sub> O	2.0
Ba(II)	BaCl <sub>2</sub> · 2H <sub>2</sub> O	20.0
Al(III)	AlCl <sub>3</sub> · 6H <sub>2</sub> O	9.0
Bi(III)	Bi(NO <sub>3</sub> ) <sub>3</sub>	7.0
Ca(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	21.0
Cr(VI)	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	none
Pb(II)	Pb(NO <sub>3</sub> ) <sub>2</sub>	10.0
Zn(II)	ZnSO <sub>4</sub> · 7H <sub>2</sub> O	10.0
Mg(II)	MgSO <sub>4</sub> · 7H <sub>2</sub> O	9.0
Cd(II)	CdSO <sub>4</sub>	18.0
W (VI)	Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O	100.0
Mo(VI)	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> · 4H <sub>2</sub> O	55.0
Pd(II)	PdCl <sub>2</sub>	0.2

contd.....

Table 3.7 contd....

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations (contd.)</u>		
Fe(II)	$\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	none
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.1
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.4
Ni(II)	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	none
Ag(I)	$\text{AgNO}_3$	none
Co(II)	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	none
<u>Anions</u>		
Citrate	Citric acid	90.0
Thiourea	Thiourea	1100.0
Oxalate	Potassium oxalate	1300.0
Persulphate	Ammonium persulphate	150.0
Tartrate	Tartaric acid	125.0
Thiosulphate	Sodium thiosulphate	95.0
EDTA <sup>-4</sup>	Disodium salt	none
Acetate	Sodium acetate	400.0
Bromate	Potassium bromate	100.0
Phosphate	Potassium dihydrogen orthophosphate	96.0
Urea	Urea	700.0

### 3.4 APPLICATIONS

#### Analysis of Manganese(II) in mild steel :

A known weight (0.10 g) of the sample of mild steel (1e, BAS, England) was dissolved in 10 ml of 1 : 1 HCl with mild heating. A few drops of concentrated  $\text{HNO}_3$  were added carefully. The resulting solution was evaporated to dryness. The residue was dissolved in 5.0 ml of 0.5 N HCl and diluted to 250 ml in volumetric flask with distilled water.

A suitable aliquot (2-3 ml) of this diluted solution was taken. The manganese was then determined as Mn(II)-SAG complex by recommended procedure and measured at 400 nm against the reagent blank. The results of analysis are summarised in table 3.8.

Table 3.8 : Analysis of mild steel

Alloy	Certified value of Mn %	Experimental value of Mn %	Relative standard deviation for 6 observations
Mild steel (1e, B.A.S. England )	0.6	0.585	0.043

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