

## Comparative Study on the Stability of Mn(III) Ion Prepared by Different Methods in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> Media

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**Abstract:** The time-periods required for the % of Mn(III) to disappear from the solution and the half-life of Mn(III) was studied in 7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 7 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub> media at ambient conditions at three different Mn(III) concentrations *viz.* 4.98, 1.94 and 1.04 mmol dm<sup>-3</sup> using spectrophotometric method. Half-life periods in the presence of 7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> are more than those in presence of 7 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub>. The time-periods required for the 1% of Mn(III) to disappear that for H<sub>2</sub>SO<sub>4</sub> medium from 1.94 mmol dm<sup>-3</sup>, Mn(III) solutions prepared from solid form is about 20 days, 10 days for electro-generated Mn(III) and 6 days for chemical oxidation method.

**Keywords:** Mn(III) in acidic media, Half-life of Mn(III), Stability of Mn(III), Trivalent manganese, Solid state Mn(III), Mn(III).

### Introduction

Trivalent manganese is frequently used as powerful oxidizing agents in analytical chemistry<sup>1-8</sup>. Significance of these ions is increased, due to their selectivity, for the oxidation of various compounds in organic synthesis<sup>9-11</sup>.

In spite of the fact that the application of strong oxidants in sulphuric acid solutions has undergone tremendous development in recent years, their stability has received comparatively little attention. The main hindrance in the way of fuller analytical usage of these ions in aqueous solutions is their instability.

Mn(III) solution can be prepared<sup>12</sup> by chemical oxidation of Mn(II) ion by KMnO<sub>4</sub> or by electrogeneration<sup>13</sup>. It has also been obtained<sup>14</sup> in the solid form as Mn<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O. Bermardini *et al.*<sup>15</sup> studied energetic stability and magnetic properties of Mn dimers in silicon. Slawomir Michalkiewicz and Jan Malyszko<sup>16</sup> have reported, the study on the stability of Co(III), Mn(III) and Tl(III) ions in anhydrous acetic acid solutions in the presence of 1 M potassium acetate as the background electrolyte. However the

stability of Mn(III) prepared by three different methods in different acidic media and surprisingly the stability Mn(III) prepared from solid manganic sulphate have not yet been explored. Mn(III) can be used as one electron oxidizing agent in various reactions. Thus, its stability is most important and crucial aspect in this regard. It was our *prima facie* observation that, the solutions of Mn(III) prepared from solid manganic sulfate showed an extra stability over the solutions prepared by other two methods. Hence, the relative stability of Mn(III) state under different conditions of preparation and concentration of acid medium would throw some light on various factors responsible for the stability. In this paper, we are reporting our results on the time-periods required for the % of Mn(III) to disappear from the solution and the half-life periods of the Mn(III) solutions prepared by three different methods at different Mn(III) concentration levels in presence of  $7 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and  $7 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$  as media using simple spectrophotometric method.

## Experimental

### *Reagents and chemicals*

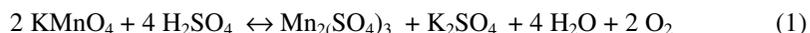
$\text{KMnO}_4$ ,  $\text{MnSO}_4$ ,  $\text{H}_2\text{SO}_4$  ( $d=1.84$ ) and  $\text{H}_3\text{PO}_4$  ( $d=1.75$ ) were obtained from Qualigens Fine Chemicals, Mumbai, India. Freshly prepared double distilled water was used through out the experimental work.

### *Apparatus*

Absorbance measurements were done with a Spectrophotometer (Hitach-330, Japan).

### *Procedures for Mn(III) synthesis*

Solid  $\text{Mn}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$  was prepared by the method described by Domange<sup>14</sup>. Briefly, 20 g of  $\text{KMnO}_4$  was introduced very carefully in small lots into 100 mL of  $\text{H}_2\text{SO}_4$  ( $d = 1.84$ ) contained a porcelain crucible with vigorous agitation. The mixture was carefully heated for 10 minutes at  $60^\circ\text{C}$  with vigorous stirring where by vapours of explosive  $\text{Mn}_2\text{O}_7$  was removed. The solution was heated to  $70^\circ\text{C}$  with continued and vigorous agitation and accurate temperature control. After about 15 minutes with most of the reaction completed the mixture was slowly brought to  $140^\circ\text{C}$  in about 10 minutes with constant stirring. It was finally raised to  $200^\circ\text{C}$  in about 15 minutes. After slow cooling, the mixture to room temperature, a semi-solid mass settled at the bottom and was washed twice by decantation with  $\text{H}_2\text{SO}_4$  to remove the  $\text{K}_2\text{SO}_4$  formed during the reaction. The product was collected on a glass filter and placed on a clay plate. The latter was placed for 3-4 days in a desiccator containing dry  $\text{P}_2\text{O}_5$ . The overall reaction is



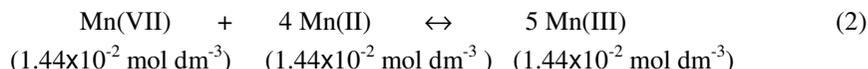
The solutions of Mn(III) ion ( $14.4 \text{ mmol dm}^{-3}$ ) in  $7 \text{ M H}_2\text{SO}_4$  were prepared using requisite amount of solid manganic sulfate.

While Mn(III) solution ( $14.4 \text{ mmol dm}^{-3}$  in  $7 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ) was prepared by electrogeneration method.<sup>13</sup> Briefly, 400 mL  $0.02 \text{ mol dm}^{-3} \text{ MnSO}_4$  prepared in  $7 \text{ mol dm}^{-3}$

$\text{H}_2\text{SO}_4$  was taken in beaker. It was closed by disc containing two holes; one was used for N.H.E. as cathode while the other for platinum Fischer electrode as an anode maintaining the current of 29-30 mA. The optimum current density was used between  $1\text{-}4 \text{ mA/cm}^2$  as reported by Selim and Lingane<sup>13</sup>. Anode consisted of platinum foil with surface area  $9 \text{ cm}^2$ .

The solutions were continuously de-aerated with  $\text{N}_2$  at constant stirring. Mn(III) ions were generated at the surface of platinum electrode as soon as the current was supplied to the cell. After 12 h of continuous electrolysis of  $\text{MnSO}_4$  solution under nitrogen atmosphere, cherry red solution was obtained. The resulting solution was found to be of Mn(III) sulfate having concentration of  $1.45 \times 10^{-2} \text{ mol dm}^{-3}$ .

Mn(III) solution prepared by chemical oxidation of Mn(II) ion as described by Grube and Huberich<sup>12</sup> and it was prepared as follows.



One part of Mn(VII) (KMnO<sub>4</sub>) prepared in distilled water was added to four parts of Mn(II) (MnSO<sub>4</sub>) prepared in 8.75 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> so as to adjust resulting concentration of H<sub>2</sub>SO<sub>4</sub> as 7 mol dm<sup>-3</sup>.

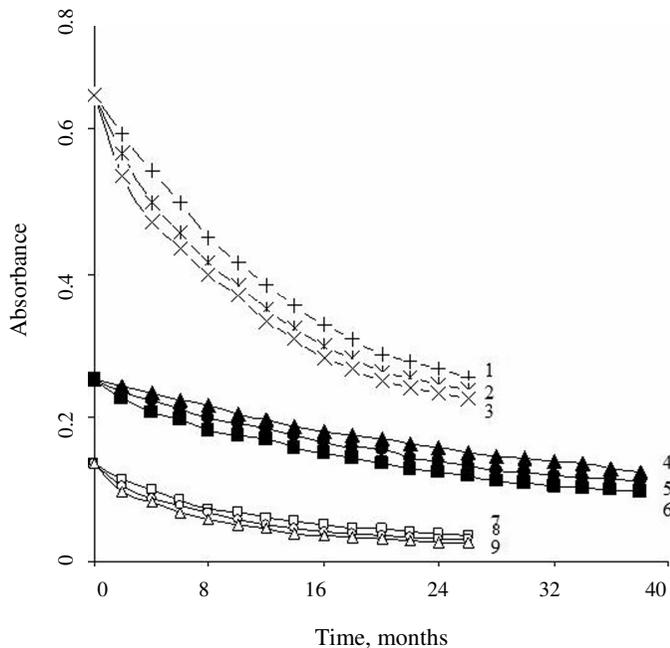
All the stock solutions so prepared were standardized against ferrous ammonium sulfate as well as by iodometric titration method. The solutions of three different concentrations (4.98, 1.94 and 1.04 mmol dm<sup>-3</sup>) of Mn(III) were prepared from the stock solutions maintaining the acid concentration (7 mol dm<sup>-3</sup>). Absorbance of these solutions were recorded<sup>17</sup> at 500 nm on Hitachi-330 Spectrophotometer using 7 mol dm<sup>-3</sup> solution of the respective acid as a reference. The solutions were stored in airtight conical flasks painted black from outside and were kept in dark cupboard to minimize light effects. Aliquots (2-3 mL) were withdrawn from time to time for absorbance as a function of time. Measurements were carried out at an interval of two months and four days for solutions in H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> respectively. Measurements were extended up to 38 months for H<sub>2</sub>SO<sub>4</sub> medium and 36 days for H<sub>3</sub>PO<sub>4</sub> medium. For computation of concentration from measured absorbance, pre-determined molar extinction coefficients  $\epsilon=130$  and 82 lit mol<sup>-1</sup>cm<sup>-1</sup> were used for H<sub>2</sub>SO<sub>4</sub> solutions and H<sub>3</sub>PO<sub>4</sub> solutions respectively. The plots of 1/conc. vs. time were straight lines, slopes of which gave half-life periods for each concentration.

## Results and Discussion

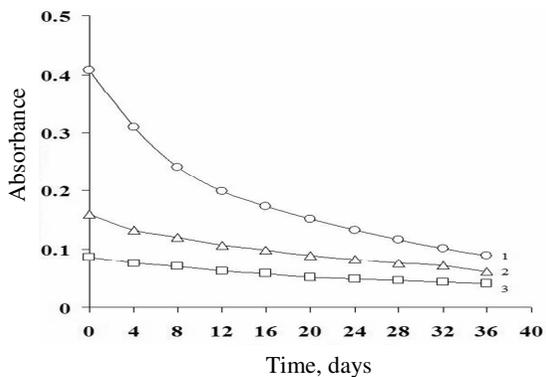
Previous investigations reported, kinetics of oxidation of *L*-aspartic acid and *L*-glutamic acid by manganese(III) ions in aqueous sulphuric acid, acetic acid, and pyrophosphate media and oxidation of *L*-serine by manganese(III) ions in aqueous sulfuric acid medium<sup>2a</sup> at 323 K, where manganese(III) solutions were prepared by known electrolytic/chemical methods<sup>2</sup>. Michalkiewicz and Malyszko<sup>16</sup> reported, the time-periods required for 1 and 10% of Mn(III) to disappear from 2.94 mmol dm<sup>-3</sup> solution were 107 and 1125 h, respectively. In other words, this solution can be used for 4 days (107 h), within that time, the concentration of Mn(III) is not changed to a significant extent. To reveal the results of our study in this regard, the plots of absorbance vs. time are shown in Figures 1 and 2 using Tables 1 and 2 for H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> solutions, respectively, while the plots of 1/conc vs. time are shown in Figures 3 and 4, which are fairly good straight lines indicating that disproportionation reaction is second order in Mn(III) concentrations. The values of half-life periods ( $t_{1/2}$ ) were obtained from the relation  $t_{1/2} = 1/\text{conc.} \times \text{slope}$ .

The calculated half-life periods are given in Table 3 for H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> media. It is seen from Table 3 that for H<sub>2</sub>SO<sub>4</sub> medium half-life period for 4.98 mmol dm<sup>-3</sup> Mn(III) solution was 16 months for solid form, 14 months for electrogenerated Mn(III) and 13 months for chemical oxidation method; for 1.94 mmol dm<sup>-3</sup> Mn(III) solution it was 36 months for solid form, 29 months for electrogenerated Mn(III) and 23 months for chemical oxidation method, where as for 1.04 mmol dm<sup>-3</sup> Mn(III) solution it was 10 months for solid form, 7 months for electrogenerated Mn(III) and 6 months for chemical oxidation method. Thus, they seem to follow the order: solid form > electrogeneration > chemical oxidation at same concentration of Mn(III) ion. However, for the solutions prepared by same method, the trend observed is moderate concentration > high concentration > low concentration for all the three methods of the preparation. This clearly shows that for H<sub>2</sub>SO<sub>4</sub> medium, solutions

prepared from solid form of manganic sulfate are most stable at all the concentrations studied here, but more stable at moderate concentration (1.94 mmol dm<sup>-3</sup>) of Mn(III) ion. However, for H<sub>3</sub>PO<sub>4</sub> medium as given in Table 3, the half-life periods and hence stability is seen to decrease with increase in concentration of Mn(III) ion in between 1.04 mmol dm<sup>-3</sup> and 4.98 mmol dm<sup>-3</sup>. A comparison of half-life periods of Mn(III) ion in 7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 7 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub> at equal concentrations of Mn(III) ion shows that Mn(III) ion is more stable in H<sub>2</sub>SO<sub>4</sub> medium than H<sub>3</sub>PO<sub>4</sub> medium .



**Figure 1.** Effect of preparation method of Mn(III) on its half-life at room temp; Series:1,4,7 (Solid form); 2,5,8 (Electrogeneration); 3,6,9 (Chemical oxidation). [Mn(III)] for Series 1, 2, 3 = 4.98 mol dm<sup>-3</sup>; [Mn(III)] for Series 4, 5, 6 = 1.94 mol dm<sup>-3</sup> and [Mn(III)] for Series 7, 8, 9 = 1.04 mol dm<sup>-3</sup>. [H<sub>2</sub>SO<sub>4</sub>] = 7 mol dm<sup>-3</sup>.



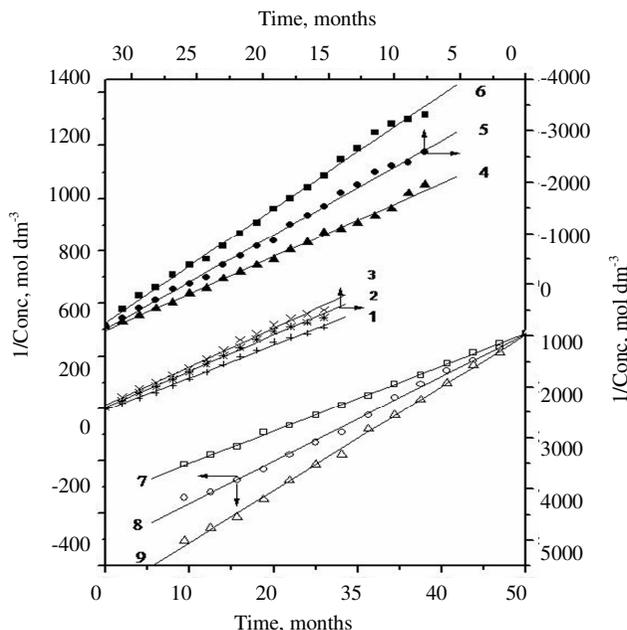
**Figure 2.** Effect of H<sub>3</sub>PO<sub>4</sub> media on Mn (III) ion (Solid form). [Mn (III)] for Series 1 = 4.98 mol dm<sup>-3</sup>; [Mn (III)] for Series 2 = 1.94 mol dm<sup>-3</sup> and [Mn (III)] for Series 3 = 1.04 mol dm<sup>-3</sup>. [ H<sub>3</sub>PO<sub>4</sub>] = 7 mol dm<sup>-3</sup>.

**Table 1.** Variation of absorbance with time at 500 nm; Effect of preparative method (solid form 1,4,7 = S; Electrogeneration 2,5,8 = E; Chemical oxidation 3,6,9 = C) of Mn(III) on its half-life period.  $[\text{H}_2\text{SO}_4] = 7 \text{ mol dm}^{-3}$  and Temp. = Room temperature.  $[\text{Mn(III)}]$  for 1,2,3 =  $4.98 \text{ mmol dm}^{-3}$ ; 4,5,6 =  $1.94 \text{ mmol dm}^{-3}$ ; 7,8,9 =  $1.04 \text{ mmol dm}^{-3}$ .

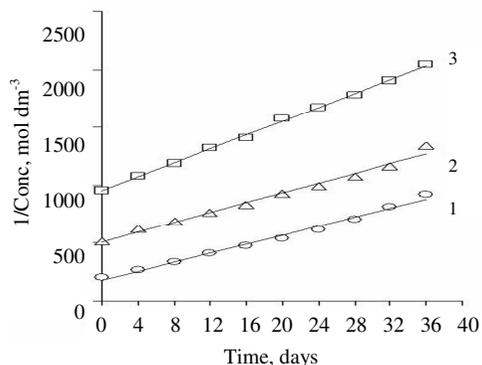
Time months	Abs. 1(S)	Abs. 2(E)	Abs. 3 (C)	Abs. 4 (S)	Abs. 5(E)	Abs. 6(C)	Abs. 7(S)	Abs. 8(E)	Abs. 9(C)
0	0.647	0.647	0.647	0.252	0.252	0.252	0.136	0.136	0.136
2	0.594	0.567	0.534	0.244	0.237	0.225	0.114	0.105	0.098
4	0.543	0.498	0.472	0.234	0.224	0.207	0.098	0.088	0.083
6	0.498	0.456	0.436	0.223	0.212	0.196	0.085	0.078	0.068
8	0.451	0.415	0.398	0.216	0.199	0.183	0.074	0.067	0.058
10	0.415	0.384	0.369	0.204	0.192	0.174	0.067	0.059	0.051
12	0.384	0.351	0.334	0.198	0.186	0.169	0.060	0.051	0.046
14	0.354	0.324	0.308	0.187	0.174	0.159	0.055	0.045	0.039
16	0.328	0.300	0.282	0.181	0.166	0.150	0.051	0.042	0.037
18	0.308	0.281	0.268	0.174	0.159	0.143	0.047	0.039	0.034
20	0.286	0.263	0.251	0.169	0.155	0.135	0.045	0.036	0.031
22	0.277	0.255	0.240	0.162	0.144	0.130	0.041	0.034	0.029
24	0.268	0.246	0.233	0.157	0.139	0.125	0.039	0.032	0.027
26	0.255	0.238	0.226	0.150	0.134	0.120	0.037	0.031	0.026
28				0.147	0.127	0.113			
30				0.143	0.124	0.109			
32				0.139	0.118	0.104			
34				0.135	0.116	0.101			
36				0.128	0.114	0.100			
38				0.124	0.111	0.098			

**Table 2.** Variation of absorbance with time at 500 nm; Effect of  $\text{H}_3\text{PO}_4$  medium on the stability of Mn(III)(Solid form)  $[\text{Mn(III)}]$  For 1 =  $4.98 \text{ mmol dm}^{-3}$ ; 2 =  $1.94 \text{ mmol dm}^{-3}$ ; 3 =  $1.04 \text{ mmol dm}^{-3}$   $[\text{H}_3\text{PO}_4] = 7 \text{ mol dm}^{-3}$  and Temp. = Room temperature.

Time, days	Absorbance 1	Absorbance 2	Absorbance 3
0	0.408	0.159	0.086
4	0.310	0.132	0.076
8	0.241	0.120	0.070
12	0.198	0.107	0.062
16	0.173	0.098	0.058
20	0.152	0.089	0.052
24	0.133	0.083	0.049
28	0.116	0.076	0.046
32	0.101	0.071	0.043
36	0.089	0.061	0.040



**Figure 3.** Variation of 1/Conc. with time; Effect of preparation method of Mn(III) ion on its half life at room temp.; Series 1,4,7 = Solid form; Series 2,5,8 = Electrogeneration; Series 3,6,9 = Chemical oxidation. [Mn(III)] for Series 1, 2, 3 = 4.98 mol dm<sup>-3</sup>; [Mn(III)] for Series 4, 5, 6 = 1.94 mol dm<sup>-3</sup> and [Mn(III)] for Series 7, 8, 9 = 1.04 mol dm<sup>-3</sup>. [H<sub>2</sub>SO<sub>4</sub>] = 7 mol dm<sup>-3</sup>.



**Figure 4.** Variation of 1 / Conc. with time; Effect of H<sub>3</sub>PO<sub>4</sub> on Mn(III) (Solid form). [Mn (III)] for Series 2 = 1.94 mol dm<sup>-3</sup> and [Mn (III)] for Series 3 = 1.04 mol dm<sup>-3</sup>. [ H<sub>3</sub>PO<sub>4</sub>] = 7 mol dm<sup>-3</sup>.

**Table 3.** Effect of preparative method of Mn(III) on its relative stability and in different acid media (7 mol dm<sup>-3</sup>) in terms of half-life periods.

[Mn(III)], mmol dm <sup>-3</sup>	Solid form		Electrogeneration	Chemical oxidation
	H <sub>2</sub> SO <sub>4</sub> Medium Months	H <sub>3</sub> PO <sub>4</sub> Medium Days	H <sub>2</sub> SO <sub>4</sub> Medium Months	H <sub>2</sub> SO <sub>4</sub> Medium Months
1.04	10	32	7	6
1.94	36	26	29	23
4.98	16	11	14	13

The % of Mn(III) to disappear from the solution after 2 months in  $\text{H}_2\text{SO}_4$  ( $7 \text{ mol dm}^{-3}$ ) media and 4 days in  $\text{H}_3\text{PO}_4$  ( $7 \text{ mol dm}^{-3}$ ) media are given in Table 4. It is seen from Table 4 that for  $\text{H}_2\text{SO}_4$  medium % disappearance of Mn(III) from  $4.98 \text{ mmol dm}^{-3}$  Mn(III) solution was 9% for solid form, 12% for electrogenerated Mn(III) and 17% for chemical oxidation method; from  $1.94 \text{ mmol dm}^{-3}$  Mn(III) solution it was 3% for solid form, 6% for electrogenerated Mn(III) and 11% for chemical oxidation method, where as from  $1.04 \text{ mM}$  Mn(III) solution it was 16% for solid form, 23% for electrogenerated Mn(III) and 28% for chemical oxidation method. Thus, they seem to follow the order: chemical oxidation > electrogeneration > solid form at same concentration of Mn(III) ion. However, for the solutions prepared by same method, the trend observed is low concentration > high concentration > moderate concentration for all the three methods of the preparation. This clearly shows that for  $\text{H}_2\text{SO}_4$  medium, solutions prepared from solid form of manganic sulfate are most stable at all the concentrations studied here, but more stable at moderate concentration ( $1.94 \text{ mmol dm}^{-3}$ ) of Mn(III) ion. However, for  $\text{H}_3\text{PO}_4$  medium as given in Table 4, the % disappearance of Mn(III) decreases with concentration of Mn(III) and hence stability is seen to decrease with increase in concentration of Mn(III) ion in between  $1.04 \text{ mmol dm}^{-3}$  and  $4.98 \text{ mmol dm}^{-3}$ . A comparison of % disappearance of Mn(III) ion in  $7 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and  $7 \text{ mol dm}^{-3}$   $\text{H}_3\text{PO}_4$  at equal concentrations of Mn(III) ion shows that Mn(III) ion is more stable in  $\text{H}_2\text{SO}_4$  medium than  $\text{H}_3\text{PO}_4$  medium.

**Table 4.** % of Mn (III) to disappear from the solution after 2 months in  $\text{H}_2\text{SO}_4$  ( $7 \text{ mol dm}^{-3}$ ) and 4 days in  $\text{H}_3\text{PO}_4$  ( $7 \text{ mol dm}^{-3}$ ).

[Mn(III)], $\text{mmol dm}^{-3}$	Solid form		Electrogeneration	Chemical oxidation
	$\text{H}_2\text{SO}_4$ Medium	$\text{H}_3\text{PO}_4$ Medium	$\text{H}_2\text{SO}_4$ Medium	$\text{H}_2\text{SO}_4$ Medium
	% Mn(III) Disappearance	% Mn(III) Disappearance	% Mn(III) Disappearance	% Mn(III) Disappearance
1.04	16	12	23	28
1.94	03	17	06	11
4.98	09	24	12	17

Table 5 describes, the time-periods required for 1% of Mn(III) to disappear that for  $\text{H}_2\text{SO}_4$  medium from  $4.98 \text{ mmol dm}^{-3}$  Mn(III) solution was 160 h for solid form, 120 h for electrogenerated Mn(III) and 85 h for chemical oxidation method; from  $1.94 \text{ mmol dm}^{-3}$  Mn(III) solution it was 480 h for solid form, 240 h for electrogenerated Mn(III) and 131 h for chemical oxidation method, where as from  $1.04 \text{ mmol dm}^{-3}$  Mn(III) solution it was 90 h for solid form, 62 h for electrogenerated Mn(III) and 51 h for chemical oxidation method. In other words, these Mn(III) solutions can be used for above mentioned hours for different methods of preparation and different media, within that time the concentration of Mn(III) is not changed to a significant extent.

**Table 5.** The time period required for 1% of Mn(III) to disappear from the solution in  $\text{H}_2\text{SO}_4$  ( $7 \text{ mol dm}^{-3}$ ) and in  $\text{H}_3\text{PO}_4$  ( $7 \text{ mol dm}^{-3}$ ).

[Mn(III)], $\text{mmol dm}^{-3}$	Solid form		Electrogeneration	Chemical oxidation
	$\text{H}_2\text{SO}_4$ Medium	$\text{H}_3\text{PO}_4$ Medium	$\text{H}_2\text{SO}_4$ Medium	$\text{H}_2\text{SO}_4$ Medium
	Hours (Days)	Hours	Hours (Days)	Hours (Days)
1.04	90 (4)	8	62 (3)	51 (2)
1.94	480 (20)	6	240 (10)	131(6)
4.98	160 (7)	4	120 (5)	85 (4)

Thus, they seem to follow the order: chemical oxidation > electrogeneration > solid form at same concentration of Mn(III) ion. However, for the solutions prepared by same method, the trend observed is low concentration > high concentration > moderate concentration for all the three methods of the preparation. This clearly shows that for H<sub>2</sub>SO<sub>4</sub> medium, solutions prepared from solid form of manganic sulfate are most stable at all the concentrations studied here, but more stable at moderate concentration (1.94 mmol dm<sup>-3</sup>) of Mn(III) ion. However, for H<sub>3</sub>PO<sub>4</sub> medium as given in Table 5, the time-periods required for 1% of Mn(III) to disappear that decreases with concentration of Mn(III) and hence stability is seen to decrease with increase in concentration of Mn(III) ion in between 1.04 mmol dm<sup>-3</sup> and 4.98 mmol dm<sup>-3</sup>. A comparison of the time-periods required for 1% of Mn(III) to disappear from these solutions of Mn(III) ion in 7 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and 7 mol dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub> at equal concentrations of Mn(III) ion shows that Mn(III) ion is more stable in H<sub>2</sub>SO<sub>4</sub> medium than H<sub>3</sub>PO<sub>4</sub> medium.

These results indicate that Mn(III) species is less stable in H<sub>3</sub>PO<sub>4</sub> medium than in H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (or HPO<sub>4</sub><sup>2-</sup>) ions have poor complexing ability as compared to HSO<sub>4</sub><sup>-</sup> (or SO<sub>4</sub><sup>2-</sup>) ions.<sup>18</sup> Moreover, *k*<sub>1</sub> and *k*<sub>2</sub> values are comparatively very low (1.1×10<sup>-2</sup> and 7.5×10<sup>-8</sup>)<sup>19</sup> rendering low H<sup>+</sup> concentration. The H<sup>+</sup> ions stabilize Mn(III) ion by suppressing the disproportionation through the reaction: 2Mn(III) + 2H<sub>2</sub>O ↔ Mn(II) + MnO<sub>2</sub> + 4H<sup>+</sup>, Mn(III) ion can exist in aqueous solution as Mn(III)(aq), [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, [Mn(OH)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>, *etc.*<sup>20-23</sup> In the presence of H<sub>2</sub>SO<sub>4</sub> binuclear species like [(H<sub>2</sub>O)<sub>4</sub>Mn(SO<sub>4</sub>)<sub>2</sub>Mn(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>, [(H<sub>2</sub>O)<sub>4</sub>Mn(OH)<sub>2</sub>Mn(H<sub>2</sub>O)<sub>4</sub>]<sup>4+</sup>, [(H<sub>2</sub>O)<sub>4</sub>Mn(H<sub>2</sub>O)<sub>2</sub>Mn(H<sub>2</sub>O)<sub>4</sub>]<sup>6+</sup> *etc.* have been identified<sup>14,23,24</sup>. The oxo-bridged dimeric species are more susceptible for electron transfer. In dilute and very dilute solutions Mn(III) ion exists probably as monomer species and hence is more stable. The stability should decrease with increasing Mn(III) ion concentration due to formation of binuclear species, which is second order in Mn(III) concentration. This trend has been observed in our results in H<sub>3</sub>PO<sub>4</sub> medium. The low stability in this medium as compared to H<sub>2</sub>SO<sub>4</sub> medium may be attributed to very low complexing ability of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (or HPO<sub>4</sub><sup>2-</sup>) ion<sup>18</sup>. Moreover H<sub>3</sub>PO<sub>4</sub> has low dissociation constants (*k*<sub>1</sub> = 1.1×10<sup>-2</sup>, *k*<sub>2</sub> = 7.5×10<sup>-8</sup>) as compared to the dissociation constants for H<sub>2</sub>SO<sub>4</sub> (*k*<sub>1</sub> >> 1, *k*<sub>2</sub> = 1.2 × 10<sup>-2</sup>)<sup>19</sup> rendering low H<sup>+</sup> concentrations. This also points out to the low stability of Mn(III) ion in H<sub>3</sub>PO<sub>4</sub> medium. Complexing ability of HSO<sub>4</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions adds extra stability to Mn(III) ion. In the case of H<sub>2</sub>SO<sub>4</sub> medium we have observed that the solution with moderate concentration (1.94 mmol dm<sup>-3</sup>) of Mn(III) ion showed maximum stability as compared to low (1.04 mmol dm<sup>-3</sup>) and high (4.98 mmol dm<sup>-3</sup>) concentrations irrespective of the method of preparation. Such trend is not observed in the case of H<sub>3</sub>PO<sub>4</sub> medium. It seems that some hitherto 'unknown' factor should also be operative to add extra stability at moderate concentrations of Mn(III) ion. Mulvany *et al.*<sup>25</sup> have reported that a colloid solution is formed in both acidic and alkaline solutions depending upon pH or pMn. It seems that MnO<sub>2</sub> formed due to disproportionation probably exists as a colloidal state. [(H<sub>2</sub>O)<sub>4</sub>Mn(H<sub>2</sub>O)<sub>2</sub>Mn(H<sub>2</sub>O)<sub>4</sub>]<sup>6+</sup> ↔ [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> + MnO<sub>2</sub> + 2H<sub>2</sub>O + 4H<sup>+</sup><sup>14</sup> At higher concentrations of Mn<sup>3+</sup> ion colloid solution may have sufficient concentration of MnO<sub>2</sub> to form crystalline precipitate of MnO<sub>2</sub> or MnO<sub>2</sub>·2H<sub>2</sub>O. Thus, the overall disproportionation reaction seems to take place stepwise as follows.



Although in our study, no such formation of visible precipitate was observed, it seems that very low colloidal state formed facilitated disproportionation reaction through adsorption of Mn(III) ion on surface. Attempts are being made in this laboratory to study the disproportionation reaction at lower concentration (< 4 mol dm<sup>-3</sup>) of H<sub>2</sub>SO<sub>4</sub> to elucidate the probable role of colloidal state. However, at present no conclusive comments can be made regarding the maximum stability

of moderate Mn(III) concentration in  $7 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . The above results indicate that the stability of Mn(III) ion is dependent on preparation method also. At equal concentration of Mn(III) ion the stability has been shown to follow the trend, solid form > electrogeneration > chemical oxidation. In the case of electrogeneration method some higher oxidation states of manganese are likely to be invariably introduced<sup>26</sup>. While in the case of chemical oxidation method, some unreacted  $\text{MnO}_4^-$  ions or  $\text{MnO}_4^{2-}$  ion, is likely to be introduced.<sup>27</sup> It seems probable that these higher oxidation states add instability to the solution. In case of solid form such higher oxidation states are get removed by repeated washing of the solid form with conc.  $\text{H}_2\text{SO}_4$ , adding thereby very high extra stability to the solution. In case of electrogeneration Mn(III) ion, high ( $0.02 - 0.45 \text{ mol dm}^{-3}$ ) concentration of Mn(II) ions used for electrolytic oxidation seem to add extra stability to these solutions over chemical oxidation method due to unreacted Mn(II) ions in solution and absence of species of higher oxidation states of manganese such as Mn(IV)- Mn(VII).

## Conclusion

The Mn(III) solutions in  $7 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  are found to be more stable than  $7 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$  media. This extra- stability of solutions prepared from solid manganic sulphate as compared to those prepared by electrogeneration or chemical oxidation seems to be due to lack of presence of higher oxidation states Mn(VI), Mn(VII) or inert ions like  $\text{K}^+$ . The time-periods required for 1% of Mn(III) to disappear that for  $\text{H}_2\text{SO}_4$  medium from 1.94 mM Mn(III) solution it was 480 h *i.e.* 20 days for solid form, 240 h *i.e.* 10 days for electrogenerated Mn(III) and 131 h *i.e.* 6 days for chemical oxidation method. In other words, within that time the concentration of Mn(III) is not changed to a significant extent. The time-periods required for 1% of Mn(III) to disappear that for  $\text{H}_2\text{SO}_4$  medium from 1.04 and  $4.98 \text{ mmol dm}^{-3}$ , Mn(III) solutions are less than  $1.94 \text{ mmol dm}^{-3}$ , Mn(III) solutions. The results indicate that in the applications of Mn(III) ion such as oxidation reactions, catalysis, coordination chemistry, oxygen evolving reactions *etc*, Mn(III) solution should be preferably prepared from solid manganic sulphate at medium concentration  $1.94 \text{ mmol dm}^{-3}$ .

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