



## KINETIC ESTIMATION OF D-XYLOSE BY ELECTRON TRANSFER INDICATOR REACTION WITH Mn(III) PYROPHOSPHATE

Anand G.Fadnis\*

Department of Chemistry, Government (autonomous) Holkar Science College, Indore-42002, (Madhya Pradesh)  
India

### ABSTRACT

*The Mn(III) in the form of pyrophosphate has been used in the present electron transfer indicator reaction with D-xylose for their kinetic estimations using following indicator reaction.*



*The rate data of present indicator reactions in the form of decreasing absorbance at 514nm ( $\lambda_{\text{max}}$  of Mn(III) pyrophosphate complex) with time given for this indicator reaction have been used for their respective estimation in simulated samples adopting (a) rate constant, (b) variation of absorbance at fixed time (c) variation of time at fixed absorbance of (d) one point and (e) two point methods using respective calibration plots. The consistency and reproducibility of these results have clearly showed that this kinetic estimations of can be used as an alternative/additional analytical method to the existing traditional estimation methods in the present day laboratory conditions and also as advance laboratory experiments*

**Keywords:** Mn(III) pyrophosphate, Kinetic estimation, Electron transfer, D-xylose, Indicator reaction

### I. INTRODUCTION

Metal ions are widely employed in kinetic, mechanistic and analytical studies function either as one-equivalent or as two-equivalent reagents[1]. Mn(III) is yet another important one equivalent electron

transfer reagent used in kinetic and mechanistic studies of monosaccharides/alditols in the past [2,3]. The Mn(III) in the form of pyrophosphate has been used in the present indicator reaction with D-xylose for its kinetic estimation.

## II. EXPERIMENTAL

The Mn(III) pyrophosphate complex was prepared immediately before its use by the reaction of  $\text{KMnO}_4$  with excess of  $\text{MnSO}_4$  and  $\text{HClO}_4$  at room temperature according to the stoichiometry (equ, 1)



The Mn(III) pyrophosphate complex is present as different pH dependent reactive species which react with D-xylose molecule to form a complex by displacing one of the pyrophosphate ligands which then disproportionate to produce lower aldose and formic acid by free radical mechanism [2,3]. The simplified present indicator reaction can be shown as in equation (2).



The kinetic/rate data of present indicator reactions in the form of decreasing absorbance at 514 nm ( $\lambda_{\text{max}}$  of Mn(III) pyrophosphate complex) with time have been obtained by using Shimadzu Pharmaspec-UV-1700 under the varying pseudo first order experimental conditions. The disappearance of Mn(III) with time is given as in Eq. 3

$$-d[\text{Mn(III)}]/dt = k_s[\text{Mn(III)}][\text{D-xylose}][\text{HClO}_4][\text{free pyrophosphate}] = k_{\text{obs}}[\text{Mn(III)}] \quad (3)$$

## III. RESULTS AND DISCUSSIONS

The results of variations of  $k_{\text{obs}}$ , the pseudo first order rate constants with initial concentrations of respective D-xylose is uniformly first order and are given in table 1, thus suitable for the kinetic estimation of D-xylose in the concentration range employed. In other kinetic runs it was observed that the values of  $k_{\text{obs}}$  increase proportionately with  $[\text{HClO}_4]$  and decrease with  $[\text{free pyrophosphate}]$ . The rate data of table 1 has been used for estimation in simulated sample of D-xylose by following the procedure adopted in the earlier reports [4,5]

**TABLE -1**

**VARIATION OF ABSORBANCE WITH D-XYLOSE CONCENTRATION**

$10^3[\text{Mn(III)}] = 0.50 \text{ mol dm}^{-3}$

$[\text{HClO}_4] = 0.731 \text{ mol dm}^{-3}$

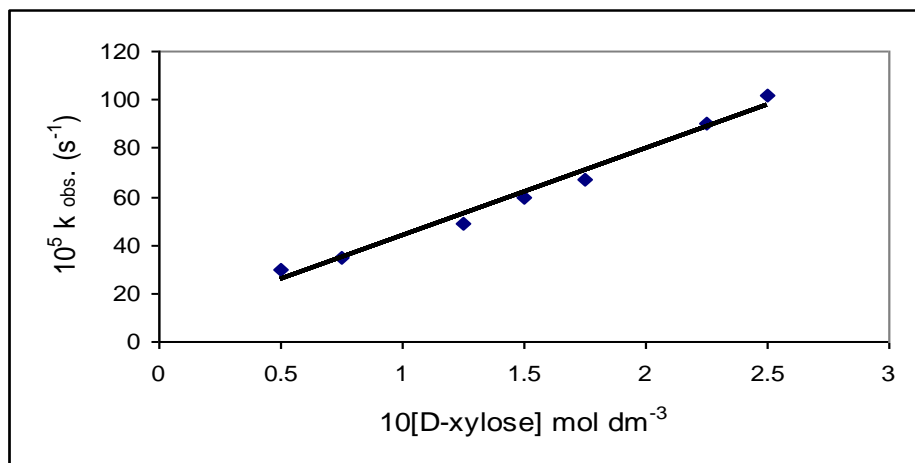
Temperature =  $313 \pm 0.5 \text{ K}$

$\lambda = 514 \text{ nm}$

10 <sup>2</sup> Time (sec.)	----- 10 [D-xylose] (mol dm <sup>-3</sup> ) -----								
	0.50	0.75	1.25	1.50	1.75	2.25	2.50	simulated -1	simulated -2
0	0.602	0.602	0.602	0.602	0.602	0.602	0.602	0.602	0.602
3	0.552	0.544	0.520	0.498	0.486	0.457	0.440	0.535	0.477
6	0.509	0.490	0.450	0.425	0.402	0.352	0.324	0.470	0.381
9	0.469	0.443	0.386	0.357	0.327	0.260	0.230	0.411	0.293
12	0.427	0.398	0.333	0.297	0.263	0.196	0.172	0.362	0.225
15	0.387	0.356	0.284	0.244	0.218	0.158	0.136	0.316	0.190
18	0.348	0.319	0.249	0.206	0.184	0.126	0.106	0.283	0.157
21	0.315	0.289	0.219	0.174	0.153	0.096	0.078	0.255	0.124
24	0.283	0.259	0.189	0.142	0.123	0.070	0.054	0.226	0.096
27	0.256	0.231	0.164	0.121	0.103	0.052	0.040	0.197	0.077
10 <sup>5</sup> k <sub>obs.</sub> (s <sup>-1</sup> )	29.68 ±0.2	34.72 ±0.03	48.87 ±0.01	59.64 ±0.05	67.32 ±0.02	90.23 ±0.06	101.4 ±0.09	<b>41.49</b> <b>±0.03</b>	<b>77.27</b> <b>±0.07</b>

### Kinetic estimation of D-Xylose

#### (A) Rate Constant Method



**Regression Equation**  $10^5 k_{obs.} = 36.312 [D\text{-xylose}] + 7.233$       **Corr. Coeff.** = 0.98

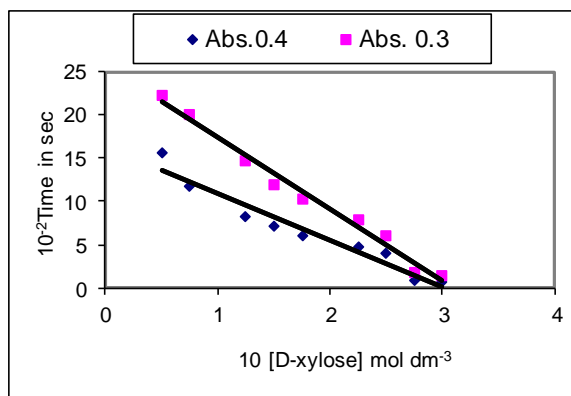
#### Results:

10[simulated -1] (mol dm <sup>-3</sup> )	0.96(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm <sup>-3</sup> )	1.94(Calculated): 2.00 (Actual)

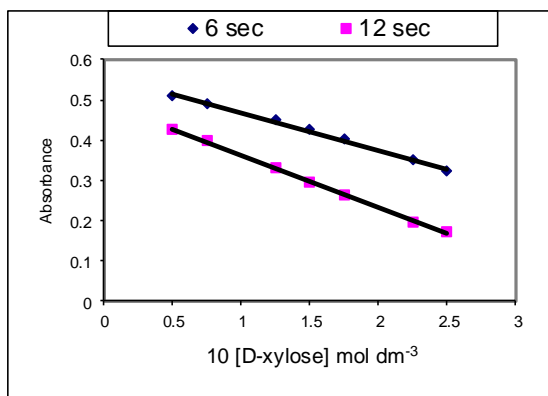
#### (B & C ) Fixed Time And Fixed Absorbance Method

10 [D-xylose] (mol dm <sup>-3</sup> )	Absorbance at fixed 10 <sup>-2</sup> time (sec)		10 <sup>-2</sup> time(sec)at fixed absorbance	
	6	12	0.4	0.3
0.50	0.509	0.427	15.60	22.20
0.75	0.490	0.398	11.70	20.10
1.25	0.450	0.333	8.25	14.70
1.50	0.425	0.297	7.05	11.85
1.75	0.402	0.263	6.00	10.20

2.25	0.352	0.196	4.65	7.80
2.50	0.324	0.172	4.05	6.00
<b>Simulated-1</b>	<b>0.470</b>	<b>0.362</b>	<b>10.50</b>	<b>16.50</b>
<b>10[simulated -1](mol dm<sup>-3</sup>)</b>	<b>1.03</b>	<b>1.04</b>	<b>1.04</b>	<b>1.08</b>
<b>simulated -2</b>	<b>0.381</b>	<b>0.225</b>	<b>5.25</b>	<b>8.70</b>
<b>10[simulated -2](mol dm<sup>-3</sup>)</b>	<b>1.95</b>	<b>2.15</b>	<b>2.05</b>	<b>2.01</b>



Absorbance at fixed 10<sup>-2</sup>time



Time at fixed absorbance

### Regression Equations

$A_{600} = -0.1832 [\text{D-xylose}] + 1.336$       Corr. Coeff. = 0.99

$A_{1200} = -0.2455 [\text{D-xylose}] + 1.289$       Corr. Coeff. = 0.99

$t_{0.4} = -1.9132 [\text{D-xylose}] + 5.473$       Corr. Coeff. = 0.97

$t_{0.3} = -4.273 [\text{D-xylose}] + 12.837$       Corr. Coeff. = 0.96

### Results:

(Fixed Time Method)	
10 [simulated -1] (mol dm <sup>-3</sup> )	1.05 ± 0.02 (Calculated): 1.00 (Actual)
10 [simulated -2] (mol dm <sup>-3</sup> )	2.07 ± 0.07 (Calculated): 2.00 (Actual)

(Fixed Abs. Method)	
10 [simulated -1] (mol dm <sup>-3</sup> )	1.03 ± 0.3 (Calculated): 1.00 (Actual)
10[simulated -2] (mol dm <sup>-3</sup> )	2.09 ± 0.03 (Calculated): 2.00 (Actual)

**(D) One Point Method**

10 <sup>-2</sup> Time (sec.)	10 [D-xylose] (mol dm <sup>-3</sup> )		
	1.00	1.50	2.00
0	0.602	0.602	0.602
3	0.535	0.498	0.477
6	0.470	0.425	0.381
9	0.411	0.357	0.293
12	0.362	0.297	0.225
15	0.316	0.244	0.190
18	0.283	0.206	0.157
21	0.255	0.174	0.124
24	0.226	0.142	0.096
27	0.197	0.121	0.077

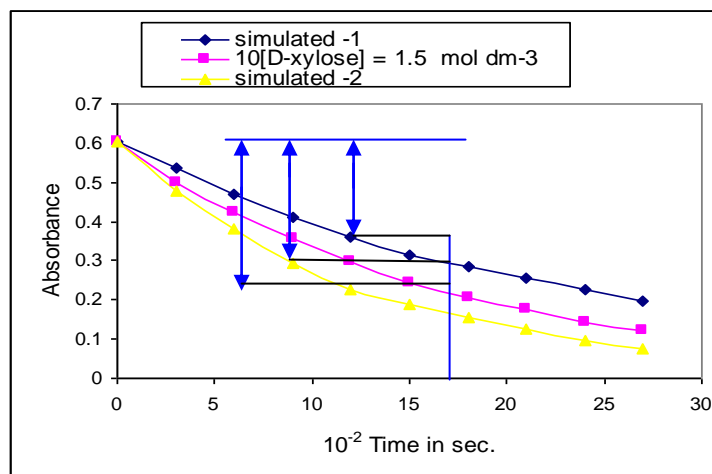
Fixed Absorbance	10 <sup>-2</sup> Time (sec.)	10[Standard] mol dm <sup>-3</sup>	10[Simulated Sample]mol dm <sup>-3</sup> C <sub>1</sub> = (t <sub>2</sub> C <sub>2</sub> /t <sub>1</sub> )
0.3	t <sub>1</sub> = 3.3 t <sub>2</sub> = 2.1	C <sub>2</sub> = 1.5	C <sub>1</sub> = 0.96 (C <sub>Actual</sub> = 1.00)
	t <sub>1</sub> = 1.2 t <sub>2</sub> = 2.1	C <sub>2</sub> = 1.5	C <sub>1</sub> = 2.12 (C <sub>Actual</sub> = 2.00)
	t <sub>1</sub> = 8.4 t <sub>2</sub> = 5.1	C <sub>2</sub> = 1.5	C <sub>1</sub> = 0.98 (C <sub>Actual</sub> = 1.00)

0.4	$t_1 = 3.0, t_2 = 5.1$	$C_2 = 1.5$	$C_1 = 2.05(C_{Actual} = 2.00)$
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**Results:**

10[simulated -1] (mol dm <sup>-3</sup> )	1.04 ± 0.02(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm <sup>-3</sup> )	2.06 ± 0.04 (Calculated): 2.00 (Actual)

**(E) TWO POINT METHOD**



$10^2$ Fixed Time (sec.)	Absorbance $\Delta A$	10[Standard] mol dm <sup>-3</sup>	10[Simulated Sample] mol dm <sup>-3</sup>  $C_1 = (\Delta A_1 C_2 / \Delta A_2)$
6	$\Delta A_1 = 0.175$ $\Delta A_2 = 0.249$	$C_2 = 1.5$	$C_1 = 1.05(C_{Actual} = 1.00)$
	$\Delta A_1 = 0.343$ $\Delta A_2 = 0.249$	$C_2 = 1.5$	$C_1 = 2.07(C_{Actual} = 2.00)$
12	$\Delta A_1 = 0.288$ $\Delta A_2 = 0.403$	$C_2 = 1.5$	$C_1 = 1.07(C_{Actual} = 1.00)$

	$\Delta A_1 = 0.561$	$C_2 = 1.5$	$C_1 = 2.09(C_{\text{Actual}} = 2.00)$
	$\Delta A_2 = 0.403$		

**Results:**

10[simulated -1] (mol dm <sup>-3</sup> )	1.07 ± 0.01(Calculated): 1.00 (Actual)
10[simulated -2] (mol dm <sup>-3</sup> )	2.04 ± 0.04 (Calculated): 2.00 (Actual)

All these results of estimations of D-xylose has been summarized in the table -2

**TABLE -2**

**Summary of Kinetic Estimation of D-xylose by Electron Transfer Reaction with Mn(III) Pyrophosphate**

Table No.		Concentration of Simulated Samples ( mol dm <sup>-3</sup> )					Average
		(Rate constant method)	(Fixed Time method)	(Fixed Abs. method)	(One point method)	(Two point method)	
		A	B	C	D	E	
1	10 <sup>2</sup> [simulated-1]	0.96	1.05	1.03	1.04	1.07	1.03±0.03
	10 <sup>2</sup> [simulated-2]	1.94	2.07	2.09	2.06	2.04	2.04±0.04



#### IV. CONCLUSION

This study is about to use rate data obtained during electron transfer reactions between D-xylose and Mn(III)(table-1) in presence of pyrophosphate for the estimations of D-xylose in simulated samples under present pseudo first order kinetic conditions using indicator reaction (equ 2).

These results and that of other reported studies [4,5] including pharmaceutical samples [6] have the potential to develop a simple, inexpensive but accurate laboratory procedure for simultaneous kinetic estimations of mixtures using differential and other chemometric methods. [7]

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