



## An improved method for determination of $Mn^{II}$ based on its catalytic effect on periodate oxidation of 2,4-xylylidine

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### ABSTRACT

The main reaction product of  $Mn^{II}$  catalysed periodate oxidation of 2,4-xylylidine in acetone-water medium is 3,5-dimethyl-1,2-benzoquinone. The progress was followed by monitoring the increase in the absorbance of reaction intermediate. The reaction was found to be first order with respect to catalyst, substrate and oxidant each. The conditions were developed for kinetic-spectrophotometric determination of  $Mn^{II}$  in the range 0.54 – 345.22 ng/ml. Molar extinction coefficient and Sandell's sensitivity for various calibration curves developed are respectively, 94149 to 148243  $L\ mol^{-1}\ cm^{-1}$  and 0.82 to 1.3  $ng\ cm^{-2}$ . The characteristics of various calibration curves, percentage recovery, effect of interferences and correlation coefficient etc have been evaluated. The method is better in terms of cost of analysis and ease of determination as well as involvement of easily available equipments and facilities.

**Keywords:** Nanogram Estimation,  $Mn^{II}$ , periodate ion, 2,4-xylylidine, 3,5-dimethyl-1,2-benzoquinone

### INTRODUCTION

There are some reports on determination of  $Mn^{II}$  based on periodate oxidation of some substrates [1-6]. A perusal of literature reveals that many methods that have been reported for determination of  $Mn^{II}$  are based on techniques such as titrimetry, spectrophotometry, pulse polarography, differential pulse anodic stripping voltametry, chromatography, flame atomic absorption spectroscopy, flow injection stopped flow spectrophotometry and Inductively coupled plasma optical emission spectrometry etc., and involve a complicated pre-treatment of samples, complex operation and use of costly equipments.  $Mn^{II}$  catalysed periodate oxidation of aromatic amines has not been explored widely for kinetic-spectrophotometric estimation of  $Mn^{II}$  and only a few attempts have been made in this direction[7-8], although there are some reports available in literature related to the  $Mn^{II}$  catalysed/ uncatalysed periodate oxidation of aromatic amines[9-22]. In continuation to our kinetic mechanistic studies made on  $Mn^{II}$  catalysed periodate oxidation of 2,4-xylylidine[18], a new method developed by us for  $Mn^{II}$  estimation based on its catalytic effect on the periodate oxidation of 2,4-xylylidine (XYL), is being reported in present communication.

### EXPERIMENTAL SECTION

#### Materials used

Thiel, Schultz and Koch buffer[23], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH. Triply distilled water was used for preparation of the solutions. Sodium metaperiodate (Loba Chemie), XYL (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization.

**Recommended Kinetic-spectrophotometric procedure**

The reaction was studied in a spectrophotometric cell and initiated by adding temperature equilibrated  $\text{NaIO}_4$  solution of known concentration to the reaction mixture containing the XYL,  $\text{Mn}^{\text{II}}$  and buffer and maintained at the desired temperature ( $\pm 0.1^\circ\text{C}$ ). The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-1700), at 474 nm, i.e., the  $\lambda_{\text{max}}$  of the reaction mixture, during the period in which  $\lambda_{\text{max}}$  remained unchanged under experimental conditions. Figure 1, shows the absorption maxima of reaction mixture at different time. Desired temperature was maintained with the help of a high precision in-built thermostatic control.

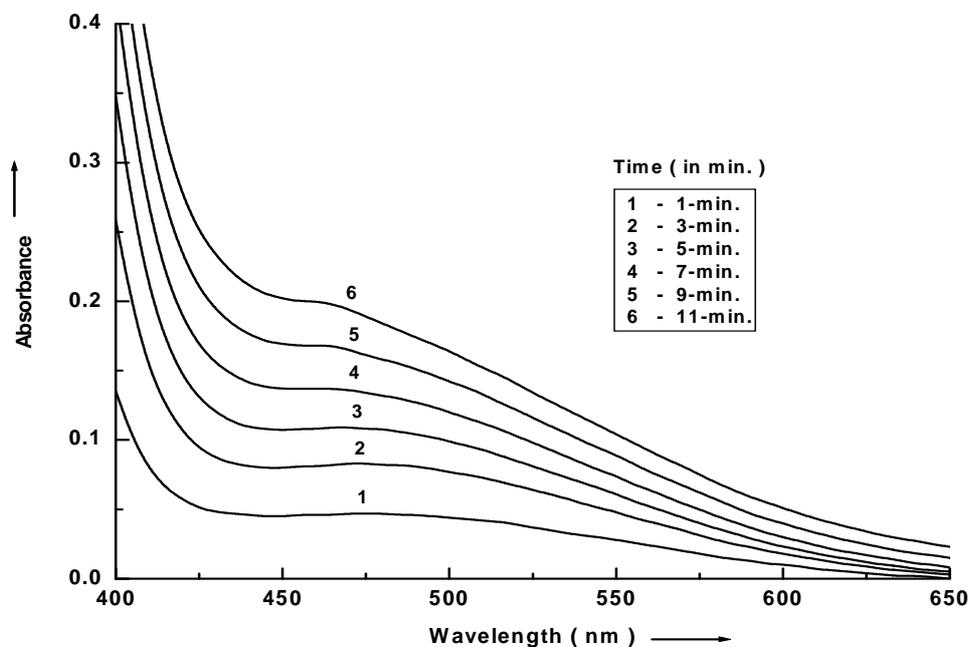


Fig. 1 - Rapid UV-VIS scan of reaction solution at different time at pH = 7.0, acetone = 10 % (v/v) and temp. = 30 °C,  $[\text{NaIO}_4] = 1.4 \times 10^{-2}$ ,  $[\text{XYL}] = 1.0 \times 10^{-3}$  and  $[\text{Mn(II)}] = 2.0 \times 10^{-7} \text{ mol dm}^{-3}$

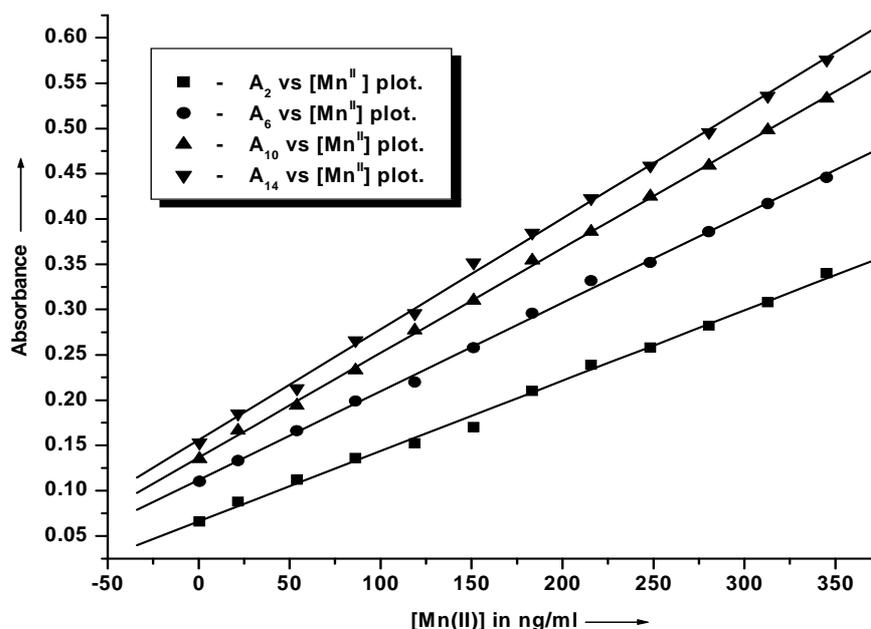


Fig.2: Calibration curves in term of Absorbance vs  $\text{Mn}^{\text{II}}$  plots  
 $[\text{NaIO}_4] = 0.01 \text{ M}$ ;  $[\text{XYL}] = 0.001 \text{ M}$ ; pH = 7.5; Acetone = 10.0%; Temp =  $35 \pm 0.1^\circ\text{C}$

A definite volume of stock solution of XYL in acetone was mixed with calculated volume of the stock solution of  $Mn^{II}$ , acetone and water and stirred a little with the help of the pipette. This mixture and stock solution of  $NaIO_4$  were then clamped in a thermostat at  $35 \pm 0.1^\circ C$ . After 30 minutes, a required amount of the periodate solution was added to the mixture and stirred to start the reaction. All additions were made in amounts calculated for maintaining the concentrations of different reagents as mentioned above. Different sets were prepared in a similar manner varying the  $[Mn^{II}]$ . The reaction mixture was transferred to the cuvette of double beam spectrophotometer immediately after start of reaction. The desired temperature was maintained in spectrophotometer cell also. The absorbance was recorded after repeated intervals of 120 seconds. The absorbance vs time plots were then made for different sets. The initial rates  $[(dA/dt)_{120}]$  were evaluated after 120 seconds from the start of the reaction by applying plane mirror method on the absorbance vs time plots. The pseudo first order rate constants ( $k_{obs}$ ) were found by Guggenheim's method. Using the method of least squares, linear calibration curves were obtained. Type 'A', type 'B', type 'C', type 'D', type 'F' and type 'G' plots were obtained in terms of  $A_2$  or  $A_6$  or  $A_{10}$  or  $A_{14}$  or initial rate or  $k_{obs}$  vs  $[Mn^{II}]$  plots respectively (Figure 2, 3). Where  $A_2$  or  $A_6$  or  $A_{10}$  or  $A_{14}$  are the absorbance values after 2, 6, 10 and 14 minutes from the start of reaction respectively.

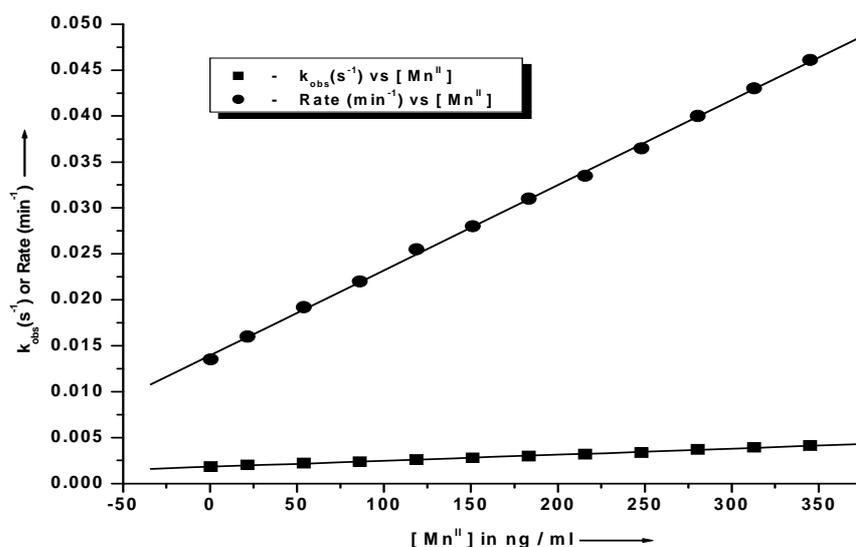


Fig.3: Calibration curves in term of rate constant or Initial rate vs.  $Mn^{II}$  plots  
 $[NaIO_4] = 0.01 M$ ;  $[XYL] = 0.001 M$ ;  $pH = 7.5$ , Acetone = 10.0%; Temp =  $35 \pm 0.1^\circ C$

Following are the finally worked out conditions for running the kinetic sets for the purpose of determination of  $Mn^{II}$  in mixed (acetone-water) medium based upon the periodate oxidation of aniline:  $[XYL] = 0.001 M$ ;  $[NaIO_4] = 0.01 M$ ; Acetone = 10% (v/v);  $pH = 6.5$ ;  $\lambda_{max} = 474 nm$ ; Temp. =  $35 \pm 0.1^\circ C$ . The method developed was suitable for estimation of  $Mn^{II}$  in the range 0.54 ng/ml to 345.22 ng/ml.

## RESULTS

### Kinetic features of the reaction involved

As already reported by us [18], the reaction was found to be first order in each reactant and catalyst with 1 mol of XYL reacting with 2 moles of periodate in initial stage of reaction and 3,5-dimethyl-1,2-benzoquinone being the main product of oxidation. Rate-pH profile showed a maximum at pH value 6.5. Increase in dielectric constant of the medium increased the rate of reaction. An attempt was made to make use of the kinetic studies to work out the best suitable conditions leading to the kinetic-spectrophotometric estimation of  $Mn^{II}$  in nanograms while it catalyses the XYL-periodate redox system in acetone-water medium. The studies were made by taking oxidant in excess.

### Validity of Beer's law and other characteristics of the method

The range of  $[Mn^{II}]$  in which the Beer's law is obeyed, molar absorptivity, Sandell's sensitivity, correlation coefficient and the coefficient of determination, value of 't' (at 0.01 significance level) and relative standard deviation for various calibration curves are given in table-1. Some of the characteristics of calibration curves can be presented in the form of equations of straight line as follows:

$$A_2 = 6.62 \times 10^{-2} + 7.77 \times 10^{-4} [Mn^{II}] \quad \text{-----(1)}$$

$$A_6 = 11.18 \times 10^{-2} + 9.78 \times 10^{-4} [Mn^{II}] \quad \text{-----(2)}$$

$$A_{10} = 13.59 \times 10^{-2} + 11.53 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad \text{----(3)}$$

$$A_{14} = 15.59 \times 10^{-2} + 12.23 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad \text{----(4)}$$

$$(dA/dt)_2 = 1.4 \times 10^{-2} + 0.93 \times 10^{-3} [\text{Mn}^{\text{II}}] \quad \text{----(5)}$$

$$k_1 = 1.87 \times 10^{-3} + 0.06 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad \text{----(6)}$$

In Eq. (5), the values of intercepts and slope are in absorbance units  $\text{min}^{-1}$  and absorbance unit  $\text{min}^{-1} \text{ng}^{-1} \text{mL}$  respectively. These are in  $\text{sec}^{-1}$  and  $\text{sec}^{-1} \text{ng}^{-1} \text{mL}$  respectively for Eq. (6). The  $[\text{Mn}^{\text{II}}]$  are in  $\text{ng/mL}$ .

**Table – 1 Characteristics of various types of calibration curves for the proposed method**  
 $[\text{XYL}] \times 10^3 = 1.0 \text{ M}$ ;  $[\text{NaIO}_4] \times 10^2 = 1.0 \text{ M}$ ;  $\text{pH} = 7.5$ ;  $\text{Acetone} = 10.0\% \text{ (v/v)}$ ;  $\text{Temp} = 35 \pm 0.1^\circ\text{C}$ ;  $\lambda_{\text{max}} = 474 \text{ nm}$

Parameter	'A' plot 2(min)	'B' plot 6(min)	'C' plot 10(min)	'D' plot 14(min)	'F' plot	'G' Plot
Beer's law limits (ng/ml)	0.54- 345.22	0.54- 345.22	0.54- 345.22	0.54- 345.22	0.54- 345.22	0.54- 345.22
Molar absorptivity $\times 10^{-4} \text{ (L mol}^{-1} \text{ cm}^{-1}\text{)}$	9.4149	11.8497	13.9809	14.8243	-----	---
Sandell's sensitivity ( $\text{ng cm}^{-2}$ )	1.3	1.02	0.87	0.82	-----	---
Slope $\times 10^4$ absorbance units $\text{ng}^{-1} \text{ cm}^3$ (from regression equation)	7.77	9.78	11.53	12.23	0.9268	0.05997
Intercept $\times 10^2$ (abs units) (from regression equation)	6.62	11.18	13.59	15.59	1.3939	0.1868
Correlation coefficient (r)	0.9981	0.9993	0.9992	0.9993	0.9996	0.9998
Coefficient of determination ( $r^2$ )	0.9962	0.9985	0.9984	0.9985	0.9992	0.9996
't' (at 0.01 significance level)	7.6033	8.4921	8.5976	8.9928	9.5786	14.4226
Relative Standard Deviation (%) (for six determinations)	0.3740	0.3180	0.3277	0.2159	0.4048	0.1417

### Effect of interferrants

The method is not applicable in presence of most of the aromatic amines/ anilines. The method may be used in presence of the ions like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  as they do not interfere in present case. However, the metals like Ag, As, B, Co, Cd, Cr, Cu, Fe, Hg, Mo, Ni, Pb, Sb, Se, U, and Zn are expected to interfere in this method. Therefore, a pretreatment is required for separating/ precipitating/ masking these ions before undertaking the proposed method. For this purpose,  $\text{H}_2\text{S}$  may be passed in presence of  $0.3 \text{ M H}^+$  solution, followed by filtration and boiling off  $\text{H}_2\text{S}$ . After it, a dilute alkaline solution of  $\alpha$ -nitroso- $\beta$ -naphthol should be added and again the solution should be filtered[24]. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method[2, 25]. In absence of the above given interferrants, the proposed method may successfully be used for the determination of nanogram quantities of  $\text{Mn}^{\text{II}}$  in water samples.

**Table – 2 Values shown are calculated from calibration curves and are mean of n = 6 in each case**

Concentration	Added (ng/ml)	Detected (ng/ml)	Recovery
A	183.4	182.92	99.74
B	183.4	183.06	99.81
C	183.4	182.98	99.77
D	183.4	183.24	99.91
F	183.4	183.25	98.92
E	183.4	182.88	98.72

### Recommended estimation procedure

$[\text{Mn}^{\text{II}}]$  may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of XYL and acetone and starting the reaction by adding  $\text{NaIO}_4$  followed by noting the absorbance of reaction mixture at different desired times as described above, or evaluating initial rate in terms of  $(dA/dt)_{120}$  by plane mirror method or evaluating  $k_{\text{obs}}$  by Guggenheim's method as discussed above. After it, different calibration curves may be used for determination of  $[\text{Mn}^{\text{II}}]$  in  $\text{ng/mL}$ .

The proposed methods were tested for many water samples containing known amounts of  $\text{Mn}^{\text{II}}$  in the range of the detection limits reported above. The results were found to be reproducible with reasonable standard deviation and low range of errors as calculated from six determinations (Table-1, 2). Various characteristics of the calibration curves indicate reasonable sensitivity, molar absorptivity, percentage recovery, and correlation in the range of  $[\text{Mn}^{\text{II}}]$  (0.54  $\text{ng/mL}$  to 345.22  $\text{ng/mL}$ ). It is clear that method is very well suited to estimation of  $\text{Mn}^{\text{II}}$  in trace amounts. The detection limit in terms of sandell's sensitivity is 0.82–1.3  $\text{ng cm}^{-2}$ , which is reasonably good.

Table – 3 Comparison with reported methods

Parameter	I <sup>26</sup>	II <sup>8</sup>	III <sup>2</sup>	IV <sup>3</sup>	V <sup>5</sup>	VI <sup>7</sup>	VII <sup>27</sup>	VIII <sup>28</sup>	IX <sup>29</sup>	X <sup>30</sup>	XI*
Beer's law limits (ng cm <sup>-3</sup> )	1000 - 25000	--	740- 10320	0.05 - 5.0	0.08- 4.0	1-120	0.00 - 3520	5 -50	5 -50	32- 200	107.88- 1294.56
Molar absorptivity x10 <sup>-3</sup> (L mol <sup>-1</sup> cm <sup>-1</sup> )	--	--	4.972	--	--	99-165	5.84- 7.24	54.945	197.8	79.2- 180	57.5- 68.1
Sandell's sensitivity (ng cm <sup>-2</sup> )	50	1x10 <sup>4</sup>	11	0.015	0.025	0.333- 0.556	7.3- 9.2	1.0	0.278	0.306- 0.694	1.78-2.11
Correlation coefficient (r)	--	--	--	--	0.998	0.998- 1.000	0.998 - 0.999	0.9333- 1.003	0.999 - 1.002	0.9951- 0.9987	0.9886- 0.9999
Coefficient of determination (r <sup>2</sup> )	--	-	--	--	0.996	0.9996- 1.000	0.996 - 0.9984	0.870 - 1.006	0.998 - 1.004	0.9902- 0.9974	0.9773- 0.9998
't' (at 0.01 significance level)	--	--	--	--	-	--	--	--	--	6.793- 8.02	6.4376- 10.026
Relative standard deviation (%)(From 6 determinations)	--	--	0.73- 1.4	--	2.7	0.353- 0.885	0.27- 0.50	1.509	1.093	--	0.107- 0.214
% error	--	--	-	-	1.7- 3.3	0.37- 0.929	0.37- 0.524	--	--	--	--
Standard deviation (%) (From six determinations)	-	--	--	--	--	--	--	--	--	0.506- 1.655	--
% Recovery	--	--	--	--	---	--	--	--	--	99.1- 100.0	98.93- 99.96

I, II, III --- X are the numbers assigned to other reported methods

\* Present method (For different type of calibration curves developed)

Note: Detection limits are also available for a few reported methods as 0.014 ng/ml<sup>31</sup>, 0.05 ng/ml<sup>32</sup>, 0.01 ng/ml (by using flow injection method)<sup>33</sup>.

## DISCUSSION

Molar absorptivity is in the range 94149 to 148243 L mol<sup>-1</sup> cm<sup>-1</sup>. Value of Sandell's sensitivity suggests that a change in absorbance by 0.001 unit is expected on changing the concentration of Mn<sup>II</sup> by 0.82-1.3 ng/ml. The correlation coefficient (r) is in the range 0.9981 to 0.9999 which indicates the high precision involved in the determination and almost perfect correlation of the data. The value of coefficient of determination (r<sup>2</sup>) suggests that 97.73% to 99.98% change in the value of absorbance or (dA/dt)<sub>i</sub> or k<sub>1</sub> is caused by Mn<sup>II</sup> and the rest 0.02% to 2.27% is the effect of unknown factors. The value of 't' as calculated for the calibration curves, are in the range 6.4376 to 14.4226 which are much higher than the tabulated critical value at 1% significance level. This suggests that there are less than 1% chances of error in drawing conclusions. The standard deviation is within reasonable limits. Percentage recovery on the basis of six parallel determinations is 98.72% to 99.96%.

A comparison of these methods for estimation of Mn<sup>II</sup> with the other reported methods based on other reactions and using high cost equipments coupled with lengthy pretreatment of samples is given in the Table-3 which includes the characteristics of other reported methods. Although lower detection limits are available for some of the reported methods involving/ not involving periodate oxidations, these methods require rarely available facilities like flow injection method. Method reported by Mutaftchiev[3,5] involves low detection limits in the range 0.015 to 0.025 ng/ml. However, the pre-treatment like complexation etc makes this method more complicated than the method being proposed by us. In general, the proposed method is fairly suitable for estimation of Mn<sup>II</sup> at nanogram level.

The methods developed by us are cost effective and involve the use of simple equipments and chemicals that are generally expected to be available in small centers of research or laboratories. The range in which Beer's law is being obeyed, molar absorptivity, Sandell's sensitivity, detection limits, reproducibility of results are good enough to make these methods competent with other reported methods. These methods are better than some of the previously reported methods in terms of the characteristics of calibration curves and the ease of the procedure involved. Further these methods are simple and less time consuming in comparison to the other available methods for estimation of Mn<sup>II</sup> in aqueous/ mixed media, as no pretreatment of the samples etc are involved except in cases where some rare interferrants are present as already discussed.

## REFERENCES

- [1] Q Wei; LG Yan; GH Chang; QY Ou, *Talanta*, **2003**, 59, 253
- [2] PD Biswas; K De, *J. Indian Chem. Soc.*, **2003**, 80, 195
- [3] KL Mutaftchiev, *Turkish J. Chem.*, **2003**, 27, 619
- [4] KL Mutaftchiev, *Chemical Papers Chemické zvesti.*, **2002**, 56, 194
- [5] KL Mutaftchiev, *Mikrochimica Acta*, **2011**, 36, 79
- [6] L Su; J. Li; H Ma; Tao G, *Analytica Chimica Acta*, **2004**, 522, 281

- [7] RD Kaushik; Shashi; S Devi; RP Singh, *Asian J. Chem.*, **2004**, 16, 837  
[8] IF Dolmanova; VP Poddubienko; VM Peshkova, *Zh Anal Khim*, **1970**, 25, 2146  
[9] RD Kaushik; AK Chaubey; PK Garg, *Asian J. Chem.*, **2003**, 15, 1655  
[10] RD Kaushik; R Joshi, *Asian J. Chem.*, **1997**, 9, 527  
[11] RD Kaushik; RP Singh; Shashi, *Asian J. Chem.*, **2003**, 15, 1485  
[12] RD Kaushik; V Kumar; RK Arya; D Singh, *Asian J. Chem.*, **2000**, 12, 1123  
[13] RD Kaushik; R Joshi; D Singh, *Asian J. Chem.*, **1998**, 10, 567  
[14] RD Kaushik; D Singh; R Joshi; S Kumar, *Asian J. Chem.*, **1998**, 10, 573  
[15] VK Pavolva; YS Sevchenko, KB Yatsimiriskii, *Zh. Fiz. Khim.*, **1970**, 44, 658  
[16] RD Kaushik; R Kumari; T Kumar, P Singh, *Asian J. Chem.*, **2010**, 22, 7959  
[17] RD Kaushik; Amrita; M Dubey; RP Singh, *Asian J. Chem.*, **2004**, 16, 831  
[18] RD Kaushik; D Kumar; A. Kumar, A. Kumar, *J. Indian Chem. Soc.*, **2010**, 87, 811  
[19] RD Kaushik; M Kaur; R. Malik; A Kumar, *Int. J. Chem. Sci.*, **2010**, 8, 1379  
[20] RD Kaushik; A Kumar; T Kumar; P Singh, *React. Kinet. Mech. Cat.*, **2010**, 101, 13  
[21] RD Kaushik; Shashi; Amrita; S Devi, *Asian J. Chem.*, **2004**, 16, 818  
[22] RD Kaushik; R Malik; T Kumar; P Singh, *Oxid. Commun.*, **2012**, 35, 316  
[23] HTS Britton. Hydrogen ions, D. Von Nostrand Co. **1956**, 354  
[24] L Meites. Handbook of Analytical Chemistry, Mc Graw-Hill book Co., INC, New York, **1963**, 3-4  
[25] AI Vogel. A Text Book of Quantitative Inorganic Analysis, Longmanns Green, London, **1961**  
[26] FN Kemmer. The Nelco Water Handbook, McGraw-Hill Co., Singapore, International edition, **1988**, 7.32  
[27] RD Kaushik; Amrita, RP Singh; S Devi, *J. Curr. Sci.*, **2004**, 5, 341  
[28] RD Kaushik; AK Chaubey; RP Singh, *Indian J. Environ. Ecoplan.*, **2003**, 7, 29  
[29] RD Kaushik; Amrita, S Devi, *J. Curr. Sci.*, **2003**, 3, 197  
[30] RD Kaushik; S Devi; Shashi; Amrita, *Indian J. Environ. Ecoplan.*, **2004**, 8, 253  
[31] P Bartkus; A Nauekaitis, Nauchn Konf Khim Anal Pribalt Resp BSSP (Tesizy Dokl.), **1974**, 190  
[32] S Rubio; AG Hens; M Valcarcel, *Analyst*, **1984**, 109, 717  
[33] IV Kolotyorkina; LK Shpigun; YA Zolotov; GI Tsysin, *Analyst*, **1991**, 116, 707