Application of periodate oxidation of N, N- diethyl-*m*-toluidine for nanogram determination of Manganese

R. D. Kaushik*, Rajdeep Malik, Om Singh, Manila and Jaspal Singh

Department of Chemistry,
Gurukul Kangri University, Haridwar -249404 (Uttarakhand), India.

*Corres.author: rduttkaushik@yahoo.co.in
Phone: +91 7351739000

Abstract: A new method based on Mn^{II} catalysed periodate oxidation of N,N-diethyl-*m*-toluidine, for the determination of Mn^{II} in aqueous/ mixed media in nanograms, has been developed. The main reaction product is 4-methyl-1, 2-benzoquinone. The progress of reaction in acetone-water medium, 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. Seven types of calibration curves were developed and tested successfully for nanogram determination of manganese in aqueous/ mixed medium. The characteristics of various calibration curves, percentage recovery, effect of interferrants 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. The conditions were developed for kinetic-spectrophotometric determination of Mn^{II} in the range 0.199 – 43.78 ng/cm^{-3}. Molar extinction coefficient and Sandell's sensitivity for various calibration curves developed are respectively, 383660 to 767320 L. mol^{-1}.cm^{-1} and 0.211 to 0.418 ng. cm^{-2}.
Keywords: Mn^{II}, periodate ion, N,N-diethyl-*m*-toluidine, Nanogram Estimation, 4-methyl-1, 2-benzoquinone.

Introduction

        Many methods reported for determination of Mn^{II} involve a complicated pre-treatment of samples, complex operation and use of costly equipments and techniques like 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. 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 determination of Mn^{II} based on periodate oxidation of other substrates[1-6] and Mn^{II} catalysed/ uncatalysed periodate oxidation of aromatic amines[9-21]. In continuation to our kinetic mechanistic studies made on Mn^{II} catalysed periodate oxidation of N,N-diethyl-*m*-toluidine [22], a new method developed for nanogram determination of Mn^{II} on the basis of periodate oxidation of N,N-diethyl-*m*-toluidine (DET), is being reported in this article.

Experimental

        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, were used for preparation of buffer[23] employed for maintaining the pH. Triply distilled water was used for preparation of the solutions. Sodium metaperiodate (CDH), DET (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. The reaction was studied in a

spectrophotometric cell and initiated by adding temperature equilibrated NaIO$_4$ solution of known concentration to the reaction mixture containing the DET, Mn^{II} and buffer and maintained at the desired temperature ($\pm$ 0.1^{0}C). The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-Pharmaspec-1700), at 535 nm, i.e., the absorption maxima of the reaction mixture. The studies were restricted to the time in which absorption maxima remained unchanged. 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.

Results

As already reported by us[22], the reaction was found to be first order in each reactant and catalyst with 1 mol of DET reacting with 2 moles of periodate in initial stage of reaction and 4-methyl-1,2-benzoquinone being the main product of oxidation. Rate-pH profile showed a maximum at pH=7.5. 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 DET–periodate redox system in acetone-water medium. The studies were made by taking oxidant in excess. The stoichiometric equation can be given as:

$$CH_3C_6H_4N(C_2H_5)_2 + 2IO_4^- + 2H^+ + 2H_2O \xrightarrow{\quad Mn^{II} \quad} CH_3C_6H_3O_2 + 2HIO_3 + NH_3 + 2C_2H_5OH$$
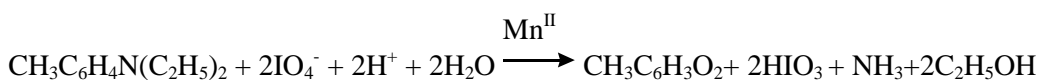
Mechanism of the reaction involved:

The faster colour changes in the reaction mixture relative to the separation of product on standing for long time indicates the formation of the colored intermediate on a time scale of minutes and that of the final product on a time scale of hours. The overall reaction appears to involve several steps and possibly several transient intermediates (C$_1$, C$_2$, C$_3$ and C$_4$), in addition to comparatively stable one C$_4$ (whose absorption maxima was used to follow the kinetics of the reaction) during the oxidation of DET into benzoquinone. Further, the kinetic order of one in periodate against the requirement of two periodate molecules for each DET molecule in the stoichiometry requires the involvement of only one periodate in the rate determining step and second IO$_4^-$ ion to be consumed in a fast step leading to the formation of C$_4$. Since the concentration of this intermediate, C$_4$, increases continuously with time and reaches a limiting value, its concentration can not be in steady state. Next important feature is the maximum obtained in the rate-pH profile of the reaction[22], which indicates the presence of at least three differently reactive species of reactant (which is periodate in this system) in the pH region chosen for study. Finally, the observation that free radical scavengers have no effect on reaction rate rules out the involvement of free radicals in the oxidation mechanism. The high negative value of entropy of activation supports the involvement of solvation effects in this reaction as given in the proposed molecular mechanism (Scheme-I). In the detailed mechanism, the catalytic role of Mn^{2+} appears to be due to the formation of a ternary complex, [(DET)Mn(H$_4$IO$_6$)]$^+$, in which Mn helps in electron transfer.

The conditions worked out for estimation of Mn^{II}:

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: [DET] = 0.0005 mol dm^{-3}; [NaIO$_4$] = 0.005 mol dm^{-3}; Acetone = 5.0% (v/v); pH = 7.0; λ_{max} = 535 nm; Temp.= 30 $\pm$ 0.1^{o}C. The method developed was suitable for estimation of Mn^{II} in the range 0.199 - 43.78 ng/ml to 1294.56 ng/ml.

Preparation of calibration curves:

A definite volume of stock solution of DET 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 30 $\pm$ 0.1^{o}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 2 minutes. The absorbance vs time plots were then made for different sets. The initial rates [(dA/dt)$_2$] were evaluated after 2 minutes 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, Seven type of linear calibration curves were obtained namely, Type 'A', Type 'B', Type 'C', Type 'D', Type 'E', Type 'F' and Type 'G' plot in terms of, respectively, A_4 or A_6 or A_8 or A_{12} or A_{16} or initial rate or k_{obs} vs [Mn^{II}] plots (where A_4, A_6, A_8, A_{12} and A_{16} are the absorbance values after 4, 6, 8, 12 and 16 minutes from the start of reaction respectively) (Figs. 2,3).
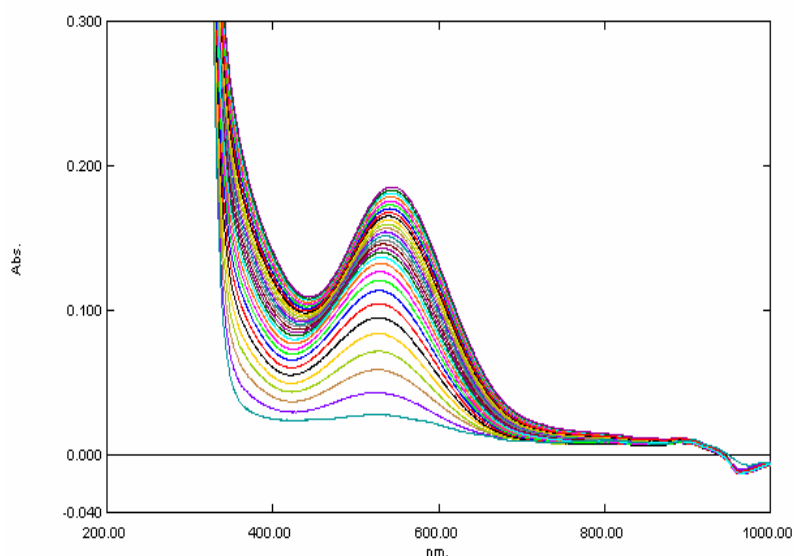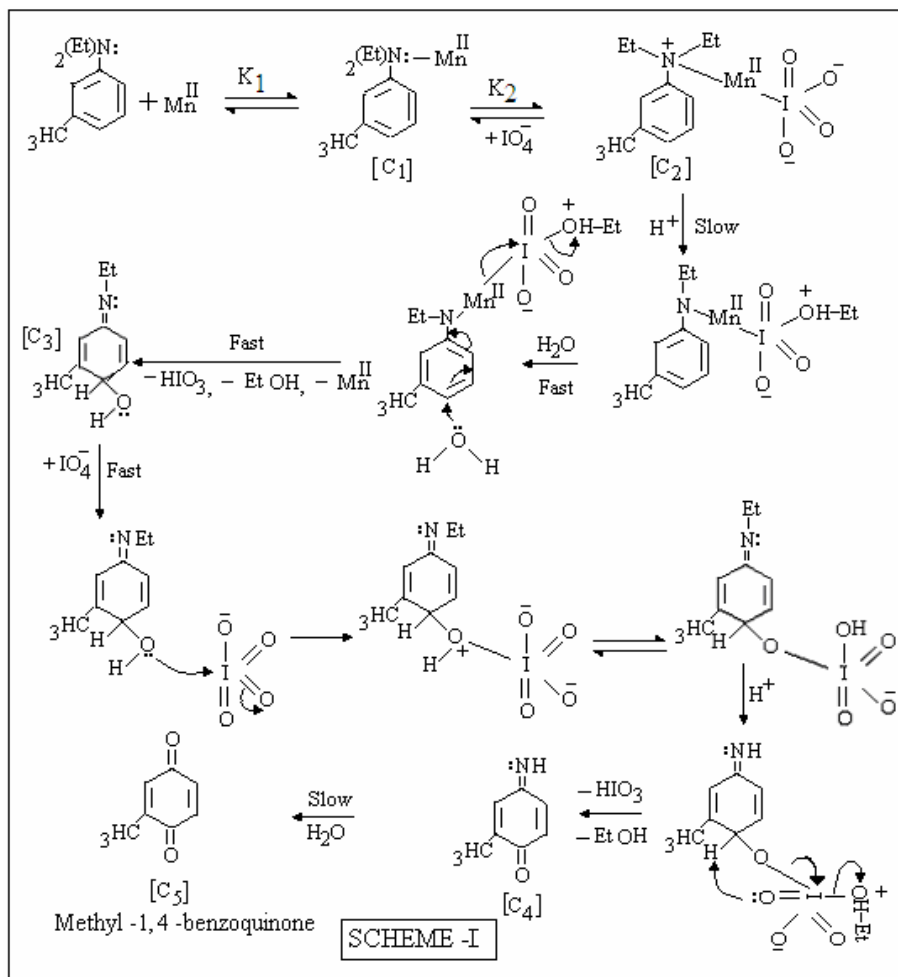

SCHEME -I

Fig.1. UV-VIS rapid scan at time interval of 60 seconds at [NaIO$_4$] = 8×10^{-3} mol dm^{-3}, [DET]=5.0×10^{-4} mol dm^{-3}, pH = 7.0, [Mn^{II}] =2.912×10^{-7} mol dm^{-3}, acetone = 5.0 % (v/v), Temp = 35.0 ± 0.1°C.
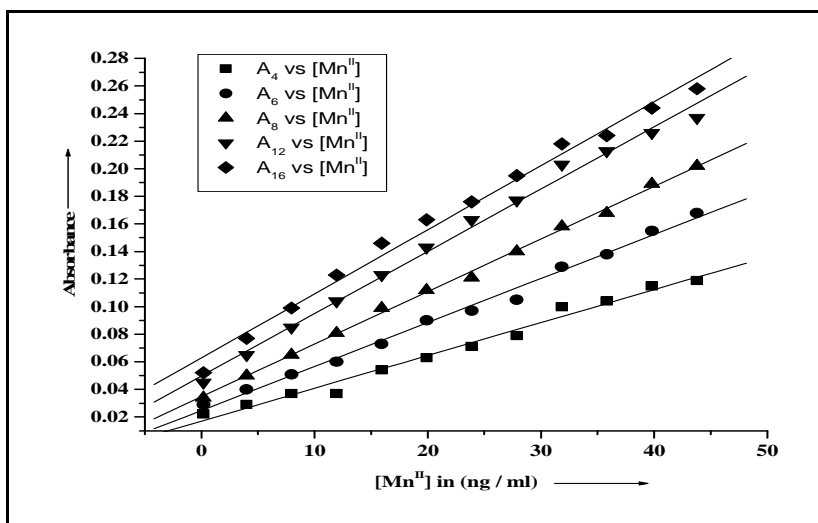
Fig. 2 Calibration curves in term of absorbance vs Mn^{II} plots at $[NaIO_4] = 5.0 \times 10^{-3}$ mol dm^{-3}, [DET] = 5.0×10^{-4} mol dm^{-3}, pH = 7.0, acetone = 5.0 % (v/v), Temp. = 30.0 ± 0.1^0C, λ_{max} = 535 nm.
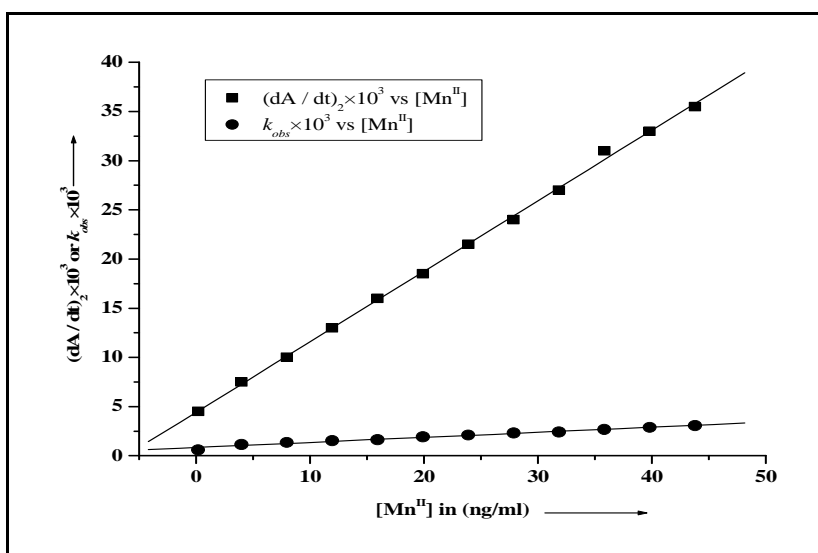

Fig.3 Calibration curves in term of initial rate or pseudo first order rate constant vs Mn^{II} plots at $[NaIO_4] = 5.0 \times 10^{-3}$ mol dm^{-3}, [DET] = 5.0×10^{-4} mol dm^{-3}, pH = 7.0, acetone = 5.0 % (v/v), Temp. = 30.0 ± 0.1^0C, λ_{max} = 535 nm.

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. The characteristics of calibration curves were evaluated in the form of equations of straight line given below:

$A_4 = 1.83 \times 10^{-2} + 2.35 \times 10^{-3}$ [Mn(II)]   -----(1)

$A_6 = 2.47 \times 10^{-2} + 3.19 \times 10^{-3}$ [Mn(II)]   -----(2)

$A_8 = 3.46 \times 10^{-2} + 3.82 \times 10^{-3}$ [Mn(II)]   -----(3)

$A_{12} = 4.97 \times 10^{-2} + 4.52 \times 10^{-3}$ [Mn(II)]   -----(4)

$A_{16} = 6.28 \times 10^{-2} + 4.54 \times 10^{-3}$ [Mn(II)]   -----(5)

$(dA/dt)_2 = 4.42 \times 10^{-3} + 7.17 \times 10^{-4}$ [Mn(II)]   -----(6)

$k_{obs} = 8.29 \times 10^{-4} + 5.4 \times 10^{-6}$ [Mn(II)]   -----(7)

In Eq. (1) to (5), the slopes and intercept are in absorbance units. ng^{-1}. cm^3 and absorbance units respectively. For equation (6), the values of slope and intercepts are in absorbance units. ng^{-1}. cm^3. min^{-1} and

absorbance units. min^{-1} respectively, while these are in absorbance units. ng^{-1}. cm^3. s^{-1} and absorbance units. s^{-1} respectively for equation (7). The [Mn^{II}] are in ng/ml.

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 Na$^+$, K$^+$, NO$_2^-$, ClO$_4^{-2}$, NO$_3^-$, and 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, H$_2$S may be passed in presence of 0.3 M H$^+$ solution, followed by filtration and boiling off H$_2$S. After it, a dilute alkaline solution of α-nitroso-β-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[4, 25]. In absence of the above given interferrants, the proposed method may successfully be used for the determination of nanogram quantities of Mn^{II} in water samples.

Procedure for estimation of Mn^{II}:

[Mn^{II}] may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of DET and acetone and starting the reaction by adding 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)$_2$ by plane mirror method or evaluating k_{obs} by Guggenheim's method as discussed above. After it, different calibration curves may be used for determination of [Mn^{II}] in ng/ml.

The proposed methods were tested for many water samples containing known amounts of Mn^{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). Various characteristics of the calibration curves indicate good sensitivity, molar absorptivity, percentage recovery, and correlation in the range of [Mn^{II}] 0.199 ng/ml to 43.78 ng/ml. It is clear that method is very well suited to estimation of Mn^{II} in trace amounts. The detection limit in terms of sandell's sensitivity is 0.211 – 0.418 ng cm^{-2}, which is reasonably good.

Discussion

Values of Sandell's sensitivity for different calibration curves obtained by using present method, suggest that a change in absorbance by 0.001 unit is expected on changing the concentration of Mn^{II} by 0.211 – 0.418 ng/ml. The molar absorptivity for sven types of calibtration curves developed are in the range 383660 to 767320 L mol^{-1} cm^{-1}. The value of 't' as calculated for the calibration curves, are in the range 6.7857 to 8.7949 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 parellel determinations is 99.21% to 99.70%. The correlation coefficient (r) is in the range 0.9886 to 0.9995 which indicates the high precision involved in the determination and almost perfect correlation of the data. The value of coefficient of determination (r^2) suggests that 98.99% to 99.89% change in the value of absorbance or (dA/dt)$_2$ or k_{obs} is caused by Mn^{II} and the rest 0.11% to 1.11% is the effect of unknown factors. A comparison of these methods 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-2. Although lower detection limits are available for some of the reported methods oxidations, these methods require rarely available facilities like flow injection method. The methods developed by us are cost effective and involve the use of simple equipments and chemicals that are generally expected to be available at 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^{II} 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. Method reported by Mutaftchiev[5,7] 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^{II} at nanogram level.

Table – 1

Characteristics of various types of calibration curves for the proposed methods

[DET]= 0.0005 mol dm^{-3}, [NaIO$_4$]= 0.005 mol dm^{-3}, acetone = 5.0% (v/v), λ_{max} = 535 nm, pH=7.0, Temp. = 30 ± 0.1^{o}C

Parameter	'A' plot	'B' plot	'C' plot	'D' plot	'E' plot	'F' plot	'G' plot
Beer's law limits (ng/ml)	0.199-43.78	0.199-43.78	0.199-43.78	0.199-43.78	0.199-43.78	0.199-43.78	0.199-43.78
Molar absorptivity x10^{-5} **(l.mol^{-1}.cm^{-1})**	3.8366	5.2079	6.2365	7.3794	7.6732	--	--
Sandell's sensitivity **(ng. cm^{-2})**	0.418	0.318	0.265	0.211	0.215	--	--
Slope x 10^3 **absorbance units. ng^{-1}.cm^3** **(from regression equation)**	2.35	3.19	3.82	4.52	4.54	7.17x10^{-1} min^{-1}	0.54x10^{-2} s^{-1}
Intercept x 10^2 (abs. units) **(from regression equation)**	1.83	2.47	3.46	4.97	6.28	4.42x10^{-1} min^{-1}	8.29 x10^{-2} s^{-1}
Correlation coefficient (r)	0.9952	0.9965	0.9981	0.9968	0.9949	0.9995	0.9974
Coefficient of determination (r^2)	0.9904	0.9930	0.9962	0.9936	0.9899	0.9989	0.9948
't' (at 0.01 significance level)	7.1569	7.1519	7.4851	7.9321	8.5252	6.7857	8.7949
Relative Standard deviation (%) **(From six determinations)**	1.1224	0.7857	0.5155	0.6296	0.4338	1.1034	0.5806
Recovery (%)	99.21	99.44	99.70	99.65	99.69	99.55	99.66

Table – 2

Comparison with other reported methods

Parameter	I[26]	II[8]	III[2]	IV[3]	V[5]	VI[7]	VII[27]	VIII[28]	IX[29]	X[30]	XI*
Beer's law limits (ng cm^{-3})	1000 – 25000	--	740 – 10320	0.05 – 5.0	0.08– 4.0	1-120	0.00 – 3520	5 –50	5 – 50	32- 200	0.199- 43.78
Molar absorptivity x10 $^{-3}$ (L mol^{-1} cm $^{-1}$)	--	--	4.972	--		99 – 165	5.84 – 7.24	54.945	197. 8	79.2- 180	383.66 - 767.32
Sandell's sensitivity (ng cm^{-2})	50	1x10^4	11	0.015	0.025	0.333 – 0.556	7.3 – 9.2	1.0	0.278	0.306- 0.694	0.211 – 0.418
Correlation coefficient (r)	--	--	--	--	0.998	0.998 – 1.000	0.998 - 0.999	0.9333- 1.003	0.999 - 1.0018	0.9951-0.9987	0.9886 - 0.9995
Coefficient of determination (r^2)	--	-	--	--	0.996	0.9996– 1.000	0.996 - 0.9984	0.870 - 1.006	0.998 - 1.0036	0.9902- 0.9974	98.99 - 99.89
't' (at 0.01 significance level)	--	--	--	--		--	--	--	--	6.793-8.02	6.7857 - 8.7949
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	0.434 – 1.122
% Recovery	--	--	--	--	---	--	--	--	--	99.1-100.0	99.21 - 99.70

I, II, III --- XI 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[31], 0.05 ng /ml [32], 0.01 ng /ml (by using flow injection method)[33].

References

1. Kaushik R.D., Shashi, Devi S. and Singh R.P., Simple kinetic-spectrophotometric method for the determination of Mn(II) in water, Asian J. Chem., 2004, 16, 837.
2. Dolmanova I.F., Poddubienko V.P. and Peshkova V.M., Determination of manganese by kinetic method using the oxidation of p-phenetidine by potassium periodate, Zh. Anal. Khim., 1970, 25, 2146.
3. Wei Q., Yan L.G., Chang G.H. and Ou Q.Y., Kinetic –spectrophotometric determination of trace manganese (II) with dahalia violet in nonionic microemulsion medium, Talenta, 2003, 59, 253
4. Biswas P.D. and De K., Extractive spectrophotometric determination of Mn(II) using 4-(methyl-phenyl)-3-oxobutanamide, J. Indian Chem. Soc., 2003, 80, 195.
5. Mutaftchiev K.L., Catalytic spectrophotometric determination of manganese in some medicinal plants and their infusions, Turkish. J. Chem., 2003, 27, 619.
6. Mutaftchiev K.L., Determination of manganese in some medicinal plants and their water extracts, Chemical Papers Chemicke zvesti., 2002, 56, 194.
7. Mutaftchiev K.L., Kinetic determination of nanogram levels of manganese(II) by naphthol blue black-potassium periodate- 1,10-phenanthroline system, Mikrochimica Acta, 2001, 36, 79-82.
8. Su L., Li J., Ma H. and Tao G., Determination of trace amounts of manganese in natural waters by flow injection stopped-flow catalytic kinetic spectrophotometry, Analytica Chimica Acta, 2004, 522, 281.
9. Kaushik R.D., Chaubey A.K. and Garg P.K., Kinetics and mechanism of periodate oxidation of p–phenetidine, Asian J.Chem., 2003, 15, 1655.
10. Kaushik R.D. and Joshi R., Kinetics and mechanism of periodate oxidation of m – toluidine in acetone – water medium, Asian J. Chem., 1997, 9, 527.
11. Kaushik R.D., Singh R.P. and Shashi, A kinetic – mechanistic study of periodate oxidation of p-chloroaniline, Asian J. Chem., 2003, 15, 1485.
12. Kaushik R.D., Kumar V., Arya R.K. and Singh D., Periodate oxidation of o-toluidine in acetone – water medium --- A kinetic and mechanistic study, Asian J. Chem., 2000, 12, 1123.
13. Kaushik R.D., Joshi R. and Singh D., Periodate oxidation of aromatic amines --- studies on the role of substituents and linear free energy relationships, Asian J. Chem., 1998, 10, 567.
14. Kaushik R.D., Singh D., Joshi R. and Kumar S., Kinetics of periodate oxidation of aromatic amines -- studies on the kinetic parameters and isokinetic relationship for few anilines, Asian J. Chem., 1998, 10, 573.
15. Pavolva V.K., Sevchenko Y.S. and Yatsimiriskii K.B., Kinetics and Mechanism of oxidation reaction of diethylaniline with periodate, Zh. Fiz. Khim. 1970, 44, 658.
16. Kaushik R.D., Kumari R., Kumar T. and Singh P., Periodate oxidation of N,N-dimethylaniline and N,N- diethylaniline, Asian J. Chem., 2010, 22, 7959.
17. Kaushik R.D., Amrita, Dubey M. and Singh R.P., Periodate oxidation of p-bromoaniline in acetone-water medium – A kinetic-mechanistic study, Asian J. Chem., 2004, 16, 831.
18. Kaushik R.D., Kumar D., Kumar Anuj and Kumar Ajay., Manganese(II) catalysed oxidation of 2,4-xylidine by periodate – A kinetic-mechanistic study, J. Indian Chem. Soc., 2010, 87, 811.
19. Kaushik R.D., Kaur M., Malik R. and , Kumar A., Studies on Manganese(II) catalysed oxidation of N-methylaniline by periodate ion, Int. J. Chem. Sci., 2010, 8, 1379.
20. Kaushik R.D., Kumar A., Kumar T. and Singh P., Manganese (II) catalysed periodate oxidation of p-toluidine- A kinetic-mechanistic study, React. Kinet. Mech. Cat., 2010, 101, 13; DOI 10.1007/s11144-010-0214-y.
21. Kaushik R.D., Shashi, Amrita and Devi S., Kinetics and mechanism of Mn (II) catalysed periodate oxidation of 4-chloro-2-methyl aniline, Asian J. Chem., 2004, 16, 818.
22. Kaushik R.D., Sundriyal P., Tyagi P., Singh P. and Singh J., Mn[II] catalyzed periodate oxidation of N, N-diethyl-*m*-toluidine – A kinetic and Mechanistic study, Int. J. Chem. Sci., In Press
23. Britton H.T.S.. Hydrogen ions, D. Von Nostrand Co.,1956, 354.
24. Meites L., Handbook of Analytical Chemistry, Mc Graw-Hill book Co., INC, New York, 1963, 3-4.
25. Vogel A.I., A Text Book of Quantitative Inorganic Analysis, Longmanns Green, London, 1961
26. Kemmer F.N., The Nelco Water Handbook, McGraw-Hill Co., Singapore, International edition, 1988, 7.32.
27. Kaushik R.D., Amrita, Singh R.P. and Devi S., Kinetic method for microgram determination of Mn(II) based on its catalytic effect on periodate oxidation of m-chloroaniline, J. Curr. Sci., 2004, 5, 341.
28. Kaushik R.D., Chaubey A.K. and Singh R.P., Indian J. Environ. Ecoplan., A new kinetic–spectro photometric method for determination of Mn(II) in micrograms in water, 2003, 7, 29.

29. Kaushik R.D., Amrita and Devi S., An improved method for nanogram determination of Mn(II) in aqueous medium, J. Curr. Sci., 2003, 3, 197.

30. Kaushik R.D., Devi S, Shashi and Amrita, Periodate oxidation of 2,3-dimethylaniline --determination of Mn (II) in nanograms in aqueous medium, Indian J. Environ. Ecoplan. 2004, 8, 253.

31. Bartkus P. and Nauekaitis A., Nauchn. Konf. Khim. Anal. Pribalt. Resp. *BSSP* (Tesizy Dokl.), 1974, 190.

32. Rubio S., Hens A.G. and Valcarcel M., Analyst, 1984, 109, 717.

33. Kolotyrkina I.V., Shpigun L.K., Zolotov Y.A. and Tsysin G.I., Analyst, 1991, 116, 707.

*****