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NEW METHOD FOR MICROGRAM DETERMINATION OF *p*-PHENETIDINE

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ABSTRACT

The reaction, Mn^{II} catalysed reduction of periodate by *p*-phenetidine in acetone-water medium is already reported by us to be first order in reactants and catalyst with main reaction product being 4-ethoxy-1, 2-benzoquinone. On the basis of best fit conditions in terms of pH, dielectric constant of medium, temperature etc., a new and simple kinetic-spectrophotometric method was developed for microgram determination of *p*-phenetidine in the range 1.29µg cm^{-3} to 9.79µg cm^{-3}. This method is being presented in present paper. Calibration curves in terms of absorbance at fix time Vs concentration of p-phenetidine as well as in terms of initial rate or pseudo first order rate constant Vs concentration, were obtained and their characteristics are being presented and discussed.

Keywords: Periodate ion, *p*-phenetidine, Mn^{II} catalysed, 4-ethoxy-1, 2-benzoquinone, Microgram

INTRODUCTION

Many workers have reported the estimation of some aromatic amines in smaller amounts in different media and using various complex reaction systems involving complicated pre-treatment and employing various techniques like NIR spectrometry, spectrophotometry, polarography, flow injection analysis, solvent extraction, Raman spectroscopy, various chromatographic techniques including TLC, gas chromatography, HPLC, reversed phase HPLC, GC-MS, GC/LC, GC-ECD, ion exchange chromatography and electrochemical detection.[1-10] There is one report available in literature regarding the kinetic-spectrophotometric estimation of some anilines based on their oxidation by periodate ion in aqueous/ mixed media.[11] Earlier reports have proposed the formation of binary or ternary complex formation as an intermediate respectively, in the reaction between aromatic amines and periodate ion either under uncatalysed[12-26] or Mn^{II} catalysed conditions.[27-36] These reactions have not been explored for estimation of *p*-phenetidine(PEA). Present paper deals with a kinetic-spectrophotometric method developed by us for determination of PEA in micrograms based on its Mn^{II}catalyzed oxidation by periodate ion. The method is new and simple in operation.

EXPERIMENTAL

Reagents

All principal chemicals like sodium metaperiodate (Loba Chemie), *p*-phenetidine (Alfa Aeser), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) were of analytical reagent/ guaranteed reagent grade. These were used after redistillation/ recrystallization for ensuring the purity. Triply distilled water was used for preparation of the solutions. pH of reaction mixtures were maintained by using Thiel, Schultz and Koch buffer.[37]

Recommended procedure for estimation of *p*-phenetidine

Reaction mixture shows the development of light pink colour changing into orange which in turn, converts into violet. Precipitation takes place in about 24 hours. The reaction was studied in a

spectrophotometric cell. For starting the reaction, $NaIO_4$ solution of known concentration (maintained at same temperature as maintained for all other reactants) was added to the reaction mixture containing the PEA, Mn^{II} and buffer. The reaction mixture was immediately transferred to the cuvette of double beam spectrophotometer (Shimadzu- UV-2550) in which the same temperature was maintained with the help of Shimadzu TCC-240 - an in-built temperature control unit with an accuracy of ± 0.1°C. The wavelength was fixed at 465 nm – which is the λ_{max} of the reaction mixture. λ_{max} was found to remain unchanged during study under experimental conditions (Fig.-1).

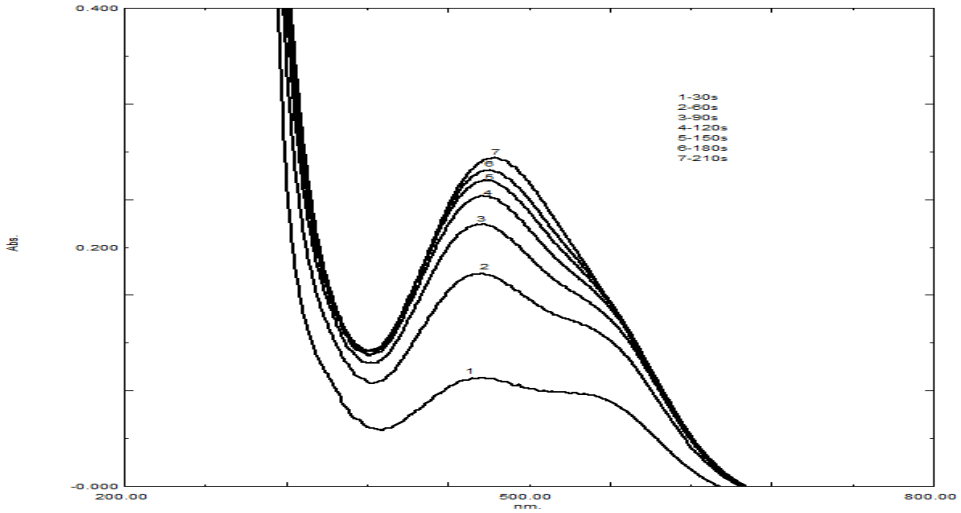

Fig.-1: Determination of absorbance maxima at [PEA] = 8.0×10^{-5} mol dm^{-3}, [$NaIO_4$] = 3.0×10^{-4} mol dm^{-3}, λ_{max} = 465 nm, [Mn^{II}] = 1.456×10^{-6} moldm^{-3}, Acetone = 5.0% (v/v), Temp. = 35 ± 0.1°C, pH = 6.5.

The finally worked out conditions for the purpose of kinetic-spectrophotometric determination of PEA in acetone-water medium as it reduces the periodate ion are, [Mn^{II}] = 7.28×10^{-7} mol dm^{-3} , [$NaIO_4$] = 1.0×10^{-3} mol dm^{-3}, Acetone = 5.0 % (v/v), pH = 6.5, λ_{max} = 465 nm, Temp.= 35.0 ± 0.1°C, [PEA] = unknown in the range of 1.29 µg $cm^{-3}$to 9.79µg cm^{-3}.

Stock solutions of PEA and Mn^{II} were prepared in respectively, acetone and water. Calculated volumes of these solutions and exxtra acetone was added for maintaining desired acetone concentration. Finally the reaction mixture was made upto required volume(less the volume of periodate to be added) by using the buffer described in reagents. This mixture and stock solution of $NaIO_4$ were then clamped in a thermostat at 35.0 ± 0.1°C. After 25 minutes, a pre-calculated amount of the periodate solution was added to the mixture and stirred to initiate the reaction. Similarly, different sets were prepared in by varying the [PEA].

The reaction mixture was transferred to the cuvette of spectrophotometer immediately. The same temperature was maintained in spectrophotometer cell too. The absorbance was recorded after repeated intervals of 30 seconds. Plane mirror method was applied on the absorbance vs time plots for different sets for evaluation of the initial rates, [$(dA/dt)_{30}$] after 30 seconds from the start of the reaction. Guggenheim's method[38] was employed for evaluation of the pseudo first order rate constants (k_{obs}). Method of least squares was used for obtaining the linear calibration curves. The calibration curves in terms of plots of type 'A', type 'B', type 'C', type 'D', type 'E' and type 'F' were obtained. These plots respectively were, in terms of A_{60} or A_{120} or A_{180} or A_{240} or initial rate or k_{obs} vs [PEA] plots (Fig. 2, 3). Here A_{60} or A_{120} or A_{180} or A_{240} are the absorbance values respectively after 60, 120, 180 and 240 seconds from the start of reaction.The sample of PEA containing unknown amount of PEA may be treated as above and [PEA] may be determined in aqueous solutions/ water samples by noting the absorbance of reaction mixture at different times or evaluating initial rate in terms of $(dA/dt)_{30}$ or k_{obs} and using different calibration curves.

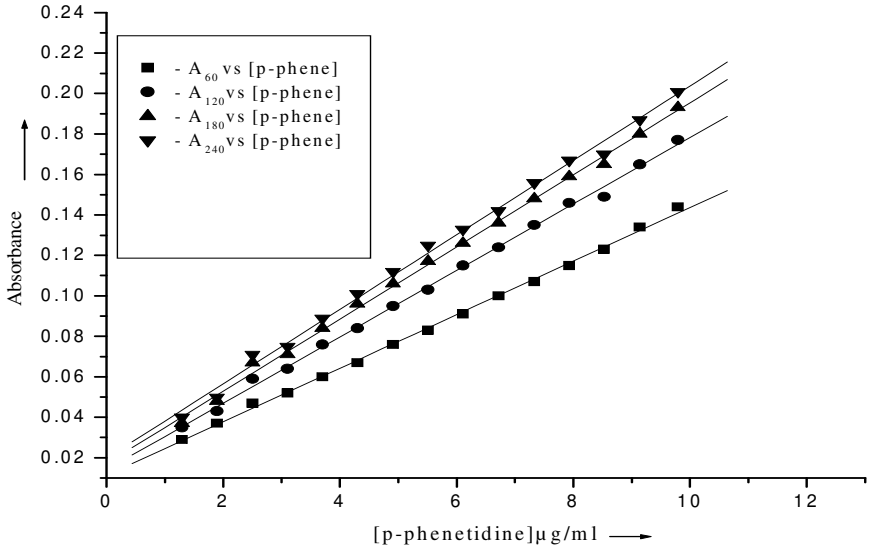

Fig.-2: Calibration curves of Type A, B, C and D
$[NaIO_4] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[Mn^{II}] = 7.28 \times 10^{-7}$ mol dm^{-3}, Acetone = 5.0 % (v/v), Temp. = 35.0 $\pm$ 0.1°C, pH = 6.5, λ_{max}= 465 nm

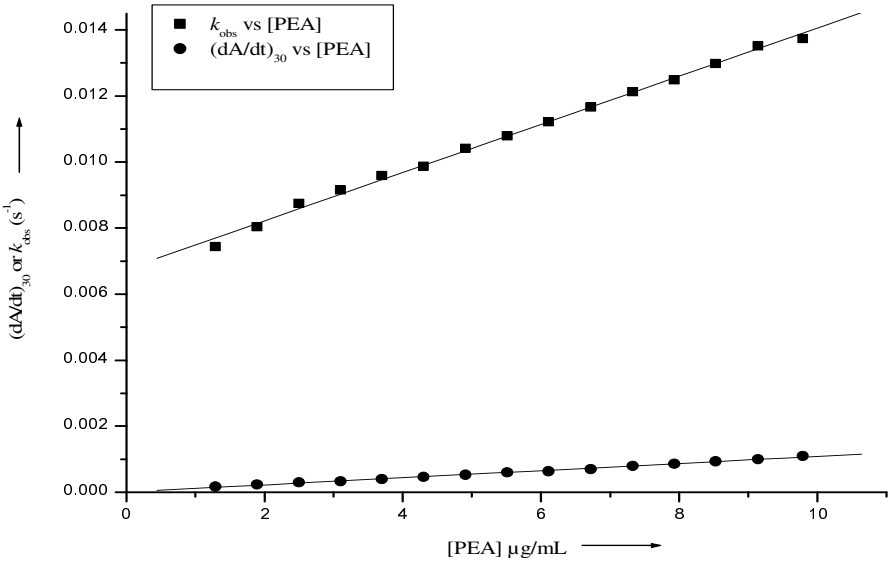

Fig.-3: Calibration curves of Type E and F
$[NaIO_4] = 1.0 \times 10^{-3}$ mol dm^{-3}, $[Mn^{II}] = 7.28\times 10^{-7}$ mol dm^{-3},acetone = 5.0 % (v/v), Temp. = 35.0 $\pm$ 0.1°C, pH = 6.5, λ_{max}= 465 nm.

Effect of interferrances

The method is not applicable in presence of most of the aromatic amines/ anilines as these might react with periodate and absorption maxima of the reaction mixture may get influenced. The ions like Na^+, NO_2^-, ClO_4^{-2}, NO_3^-, K^+, and SO_4^{-2} were found not interfering the procedure developed. A pretreatment is required for separating/ precipitating/ masking metals like, Fe, Hg, Mo, Ni, Pb, Sb, Se, U, Ag, As, Zn, Co, Cd, Cr, Cu and B as these are expected interferrants in this method. For this purpose, H_2S may be passed in presence of 0.3 M H^+ solution, followed by filtration and boiling off H_2S, addition of a dilute alkaline

solution of α-nitroso-β-naphthol and filtering the solution followed by its neutrallisation[39]. Fe may be removed by precipitation using basic formate method.[40-42] In absence of these given interferences, the method proposed by us may successfully be used for the determination of [PEA] in micrograms.

RESULTS AND DISCUSSION

The reaction under consideration (under uncatalysed and catalysed conditions) is already reported[17, 43] to show first order in PEA, periodate and Mn^{II}. Optimum value of rate has been reported at pH = 6.5. Negative solvent effect or an increase in rate with increase in dielectric constant of medium as another characteristic feature of this reaction. The reaction is not influenced by free radical scavengers and the main product of the reaction is 4-ethoxy-1, 2-benzoquinone. Fir initial part of reaction, 1 mol of PEA consumes 2 moles of periodate as given by the equation:

$$C_2H_5OC_6H_4NH_2 + 2IO_4^- + 2H^+ \xrightarrow{Mn^{II}} C_2H_5OC_6H_3O_2 + 2HIO_3 + NH_3 \quad (1)$$

The rate law can be given by Eq. (1),

$$d[C]/dt = k_{cat}\,[PEA]_0\,[IO_4^-]_0[Mn^{II}] \quad (2)$$

Where k_{cat} is the rate constant. $[IO_4^-]_0$and $[PEA]_0$ represent respectively, the initial concentration of periodate and substrate.

As already reported[44], the probable mechanism based on kinetic and other studies, is as follows:

$$C_2H_5OC_6H_4NH_2 + Mn^{2+} \overset{K_1}{\rightleftharpoons} [C_1] \quad (3)$$

$$[C_1] + [IO_4^-] \overset{K_2}{\rightleftharpoons} [C_2]\ (fast) \quad (4)$$

$$[C_2] + H^+ \xrightarrow{k} [C_3] + HIO_3 + Mn^{2+}\ (slow) \quad (5)$$

$$[C_3] + IO_4^- + H^+ \longrightarrow [C_4] + H_2O + HIO_3\ (fast) \quad (6)$$

In steps (1-6), $[C_1]$, $[C_2]$, $[C_3]$ and $[C_4]$ are intermediates, out of which $[C_4]$ appears to undergo very slow reorganization/ hydrolysis to yield the reaction product, C_5.

$$[C_4] \longrightarrow [C_5]\ (Product) \quad (7)$$

The formation of intermediates $[C_1]$ and $[C_2]$ in a rapid step having low values of equilibrium constants, K_1 and K_2, is assumed in the proposed mechanism. Mn^{2+} appears to play an important role in formation of ternary complex, $[(PEA)Mn(H_4IO_6)]^+$, in which Mn is important for electron transfer. High negative value of entropy of activation and the effect of dielectric constant on the reaction rate that support the solvation effects operating, as well as the formation of a charged intermediate complex C_2 by the attack of IO_4^- on the nitrogen of anilino group due to stabilization of positive charge on aniline nitrogen, have already been reported for the uncatalyzed/ catalyxed periodate oxidation of anilines.[22, 42-44]

Following equations of straight line describe the speciality of various calibration curves:

$$A_{60} = 1.13 \times 10^{-2} + 13.23 \times 10^{-3}\,[PEA] \quad (8)$$

$$A_{120} = 1.40 \times 10^{-2} + 16.42 \times 10^{-3}\,[PEA] \quad (9)$$

$$A_{180} = 1.73 \times 10^{-2} + 17.85 \times 10^{-3}\,[PEA] \quad (10)$$

$$A_{240} = 1.98 \times 10^{-2} + 18.39 \times 10^{-3}\,[PEA] \quad (11)$$

$$(dA/dt)_{30} = 0.0012 \times 10^{-2} + 0.11 \times 10^{-3}\,[PEA] \quad (12)$$

$$k_{obs} = 0.68 \times 10^{-2} + 0.73 \times 10^{-3}\,[PEA] \quad (13)$$

In equation 8-11, the values of intercept and slope are in absorbance units and absorbance units $\mu g^{-1} cm^3$ respectively while these are absorbance units s^{-1} and $cm^3\ \mu g^{-1}\ s^{-1}$ in equation 12-13. The [PEA] are in $\mu g\ cm^{-3}$.

Table-1: Kinetics runs for the preparation of calibration curves
$[Mn^{II}] = 7.28 \times 10^{-7}$ mol dm^{-3}, $[NaIO_4] = 1.0 \times 10^{-3}$ mol dm^{-3}, Acetone = 5.0 % (v/v), λ_{max}= 465 nm, pH = 6.5, Temp. = 35 $\pm$ 0.1°C

Parameter	Plot A (60 s)	Plot B (120 s)	Plot C (180 s)	Plot D (240 s)	Plot E (k_{obs})	Plot F (*rate*)
Linear range of [PEA] ($\mu g\ cm^{-3}$)	1.29-9.79	1.29-9.79	1.29-9.79	1.29-9.79	1.29-9.79	1.29-9.79
Molar absorptivity ($dm^3.mol^{-1}.\ cm^{-1}$)	1814.89	2252.49	2448.66	2522.74	---	---
Sandell's sensitivity($\mu g.cm^{-2}$)	0.07559	0.0609	0.05602	0.05438	---	---
Slope $\times 10^3$ absorbance units. $\mu g^{-1}cm^3$ (from regression equation)	13.23	16.42	17.85	18.39	0.728	0.107
Intercept $\times 10^2$(abs. units) (from regression equation)	1.134	1.409	1.725	1.979	0.676	0.0012
Correlation coefficient	0.9917	0.9989	0.9988	0.9979	0.9983	0.9979
Coefficient of determination	0.9835	0.9978	0.9976	0.9958	0.9966	0.9958
t*	9.0080	9.00953	9.1638	9.3156	20.8697	7.9517
Relative standaredDeviation(%) (for six determinations)	0.4200	0.5215	0.4550	0.3248	2.4507	0.3216
Recovery(%)	99.77	99.55	99.55	99.06	99.55	99.71

* at 0.01 significance level

A perusal of the data in table-1, shows a reasonable sensitivity, good correlation and excellent percentage recovery in the range of [PEA] = 1.29 - 9.79$\mu g\ cm^{-3}$. A change in absorbance by 0.001 units is caused by change in concentration of PEA by 0.054-0.076 $\mu g\ cm^{-3}$ as indicated by the Sandell's sensitivity. The correlation coefficient indicates the high precision involved in the determination. 98.35% to 99.78% change in the value of absorbance or $(dA/dt)_i$ or k_{obs} is caused by PEA and the rest 0.22% to 1.65% is the effect of unknown factors as suggested by the value of coefficient of determination. The value of 't' at 0.01 significance level are in the range 7.9517 to 20.8697 i.e. much higher than the tabulated critical value at 1% significance level indicating thereby less than 1% chances of error in drawing conclusions. The standard deviation is within reasonable limits for a simple method. Percentage recovery in the range 99.06% to 99.77% , is quite good.

Although lower detection limits and linear range of concentrations are available for estimation of some of the aromatic amines by using other reported methods involving/ not involving periodate oxidations[1-7], all of these methods require lengthy preconcentration and pretreatment of the samples including many complex reactions of the sample with oxidants and chromogenic substances. Further, most of these methods require not-readily available facilities like GC-ECD, GC-MS, solid phase extraction coupled with HPLC, differential pulse voltammetry and adsorptive stripping voltammetry, flow injection method etc. However, the requirement of cumbersome pre-treatments makes these methods more complicated.

The method proposed in present communication is fairly suitable for estimation of PEA at microgram level. It can be said that it is better than some of the reported methods which are applicable for estimation of *o*-anisidine and hydroxyanilines in the much higher range i.e. 1992- 9960 μg[7] and 1090 – 6560 μg[8], respectively. Likewise, our method will be suitable for estimation in the procedures for removal of anilines from wastewater for the initial amounts 2.5 x 10^{-6} moles of anilines (corresponding to 342.5 μg of PEA).[9, 10]

The method presented in this communication is simple, cost effective, involves the use of simple equipment (like a VIS-spectrophotometer) and chemicals that are generally available at small centers of testing and less time consuming in comparison to some of the other available methods for estimation of PEA. The characteristics of various calibration curves as given in table-1 make these methods competent for analysis. Further, no pretreatment of the samples is required except in presence of some rare interferrants.

REFERENCES

1. T.C. Schmidt, R. Haas, K. Steinbach and E.V. Low, Fresenius *J. Anal. Chem.,***357**, 909(1997)
2. L. Copolovici and I. Baldea, *Anal. Bioanal. Chem*., **374**,13(2002)
3. R. Haas, T.C. Schmidt, K. Steinbach and E.V. Low, *Fresenius J. Anal. Chem*., **359**,497-501(1997)
4. H. Bornick, T. Grischek and E. Worch, *Fresenius J. Anal. Chem*., **371**, 607 (2001)
5. X.N. Cao, J.H. Li, H.H. Xu, J.R. Zhan, L. Lin, K. Yamamoto and L.T. Jin, *Chromatographia,* **59**, 167 (2004)
6. J. Barek, J. Cvacka, A. Muck, V. Quaiserova and J. Zima, *Fresenius J. Anal. Chem.,***369,** 556 (2001)
7. M.A. Zayed, H. Khalifa and F.A.N. El-Dien, *Microchem. J.,* **34**,204 (1986)\M.Q. Al-Abachi, T.S. Al-Ghabsha and E.S. Salih, *Microchem. J.,* **41**, 64 (1990)
8. C.K. Sastri, B.S.A. Andrews and K.M.M.K. Prasad, *J. Indian Council Chemists*, **19**,59 (2002)
9. J.H. Weisburger, *Mutation Res.,* **376**,261 (1997)
10. Z. Karim and Q. Husain, *Int. J. Biodeterioration & Biodegradation*, **63**, 587 (2009)
11. R.D. Kaushik and R. Joshi, *Asian J.Chem.,***10**, 328(1998)
12. R.D. Kaushik , Amrita, M. Dubey and R.P. Singh, *Asian J. Chem.,***16**, 831 (2004).
13. R.D. Kaushik , V. Kumar, R.K. Arya, and D. Singh, *Asian J. Chem.,***12**, 1123(2000).
14. R.D. Kaushik , R.P. Singh, and Shashi, *Asian J. Chem.,***15**, 1485 (2003).
15. R.D. Kaushik , R. Malik, and A. Kumar, *J. Indian Chem. Soc.,***87**, 317 (2010).
16. R.D. Kaushik , R. Kumari, T. Kumar, and P. Singh, *Asian J. Chem.,***22**, 7959 (2010).
17. R.D. Kaushik , A.K. Chauby, and P. K. Garg, *Asian J. Chem.,***15**, 1655 (2003).
18. R.D. Kaushik , R.K. Arya. and S. Kumar, *Asian J. Chem.,***12**, 1229 (2000).
19. R.D. Kaushik , S.D. Oswal, and D. Singh, *Asian J. Chem.,***12**, 1129 (2000).
20. R.D. Kaushik , V. Kumar. and S. Kumar, *Asian J. Chem.,***11**, 633 (1999).
21. R.D. Kaushik , D. Singh. R. Joshi, and S. Kumar, *Asian J. Chem.,* **10**, 573 (1998).
22. R.D. Kaushik , R. Joshi, and D. Singh, *Asian J. Chem.,***10**, 567 (1998).
23. R.D. Kaushik and R. Joshi, *Asian J. Chem.,* **9**, 527 (1997).
24. R.D. Kaushik , P. Rathi, Manila, J. Singh, and R. Yadav, *J. Chem. Pharm. Res.,***6**, 2752 (2014).
25. R.D. Kaushik , R. Malik, R. Aggarwal, and J. Singh, *Res. J. Pharm. Biol. Chem. Sci.,***5**, 1644 (2014)
26. R.D. Kaushik , Shashi, Amrita and S. Devi, *Asian J. Chem.,***16**, 818 (2004).
27. R.D. Kaushik , D. Kumar, A. Kumar and A. Kumar, *J. Indian Chem. Soc.,***87**, 811 (2010).
28. R.D. Kaushik , A. Kumar, T. Kumar, and P. Singh, *React. Kinet. Mech. Cat.,***101**, 13 (2010).
29. R.D. Kaushik , R. Malik, T. Kumar, and P. Singh, *Oxid. Commun.,***35**, 316 (2012).
30. J. Singh, R. Malik, O. Singh, Sushma, and R.D. Kaushik , *Int. J. Chem. Sci.,***12**, 445 (2014)
31. R.D. Kaushik , P. Sundriyal, P. Tyagi, P. Singh, and J. Singh, *Int. J. Chem. Sci.,***12**, 600 (2014).
32. R.D. Kaushik , J. Singh, Manila, M. Kaur, and P. Singh, *Bull. Chem. React. Eng. & Cat.,* **9**, 182 (2014,)
33. R.D. Kaushik , R. Malik, O. Singh, Manila and J. Singh, *Int. J. ChemTech. Res.,***6**, 2695 (2014)
34. R.D. Kaushik , R. Yadav, M.M. Tiwari, P. Rathi and J. Singh, *Der Pharmacia Lettre,* **6**, 78 (2014),

35. R.D. Kaushik , R. Malik, M.M. Tiwari, J. Singh, and P. Singh, *Res. J. Pharm. Biol. Chem. Sci.,***5**, 1963(2014)
36. R.D. Kaushik, J. Singh, R. Agarwal, P. Rathi and E. Kumari, *Accepted for publication in Rasayan J. Chem,* **10(2)**,(2017)
37. H.T.S. Britton, "Hydrogen Ions", D. Von Nostrand Co., , pp. 354(1956)
38. E.A. Guggenheim, *Phil. Mag.*, 7, 538(1926)
39. L. Meites, Handbook of Analytical Chemistry, Mc Graw-Hill book Co., INC, New York, pp.3-4(1963)
40. P.D. Biswas and K. De, *J. Indian Chem. Soc.*, **80**, 195(2003)
41. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmanns Green, London,(1961)
42. R.D. Kaushik , J. Singh, Manila, P. Tyagi and P. Singh, *J. Indian Chem. Soc.*,**91**, 1483(2014)
43. R.D. Kaushik, J. Singh, P. Tyagi and E. Kumari, *Accepted for publication in J. Indian Chem. Soc.,* **94(6)**, (2017)
44. R.D. Kaushik , O. Singh, P. Tyagi, R. Yadav and J. Singh, *J. Indian Chem. Soc.*, **91**, 1959(2014)

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