



Application of Periodate - p-Phenetidine Reaction for Nanogram Determination of Mn^{II}

Jaspal Singh¹, RD Kaushik^{1*}, Priyanka Tyagi¹, Richa Saini² and Ekata Kumari³

¹Department of Chemistry, Gurukul Kangri University, Haridwar (Uttarakhand) India

²Department of Physics, Gurukul Kangri University, Haridwar (Uttarakhand) India

³Uttaranchal College of Science and Technology, Dehradun (Uttarakhand), India

ABSTRACT

On the basis of best fit conditions in terms of pH, dielectric constant of medium, temperature etc., a new and simple kinetic-spectrophotometric method has been developed for nanogram determination of Mn^{II} in the range 1.23 – 190.98 ng cm³ with molar extinction coefficient and Sandell's sensitivity for various calibration curves developed being respectively, 55600 to 72340 L mol⁻¹ cm⁻¹ and 2.34 to 3.04 ng cm⁻² using the reaction Mn^{II} catalysed periodate oxidation of p-phenetidine. Calibration curves in terms of absorbance at fix time vs [Mn^{II}] as well as in terms of initial rate or pseudo first order rate constant vs [Mn^{II}], were obtained and their characteristics are being presented and discussed. This reaction is already reported by us to be first order in reactants and catalyst with main reaction product 4-ethoxy-1, 2-benzoquinone.

Keywords: Nanogram; Periodate ion; p-phenetidine; Mn^{II}; 4-ethoxy-1,2-benzoquinone

INTRODUCTION

While there are many available reports related to kinetic-mechanistic studies on catalysed or uncatalysed non-Malapradian periodate oxidation of some aromatic amines [1-23], only some of these reactions have been explored for estimation of Mn^{II} [24-26]. It is worth mentioning that some methods have been developed for determination of Mn^{II} by employing the reactions of periodate with other substrates [27-32]. However, these methods involve complicated pre-treatment of samples and costly equipments. We have already reported the kinetic mechanistic studies on Mn^{II} catalysed reduction of periodate by p-phenetidine(PEA) [15]. This reaction has already been explored by us for developing method for determination of p-phenetidine. In this communication, it is being employed for the first time for developing a new method for nanogram determination of Mn^{II}.

EXPERIMENTAL SECTION

Materials

The 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 [33].

Recommended Procedure for Estimation of Mn^{II}

For starting the reaction, NaIO₄ 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 $\pm 0.1^\circ\text{C}$. 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 (Figure 1). Reaction mixture shows the development of light pink colour changing into orange which finally 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 $\pm 0.1^\circ\text{C}$. 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 (Figure 1).

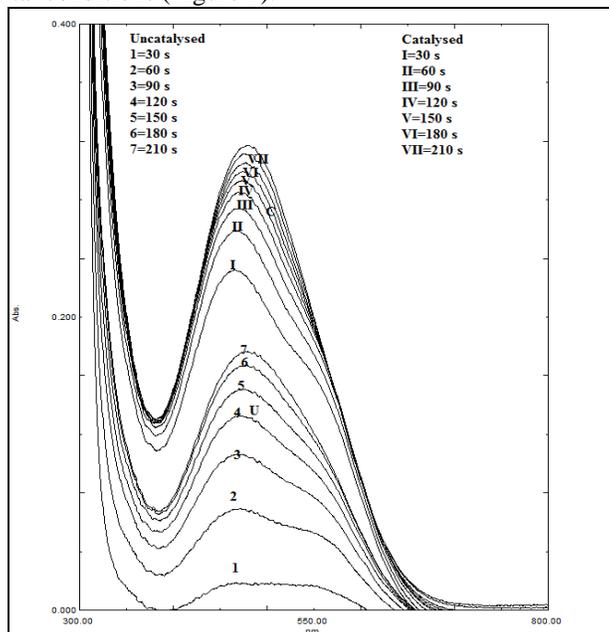


Figure 1: Determination of absorbance maxima for Mn^{II} catalysed and uncatalysed periodate oxidation of *p*-phenetidine

$$[\text{PEA}] = 8.0 \times 10^{-5} \text{ mol dm}^{-3}, [\text{NaIO}_4] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}, \lambda_{\text{max}} = 465 \text{ nm}, \\ [\text{Mn}(\text{II})] = 1.456 \times 10^{-6} \text{ mol dm}^{-3}, \text{Acetone} = 5.0\%, \text{Temperature} = 35 \pm 0.1^\circ\text{C}, \text{pH} = 6.5$$

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, $[\text{PEA}] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{NaIO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, Acetone = 10% (v/v), pH = 6.5, $\lambda_{\text{max}} = 465 \text{ nm}$, Temperature = $35 \pm 0.1^\circ\text{C}$. The methods developed were suitable for estimation of Mn^{II} in the range 1.23 ng cm^{-3} to $190.98 \text{ ng cm}^{-3}$.

Stock solutions of PEA and Mn^{II} were prepared respectively, in acetone and water. Calculated volumes of these solutions and extra acetone were 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 $35.0 \pm 0.1^\circ\text{C}$. 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 $[\text{Mn}^{\text{II}}]$.

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 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. Graphical plot between absorbance and time are given in Figure 2.

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_{30} or A_{60} or A_{90} or A_{120} or k_{obs} or initial rate vs $[\text{Mn}^{\text{II}}]$ plots

respectively (Figures 3 and 4). Where A_{30} or A_{60} or A_{90} or A_{120} are respectively, the absorbance values after 30, 60, 90 and 120 seconds from the start of reaction.

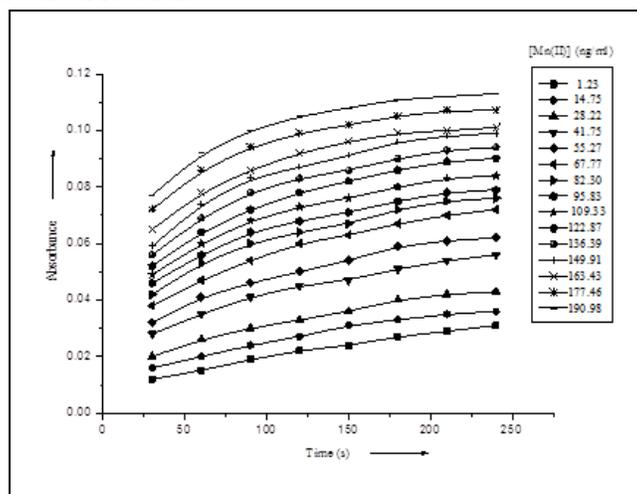


Figure 2: Absorbance vs. time plots

$[PEA] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[NaIO_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$,
Acetone = 5.0% (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 6.5, $\lambda_{\text{max}} = 465 \text{ nm}$.

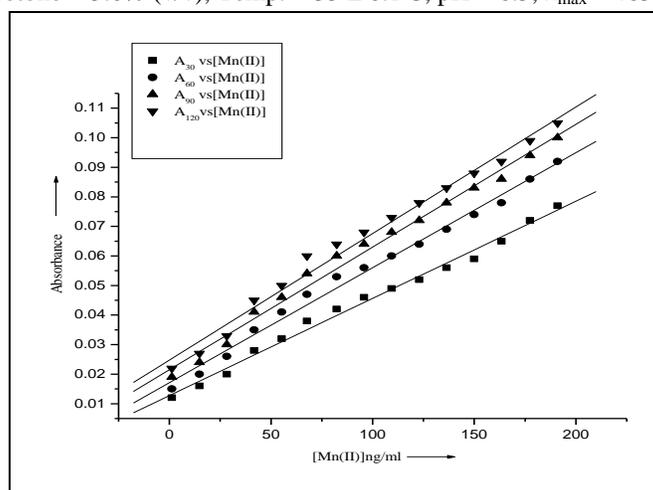


Figure 3: Calibration curves of type - A, B, C and D

$[PEA] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[NaIO_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$,
Acetone = 5.0% (v/v), Temperature = $35 \pm 0.1^\circ\text{C}$, pH = 6.5, $\lambda_{\text{max}} = 465 \text{ nm}$.

Effect of Interferences

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^- , NO_3^- , K^+ , and SO_4^{2-} were found not interfering with 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 interferences 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 neutralisation [33,34]. Fe may be removed by precipitation using basic formate method [28,35]. In absence of these given interferences, the method proposed by us may successfully be used for the determination of $[\text{Mn}^{\text{II}}]$ in nanograms.

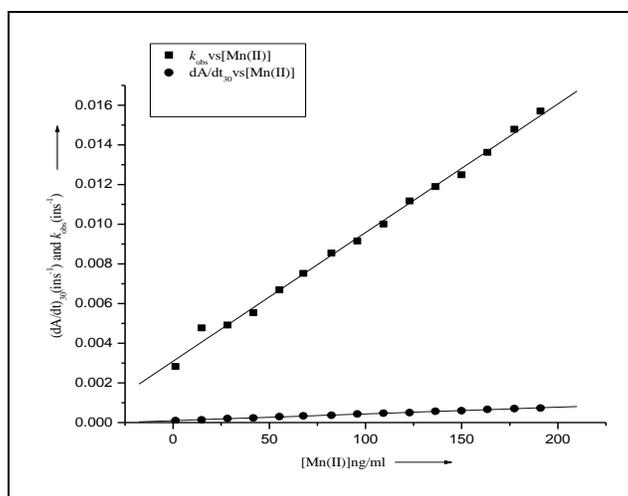


Figure 4: Calibration curves of type-E and F

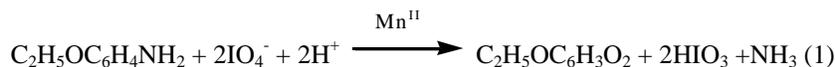
$$[\text{PEA}] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}, [\text{NaIO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3},$$

$$\text{Acetone} = 5.0\% \text{ (v/v)}, \text{Temperature} = 35 \pm 0.1^\circ\text{C}, \text{pH} = 6.5, \lambda_{\text{max}} = 465 \text{ nm}.$$

The sample of Mn^{II} containing unknown amount of Mn^{II} may be treated as above and $[\text{Mn}^{\text{II}}]$ 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.

RESULTS

The reaction under consideration (under uncatalysed and catalysed conditions) is already reported [15,35-40] to show first order in PEA, periodate and Mn^{II} . Optimum value of rate has been reported at $\text{pH} = 6.5$. Negative solvent effect or an increase in rate with increase in dielectric constant of medium is 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. For initial part of reaction, 1 mol of PEA consumes 2 moles of periodate as given by the equation:



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

$$A_{30} = 1.28 \times 10^{-2} + 3.29 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad (1)$$

$$A_{60} = 1.71 \times 10^{-2} + 3.89 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad (2)$$

$$A_{90} = 2.15 \times 10^{-2} + 4.15 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad (3)$$

$$A_{120} = 2.48 \times 10^{-2} + 4.29 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad (4)$$

$$(dA/dt)_{30} = 0.0097 \times 10^{-2} + 0.034 \times 10^{-3} [\text{Mn}^{\text{II}}] \quad (5)$$

$$k_{\text{obs}} = 0.3100 \times 10^{-2} + 0.648 \times 10^{-4} [\text{Mn}^{\text{II}}] \quad (6)$$

In equation 5, the values of intercepts and slope are in absorbance units sec^{-1} and absorbance unit $\text{sec}^{-1} \text{ ng}^{-1} \text{ cm}^{-3}$ respectively. These are in sec^{-1} and $\text{sec}^{-1} \text{ ng}^{-1} \text{ mL}$ respectively for equation 6. The $[\text{Mn}^{\text{II}}]$ are in ng cm^{-3} .

Table 1: Characteristic of various types of calibration curves for the proposed method

$$[\text{PEA}] = 3.0 \times 10^{-5} \text{ mol dm}^{-3}, [\text{NaIO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}, \text{Acetone} = 5.0\% \text{ (v/v)},$$

$$\text{Temperature} = 35 \pm 0.1^\circ\text{C}, \text{pH} = 6.5, \lambda_{\text{max}} = 465 \text{ nm}.$$

Parameter	A plot	B Plot	C plot	D plot	E plot	F plot
Linear range of $[\text{Mn}^{\text{II}}]$ (ng cm^{-3})	1.23-190.98	1.23-190.98	123-190.98	1.23-190.98	1.23-190.98	1.23-190.98
Molar absorptivity $\times 10^{-3}$ ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	55.6	65.74	70.14	72.34	---	---
Sandells sensitivity ($\text{ng} \cdot \text{cm}^{-2}$)	3.04	2.57	2.41	2.34	---	---
Slope $\times 10^4$ absorbance units. $\text{ng}^{-1} \text{ cm}^3$ (from regression equation)	3.29	3.89	4.15	4.29	0.648	0.034
Intercept $\times 10^2$ (absorbance units) (from regression equation)	1.28	1.71	2.15	2.48	0.31	0.0097
Correlation coefficient (r)	0.9959	0.9956	0.9944	0.9934	0.9977	0.9988
Coefficient of determination (r^2)	0.9916	0.9912	0.9888	0.9868	0.9954	0.9976
t (at 0.01 significance level)	8.5129	8.8385	9.328	9.7166	9.072	7.87
Relative standard Deviation (%) (for six determinations)	0.4201	0.5215	0.455	0.3247	0.6704	0.3216
Recovery (%)	99.97	99.77	99.42	97.32	98.49	99.39

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

Plots	Added (ng/ml)	Detected (ng/ml)	Recovery (%)
A	67.77	67.75	99.97
B	67.77	67.57	99.71
C	67.77	67.38	99.42
D	67.77	67.95	99.32
E(Rate)	67.77	67.56	99.69
F(k_{obs})	67.77	66.75	98.49

DISCUSSION AND CONCLUSION

A perusal of the data in Table 1, shows a reasonable sensitivity, good correlation and excellent percentage recovery in the range of $[Mn^{II}] = 1.23-190.98 \text{ ng cm}^{-3}$. Molar absorptivity is in the range $55600 \text{ to } 72340 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ which indicates good sensitivity. A change in absorbance by 0.001 units is caused by change in concentration of PEA by $2.34-3.04 \text{ ng cm}^{-3}$ as indicated by the Sandell's sensitivity. The correlation coefficient indicates the high precision involved in the determination. 98.68% to 99.76% change in the value of absorbance or $(dA/dt)_i$ or k_{obs} is caused by PEA and the rest 0.24% to 1.32% 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 7.8700 to 9.7166 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 97.32% to 99.77% is quite good. 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 (Tables 1 and 2). Various characteristics of the calibration curves indicate reasonable sensitivity, molar absorptivity, percentage recovery, and correlation in the range of $[Mn^{II}]$ (1.23 ng cm^{-3} to $190.98 \text{ ng cm}^{-3}$). 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 $2.34-3.04 \text{ ng cm}^{-2}$, which is reasonably good. A comparison of these methods for estimation of Mn^{II} 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 [16-19,24-26,28-29,31,36,39]. Although lower detection limits are available for some of the reported methods involving/ not involving periodate oxidations, not-readily available facilities like flow injection method etc and the requirement of cumbersome pre-treatments makes these methods more complicated. 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} in nanograms.

Table 3: Comparison with other reported methods

Parameter	I [36]	II [25]	III [28]	IV [29]	V [31]	VI [24]	VII [16]	VIII [17]	IX [18]	X [19]	XI [26]	XII*
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	0.54-345.22	1.23-190.98
Molar absorptivity $\times 10^{-3}$ ($\text{L mol}^{-1} \text{ cm}^{-1}$)	--	--	4.972	--	--	99-165	5.84-7.24	54.945	197.8	79.2-180	94.15-148.24	55.60-72.34
Sandell's sensitivity (ng cm^{-2})	50	1×10^4	11	0.015	0.025	0.333-0.556	7.3-9.2	1	0.278	0.306-0.694	0.82-1.3	2.34-3.04
Correlation coefficient (r)	--	--	--	--	0.998	0.998-1	0.998- 0.999	0.9333- 1.003	0.999- 1.002	0.9951- 0.9987	0.9981-0.9998	0.9934- 0.9988
Coefficient of determination (r^2)	--	-	--	--	0.996	0.9996- 1.000	0.996- 0.9984	0.870-1.006	0.998- 1.004	0.9902- 0.9974	0.9962-0.9996	0.9868- 0.9976
't' (at 0.01 significance level)	--	--	--	--	-	--	--	--	--	6.793-8.02	7.6033- 14.4226	7.8700- 9.7166
Relative standard deviation (%)(From 6 determinations)	--	--	0.73-1.4	--	2.7	0.353-0.885	0.27-0.5	1.509	1.093	--	0.1417-0.4048	0.322-0.670
% 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	98.72-99.91	97.32-99.97

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 33, 0.05 ng/ml 34, 0.01 ng/ml (by using flow injection method)[39].

REFERENCES

- [1] RD Kaushik; AK Chaubey; PK Garg. *Asian J Chem.* **2003**, 15, 1655.
- [2] RD Kaushik; R Joshi. *Asian J Chem.* **1997**, 9, 527.
- [3] RD Kaushik; RP Singh; Shashi. *Asian J Chem.* **2003**, 15, 1485.
- [4] RD Kaushik; V Kumar; RK Arya; D Singh. *Asian J Chem.* **2000**, 12, 1123.
- [5] RD Kaushik; R Joshi; D Singh. *Asian J Chem.* **1998**, 10, 567.
- [6] RD Kaushik; D Singh; R Joshi; S Kumar. *Asian J Chem.* **1998**, 10, 573.
- [7] VK Pavolva; YS Sevchenko; KB Yatsimiriskii. *Zh Fiz Khim.* **1970**, 44, 658.
- [8] RD Kaushik; R Kumari; T Kumar; P Singh. *Asian J Chem.* **2010**, 22, 7959.
- [9] RD Kaushik; Amrita; M Dubey; RP Singh. *Asian J Chem.* **2004**, 16, 831.
- [10] RD Kaushik; D Kumar; A Kumar; A Kumar. *J Indian Chem Soc.* **2010**, 87, 811.
- [11] RD Kaushik; M Kaur; R Malik; A Kumar. *Int J Chem Sci.* **2010**, 8, 1379.
- [12] RD Kaushik; A Kumar; T Kumar, P Singh. *React Kinet Mech Cat.* **2010**, 101, 13.
- [13] R.D. Kaushik; Shashi; Amrita, S. Devi. *Asian J Chem.* **2004**, 16, 818.
- [14] RD Kaushik; R Malik; T Kumar, P Singh. *Oxid Commun.* **2012**, 35, 316.
- [15] RD Kaushik; J Singh; P Tyagi; E Kumari. *J Indian Chem. Soc.* **2017**, 94(6).
- [16] RD Kaushik; Amrita; RP Singh; S. Devi. *J Curr Sci.* **2004**, 5, 341.
- [17] RD Kaushik; AK Chaubey; RP Singh. *Indian J Environ Ecoplan.* **2003**, 7, 29.
- [18] RD Kaushik; Amrita; S Devi. *J Curr Sci.* **2003**, 3, 197.
- [19] RD Kaushik; S Devi; Shashi; Amrita. *Indian J Environ Ecoplan.* **2004**, 8, 253.
- [20] RD Kaushik; V Kumar; S Kumar. *Asian J Chem.* **1999**, 11, 633.
- [21] RD Kaushik; SD Oswal; D Singh. *Asian J Chem.* **2000**, 12, 1129.
- [22] RD Kaushik; RK Arya; S Kumar. *Asian J Chem.* **2000**, 12, 1229.
- [23] RD Kaushik; R Malik; A Kumar. *J Indian Chem Soc.* **2010**, 87, 317.
- [24] RD Kaushik; Shashi; S Devi; RP Singh. *Asian J Chem.* **2004**, 16, 837.
- [25] IF Dolmanova; VP Poddubienko; VM Peshkova. *Zh Anal Khim.* **1970**, 25, 2146.
- [26] RD Kaushik; E Kumari. *J Chem Pharm Res.* **2014**, 6, 150.
- [27] Q Wei; LG Yan; GH Chang; QY Ou. *Talanta.* **2003**, 59, 253.
- [28] PD Biswas; K De. *J Indian Chem Soc.* **2003**, 80, 195.
- [29] KL Mutaftchiev. *Turkish J Chem.* **2003**, 27, 619.
- [30] KL Mutaftchiev. *Chemical Papers Chemicke zvesti.* **2002**, 56, 194.
- [31] KL Mutaftchiev, *Mikrochimica Acta*, **2011**, 36, 79
- [32] L Su; J Li; H Ma; G Tao. *Analytica Chimica Acta.* **2004**, 522, 281.
- [33] HTS Britton. Hydrogen ions, D. Von Nostrand Co. **1956**, 354.
- [34] L Meites. Handbook of Analytical Chemistry, Mc Graw-Hill book Co., INC, New York, **1963**, 3-4.
- [35] AI Vogel. A Text Book of Quantitative Inorganic Analysis, Longmanns Green, London, **1961**.
- [36] FN Kemmer. The Nelco Water Handbook, McGraw-Hill Co., Singapore, International edition, **1988**, 7.32.
- [37] P Bartkus; A Nauekaitis. *Nauchn Konf Khim Anal Pribalt Resp BSSP (Tesizy Dokl.)*, **1974**, 190.
- [38] S Rubio; AG Hens; M Valcarcel. *Analyst.* **1984**, 109, 717.
- [39] IV Kolotyrkina; LK Shpigun, YA Zolotov, GI Tsysin, *Analyst.* **1991**, 116, 707.
- [40] RD Kaushik; J Singh; Manila; P Tyagi; P Singh. *J Indian Chem Soc.* **2014**, 91, 1483.