Kinetic-spectrophotometric determination of Mn^{II} in nanograms based on its catalytic effect on periodate oxidation of N, N-dimethyl-p-toluidine.

Rd Kaushik[1]*, Jaspal Singh[1], Payal Rathi[2], Richa Saini[3], and Ekata Kumari[4]

[1]Department of Chemistry, Gurukul Kangri University, Haridwar (Uttarakhand) India
[2]Krishna College of Science & Information Technology, Bijnor(U.P.), India
[3]Department of Physics, Gurukul Kangri University, Haridwar (Uttarakhand) India
[4]Uttaranchal College of Science and Technology, Dehradun (Uttarakhand), India

ABSTRACT

The main reaction product of Mn^{II} catalysed periodate oxidation of N, N-dimethyl-p-toluidine in acetone-water medium is 4-methyl-1,2-benzoquinone. The progress of the reaction 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 5.49 – 357.11 ng/mL. Molar extinction coefficient and Sandell's sensitivity for various calibration curves developed are respectively, 85500 to 132400 L mol^{-1} cm^{-1} and 1.0 to 1.6 ng cm^{-2}. The characteristics of various calibration curves, percentage recovery, effect of interferrants and correlation coefficient etc have been evaluated. A comparison with other reported methods is also presented. It 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, N, N-dimethyl-p-toluidine, 4-methyl-1,2-benzoquinone

Corresponding author

INTRODUCTION

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. There are some reports on determination of Mn^{II} based on periodate oxidation of some substrates [1-6]. 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[7-9], although there are some reports available in literature related to the Mn^{II} catalysed/ uncatlysed periodate oxidation of aromatic amines[10-24, 29-32, 36-39]. In continuation to our kinetic mechanistic studies made on Mn^{II} catalysed periodate oxidation of N, N-dimethyl-p-toluidine [40], a new method developed by us for Mn^{II} estimation based on its catalytic effect on the periodate oxidation of N, N-dimethyl-p-toluidine (DMT), is being reported in present communication.

EXPERIMENTAL

Materials used

Triply distilled water was used for preparation of the solutions. Sodium metaperiodate(Loba Chemie), PEA(Aldrich), acetone(E. Merck), manganese sulphate monohydrate(Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. Thiel, Schultz and Koch buffer[25], consisting of different volumes of 0.05 mol dm^{-3} oxalic acid, 0.02 mol dm^{-3} boric acid, 0.05 mol dm^{-3} succinic acid, 0.05 mol dm^{-3} sodium sulphate and 0.05 mol dm^{-3} borax, was used for maintaining the pH.

Recommended Kinetic-spectrophotometric procedure

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 DMT, 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-1700), at 570 nm, i.e., the λ_{max} of the reaction mixture, during the period in which λ_{max} remained unchanged under experimental conditions. Figure 1, shows the absorption maxima of reaction mixture at different time[40]. Desired temperature was maintained with the help of a high precision in-built thermostatic control.

A definite volume of stock solution of DMT 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^{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 with the help of an in built temperature control unit Shimadzu TCC-240 with an accuracy of $\pm$ 0.1^{o}C. The absorbance was recorded after repeated intervals of 30 seconds. The absorbance vs time plots were then made for different sets. The initial rates [$(dA/dt)_{30}$] were evaluated after 30 seconds from the start of the reaction by applying plane mirror method on the absorbance vs time plots. Graphical plot between absorbance and time are given in Figure 2. 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 'E' and type 'F' plots were obtained in terms of A_{30} or A_{60} or A_{90} or A_{120} or initial rate or k_{obs} vs [Mn^{II}] plots respectively (Figure 2, 3). Where A_{30} or A_{60} or A_{90} or A_{120} are respectively, the absorbance values after 30, 60, 90 and 120 sceonds from the start of reaction.
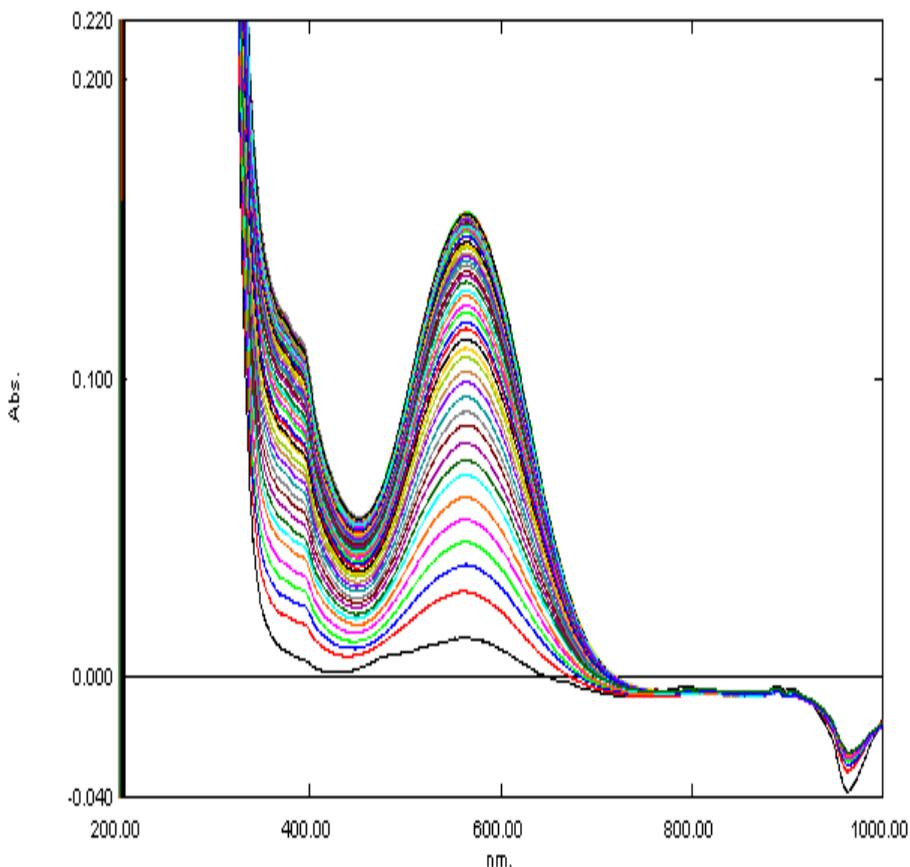
Fig 1: UV-VIS rapid scan at time interval of 60 seconds at [NaIO$_4$] = 8.0 × 10^{-3} moldm^{-3}, [DMT] = 3.0 × 10^{-4} mol dm^{-3}, pH = 5.5, [Mn^{II}] = 1.456 × 10^{-7} mol dm^{-3}, acetone = 10.0 % (v/v), Temp = 35.0 ± 0.1ºC [40]
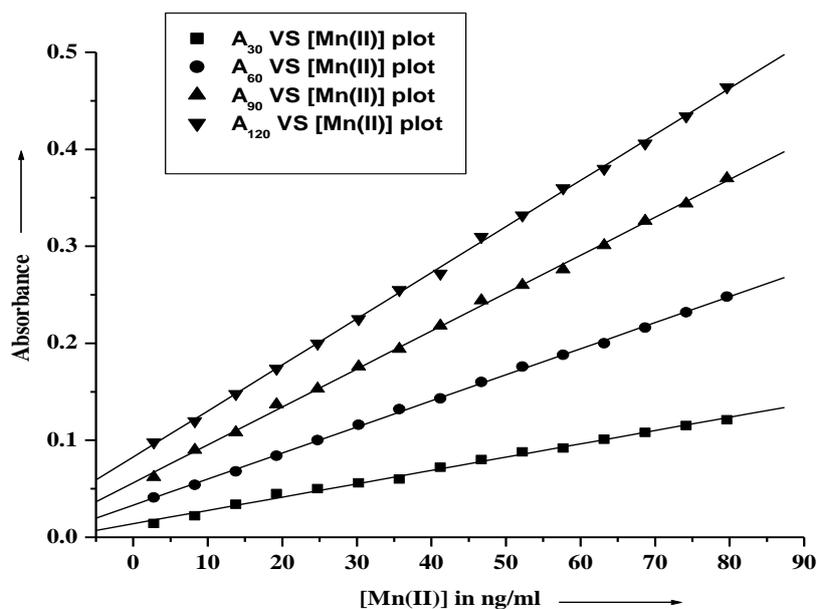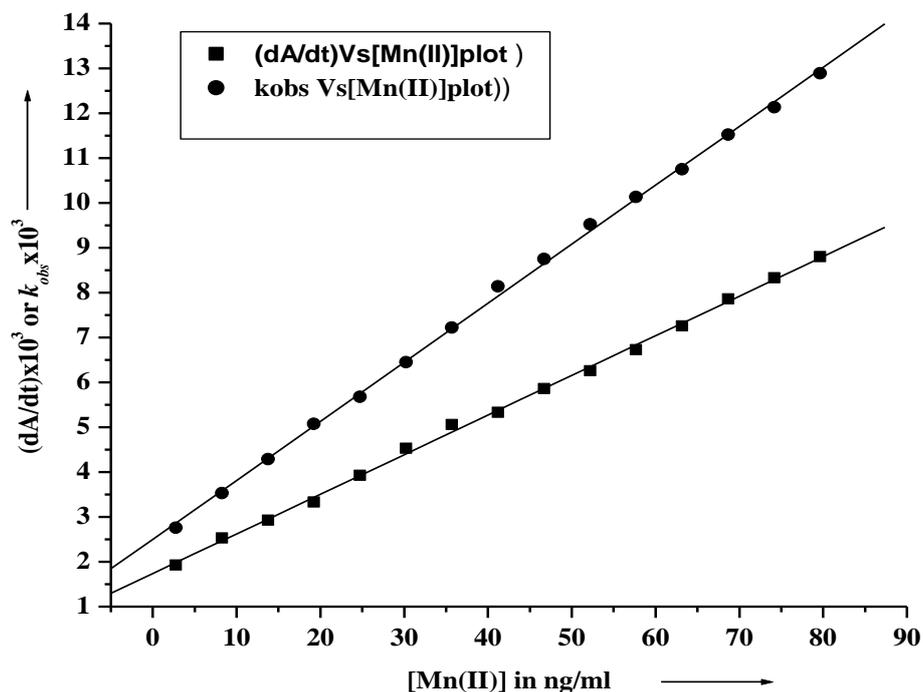

Figure 2: Calibration curves in terms of absorbance vs [Mn^{II}] plots
[DMT] ×10^4 = 3.0 M; [NaIO$_4$] ×10^3 = 3.0; Temp = 30 ± 0.1°C;
pH = 5.5; Acetone = 5.0% (v/v); λ$_{max}$ = 570 nm

Figure 3: Calibration curves in terms of Initial Rate vs [Mn^{II}] or pseudo first order rate constant vs [Mn^{II}] plot [DMT]×10^4 =3.0 M; [NaIO$_4$] ×10^3 = 3.0 M; Temp = 30 ± 0.1°C, pH = 5.5, Acetone = 5.0% (v/v); λ$_{max}$ = 570 nm]

The conditions worked out for determination 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 N, N-dimethyl-p-toluidine:

[NaIO$_4$)]× 10^3 = 3.0 mol dm^{-3}, [DMT] × 10^4 = 3.0 mol dm^{-3}, Acetone = 5.0% (v/v), pH = 5.5, λ$_{max}$ = 570 nm, Temp.= 30.0 ± 0.1°C, [Mn^{II}] = unknown in the range of 5.49 ng/ml – 357.11 ng/ml.

RESULTS

Kinetic features of the reaction involved

As already reported by us[40], the reaction was found to be first order in each reactant and catalyst with 1 mol of DMT reacting with 2 moles of periodate in initial stage of reaction and 4-methyl-1,2-benzoquinone being the main product of oxidation. The main reaction product is 4-methyl-1,2-benzoquinone. Rate-pH profile showed a maximum at pH value 7.0. 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 DMT−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:

$$A_{30} = 4.94 \times 10^{-2} + 6.32 \times 10^{-4} \, [Mn^{II}] \qquad -----(1)$$
$$A_{60} = 10.0 \times 10^{-2} + 9.23 \times 10^{-4} \, [Mn^{II}] \qquad -----(2)$$
$$A_{90} = 14.43 \times 10^{-2} + 9.75 \times 10^{-4} \, [Mn^{II}] \qquad -----(3)$$
$$A_{120} = 16.41 \times 10^{-2} + 9.79 \times 10^{-4} \, [Mn^{II}] \qquad -----(4)$$
$$(dA/dt)_{30} = 0.10 \times 10^{-2} + 8.96 \times 10^{-6} \, [Mn^{II}] \qquad -----(5)$$
$$k_{obs} = 0.43 \times 10^{-2} + 2.51 \times 10^{-5} \, [Mn^{II}] \qquad -----(6)$$

In equation 1-4, the values of intercept and slope are in absorbance units and absorbance units ng^{-1} mL respectively while in equation 5, the values of intercepts and slope are in absorbance units sec^{-1} and absorbance unit sec^{-1} ng^{-1} mL respectively. These are in sec^{-1} and sec^{-1} ng^{-1} mL respectively for equation 6. 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_2S may be passed in presence of 0.3 M H^+ solution, followed by filtration and boiling off H_2S. After it, a dilute alkaline solution of α-nitroso-β-naphthol should be added and again the solution should be filtered[26]. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method[2, 27]. 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.

Recommended estimation procedure

$[Mn^{II}]$ may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of DMT 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 $(dA/dt)_{30}$ 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 reasonable sensitivity, molar absorptivity, percentage recovery, and correlation in the range of $[Mn^{II}]$ (5.49 ng/mL-357.11 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 1.0-1.6 ng cm^{-2}, which is reasonably good.

DISCUSSION

Molar absorptivity is in the range 85500 to 132400 L mol^{-1} cm^{-1}. Value of Sandell's sensitivity suggests that a change in absorbance by 0.001 units is expected on changing the concentration of Mn^{II} by 1.0-1.6 ng/mL. Further, on changing concentration of Mn^{II} by 1 ng/mL, the value of k_{obs} will change by 2.51×10^{-5} in 1 second. This change is quite satisfactory and can be easily detected by using the methods under consideration. The correlation coefficient (r) is in the range 0.9992 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^2) suggests that 99.84% to 99.98% change in the value of absorbance or $(dA/dt)_i$ or k_{obs} is caused by Mn^{II} and the rest 0.02% to 0.16% is the effect of unknown factors. The values of 't' at 0.01 significance level, as calculated for the calibration curves, 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 98.53% to 99.93%.

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

Parameter	'A' Plot	'B' Plot	'C' Plot	'D' Plot	'E' Plot(dA/dt)	'F' Plot k_{obs}
Beer's law limits (ng/ml)	5.49-357.11	5.49-357.11	5.49-357.11	5.49-357.11	5.49-357.11	5.49-357.11
Molar absorptivity$\times10^{-4}$ (L mol^{-1} cm^{-1})	8.55	12.48	13.18	13.24	------	-----
Sandell's sensitivity (ng cm^{-2})	1.6	1.1	1.0	1.0	------	-----
Slope$\times10^4$ absorbance units ng^{-1} cm^3 (from regression equation)	6.32	9.23	9.75	9.79	8.96×10^{-2}	2.51×10^{-1}
Intercept $\times10^2$ absorbance units µg^{-1} cm^3 (from regression equation)	4.94	10.00	14.43	16.41	0.10	0.43
Correlation coefficient(r)	0.9998	0.9998	0.9998	0.9996	0.9992	0.9999
Coefficient of determination(r^2)	0.9996	0.9996	0.9996	0.9992	0.9984	0.9998
't' (at 0.01 significance level)	8.4179	9.4078	10.7057	11.3437	9.5619	11.4362
Relative Standard deviation(%) (from six determinations)	0.8319	0.4683	0.2041	0.1847	1.4709	0.8132
Recovery(%)	99.41	99.67	99.92	99.93	99.15	98.53

[DMT]$\times10^4$ = 3.0 M, [NaIO$_4$] x 10^3 = 3.0 M, Temperature = 30.0 ± 0.1°C, pH = 5.5, Acetone = 5.0% (v/v), λ$_{max}$ = 570 nm

Table-2: Comparison with other reported methods

Parameter	I [28]	II [8]	III [2]	IV [3]	V [5]	VI [7]	VII [29]	VIII [30]	IX [31]	X [32]	XI [9]	XII [40]	XIII*
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	5.49-357.11

Parameter													
Molar absorptivity $\times 10^{-3}$ (L mol^{-1} 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	85.5-132.4
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	0.82-1.3	2.34-3.04	1.0-1.6
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	0.9981-0.9998	0.9934-0.9988	0.9992-0.9999
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	0.9984-0.9998
											0.9996	0.9976	0.9998
't' (at 0.01 significance level)	--	--	--	--		--	--	--	--	6.793 -8.02	7.6033-14.4226	7.8700-9.7166	8.4179-11.4362
Relative standard deviation (%)(From 6 determinations)	--	--	0.73-1.4	--	2.7	0.353-0.885	0.27-0.50	1.509	1.093	--	0.1417-0.4048	0.322-0.670	0.185-1.471
% 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	98.53-99.93

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)[35].

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^{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.

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-2 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^{II} at nanogram level.

REFERENCES

[1]   Wei Q, Yan LG, Chang GH, Ou QY. Talenta 2003; 59: 253
[2]   Biswas PD, De K. J Indian Chem Soc 2003; 80: 195
[3]   Mutaftchiev KL. Turkish J Chem. 2003l; 27: 619
[4]   Mutaftchiev KL. Chemical Papers Chemicke zvesti 2002; 56: 194
[5]   Mutaftchiev KL. Mikrochimica Acta 2011; 36: 79
[6]   Su L, Li J, Ma H, Tao G. Analytica Chimica Acta 2004; 522: 281
[7]   Kaushik RD, Shashi, Devi S, Singh RP. Asian J Chem 2004; 16: 837
[8]   Dolmanova IF, Poddubienko VP, Peshkova VM. Zh Anal Khim 1970; 25: 2146
[9]   Kaushik RD, Kumari E. J Chem Pharm Res 2014; 6: 150
[10]   Kaushik RD, Chaubey AK, Garg PK. Asian J Chem 2003; 15: 1655
[11]   Kaushik RD, Joshi R. Asian J Chem 1997; 9: 527
[12]   Kaushik RD, Singh RP, Shashi. Asian J Chem 2003; 15:1485
[13]   Kaushik RD, Kumar V, Arya RK, Singh D. Asian J Chem 2000; 12: 1123
[14]   Kaushik RD, Joshi R, Singh D. Asian J Chem 1998; 10: 567
[15]   Kaushik RD, Singh D, Joshi R., Kumar S. Asian J Chem 1998; 10: 573
[16]   Pavolva VK, Sevchenko YS, Yatsimiriskii KB. Zh Fiz Khim 1970; 44: 658
[17]   Kaushik RD, Kumari R., Kumar T, Singh P. Asian J Chem 2010; 22:7959
[18]   Kaushik RD, Amrita, Dubey M, Singh RP. Asian J Chem 2004; 16: 831
[19]   Kaushik RD, Kumar D, Kumar A, Kumar A. J Indian Chem Soc 2010; 87: 811
[20]   Kaushik RD, Kaur M, Malik R, Kumar A, Int J Chem Sci 2010; 8: 1379
[21]   Kaushik RD, Kumar A, Kumar T, Singh P. React Kinet Mech Cat 2010; 101: 13
[22]   Kaushik RD, Shashi, Amrita, Devi S. Asian J Chem 2004; 16: 818
[23]   Kaushik RD, Malik R, Kumar T, Singh P. Oxid Commun 2012; 35: 316
[24]   Kaushik RD, Singh J, Tyagi P, Kumari E. Accepted for publication in J Indian Chem Soc 2017
[25]   Britton HTS. "Hydrogen Ions", D. Von Nostrand Co. 1956; p. 354
[26]   Meites L. Handbook of Analytical Chemistry, Mc Graw-Hill book Co., INC, New York. 1963; p.3-4
[27]   Vogel AI. A Text Book of Quantitative Inorganic Analysis. Longmanns Green, London. 1961
[28]   Kemmer FN. The Nelco Water Handbook, McGraw-Hill Co., Singapore, International edition 1988; 7.32
[29]   Kaushik RD, Amrita, Singh RP, Devi S. J Curr Sci 2004; 5: 341
[30]   Kaushik RD, Chaubey AK, Singh RP. Indian J Environ Ecoplan 2003; 7: 29
[31]   Kaushik RD, Amrita, Devi S. J Curr Sci 2003; 3: 197
[32]   Kaushik RD, Devi S, Shashi, Amrita. Indian J Environ Ecoplan 2004; 8: 253
[33]   Bartkus P, Nauekaitis A. Nauchn Konf Khim Anal Pribalt Resp BSSP (Tesizy Dokl.) 1974; 190
[34]   Rubio S, Hens AG, Valcarcel M. Analyst 1984; 109: 717
[35]   Kolotyrkina IV, Shpigun LK, Zolotov YA, Tsysin GI. Analyst 1991; 116: 707
[36]   Kaushik RD, Kumar V, Kumar S. Asian J Chem, 1999; 11, 633
[37]   Kaushik RD, Oswal SD, Singh D. Asian J Chem 2000; 12: 1129
[38]   Kaushik RD, Arya RK, Kumar S. Asian J Chem 2000; 12: 1229
[39]   Kaushik RD, Malik R., Kumar A. J Indian Chem Soc 2010; 87: 317
[40]   Kaushik RD, Manila, Malik R, Kaur M, Sundriyal P. Res J Pharm Biol Chem Sci 2014; 5: 1261