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NEW METHODS FOR NANOGRAM ESTIMATION OF Mn(II) IN AQUEOUS/ MIXED MEDIA

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Abstract: A less cost effective method based on Mn(II) catalyzed periodate oxidation of o-toluidine for the determination of Mn (II) in aqueous / mixed media in nanogram 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 is found to be the first order with respect to catalyst, substrate and oxidant each. Different types of calibration curves were developed and tested successfully for nanogram determination of manganese (II) in aqueous/mixed medium. 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: Mn(II), periodate ion, o- toluidine, nanogram estimation.

Introduction:

Keeping in view the reported less cost effective methods involving costly instrumentation not available at all places of researches/ scientific institutions/ testing laboratories in India, an attempt has been made to work out the best suitable conditions leading to the kinetic spectrophotometric estimation of Mn (II) in nanograms while it catalyzes the o- toluidine (o-TOL)- periodate or p-toluidine (p-Tol) – periodate redox systems in acetone -water medium. While p-Tol – periodate system has been studied at absorption maxima 490 nm, the o-TOL – periodate system has been used for estimation of Mn (II) at two absorption maxima of reaction mixtures i.e. 475 nm and 525 nm.

The conditions worked out for estimation of Mn(II):

Three methods were developed for the estimation of Mn (II) in various ranges of concentration. In **method- I**, 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 o-TOL: [o-TOL] = 0.001 M; [$NaIO_4$] = 0.01 M; Acetone = 10% (v/v); pH 5.5; **λ**max = 525 nm; Temp. 35 ± 0.1°C. The reaction was found to follow second order kinetics with order being one in each reactant. The method developed was fit for estimation of Mn(II) in the range **52.0 ng/ml to 109.8 ng/ml**.

In **method II**, the Mn(II) estimation could be achieved in same medium but in the range **109.8 ng/ml to 2635.2 ng/ml** by making use of periodate oxidation of o-TOL. The conditions worked out and found suitable are: [o-TOL] = 0.0005 M; [$NaIO_4$] = 0.005M; Acetone = 5% (v/v); pH 6.5; **λ**max= 475 nm; Temp. 35 ± 0.1°C.
Third method for estimation of Mn(II) in same medium in the range **0.5 ng/ml to 48.0 ng/ml** was developed by using p-TOL - periodate redox system. This method was worked out under following conditions: [p-TOL] = 0.001 M; [$NaIO_4$] = 0.02M; Acetone = 15% (v/v); pH 8.0; λ_{max} = 490 nm; Temp. 35 ± 0.1°C. The reaction has also been found to be first order w.r.t. periodate and p-TOL.

Preparation of calibration curves:

A definite volume of stock solution of o-TOL or p-TOL 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 ± 0.1°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)]. Aliquots were withdrawn from the reaction mixture after repeated intervals of 0.5 or 1 or 5 minutes and the absorbance was recorded on double beam spectrophotometer. The absorbance vs time plots were then made for different sets. The initial rates [$(dA/dt)_i$] were evaluated after 0.5 or 1 or 5 minute from the start of the reaction by applying plane

mirror method on the absorbance vs time plots. The pseudo first order rate constants (k_1) were found by Guggenheim's method.

Using the method of least squares, linear calibration curves were obtained. For method I, type 'A', type 'B', type 'C', type 'D', type 'E' and type 'F' plots were obtained in terms of A_{10} or A_{20} or A_{30} or A_{40} or initial rate or k_1 vs [Mn (II)] plots respectively (where A_{10}, A_{20}, A_{30} and A_{40} are the absorbance values after 10, 20, 30 and 40 minutes from the start of reaction respectively) for the oxidation of o-TOI studied at absorption maxima 525 nm. In method - II, type 'A', type 'B', type 'C', type 'D', type 'E', type 'F' and type 'G' plots were obtained in terms of A_2 or A_4 or A_6 or A_8 or A_{10} or initial rate or k_1 vs [Mn (II)] plots respectively (where A_2 or A_4 or A_6 or A_8 or A_{10} are the absorbance values after 2, 4, 6, 8 and 10 minutes from the start of reaction respectively) for the oxidation of o-TOI studied at absorption maxima 475 nm. In method - III, type 'A', type 'B', type 'C', type 'D', type 'E' and type 'F' plots were obtained in terms of A_2 or A_4 or A_6 or A_8 or initial rate or k_1 vs [Mn (II)] plots respectively.

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 0.05 significance level), relative standard deviation and % error for various calibration curves are given in table. For the method - I, involving the oxidation of o-TOL that was studied at absorption maxima 525 nm, the characteristics of calibration curves were evaluated in the form of equations of straight line as follows:

$A_{10} = 2.44 \times 10^{-2} + 6.87 \times 10^{-4}$ [Mn(II)] -----(1)
$A_{20} = 5.735 \times 10^{-2} + 9.11 \times 10^{-4}$ [Mn(II)] -----(2
$A_{30} = 8.81 \times 10^{-2} + 1.05 \times 10^{-3}$ [Mn(II)] -----(3)

$A_{40} = 11.81 \times 10^{-2} + 1.1 \times 10^{-3}$ [Mn(II)] -----(4)

(dA/dt)i $1.75 \times 10^{-2} + 3.86 \times 10^{-3}$ [Mn(II)] -----(5)

$k_1 = 1.196 \times 10^{-4} + 2.67 \times 10^{-6}$ [Mn(II)] -----(6)

For the method II, involving the oxidation of o-TOL that was
studied at absorption maxima 475 nm, the characteristics of calibration curves were evaluated in the form of equations of straight line as follows:

$A_2 = 2.67 \times 10^{-2} + 3.147 \times 10^{-4}$ [Mn(II)] -----(7)

$A_4 = 6.854 \times 10^{-2} + 3.724 \times 10^{-4}$ [Mn(II)] -----(8)

$A_6 = 10.24 \times 10^{-2} + 4.171 \times 10^{-4}$ [Mn(II)] -----(9)

$A_8 = 11.86 \times 10^{-2} + 4.45 \times 10^{-4}$ [Mn(II)] -----(10)

$A_{10} = 12.32 \times 10^{-2} + 5.48 \times 10^{-4}$ [Mn(II)] -----(11)

(dA/dt)i = $-2.2 \times 10^{-3} + 1.83 \times 10^{-4}$ [Mn(II)] -----(12)

$k_1 = 7.36 \times 10^{-4} + 4.1 \times 10^{-6}$ [Mn(II)] -----(13)
Similarly, for the method - III, involving the oxidation of p-TOL
that was studied at absorption maxima 490 nm, the characteristics of calibration curves were evaluated in the form of equations of straight line as follows:

$A_2 = 8.55 \times 10^{-2} + 3.67 \times 10^{-3}$ [Mn(II)] -----(14)

$A_4 = 11.75 \times 10^{-2} + 6.2 \times 10^{-3}$ [Mn(II)] -----(15)

$A_6 = 15.61 \times 10^{-2} + 7.6 \times 10^{-3}$ [Mn(II)] -----(16)

$A_8 = 18.84 \times 10^{-2} + 9.2 \times 10^{-3}$ [Mn(II)] -----(17)

$(dA/dt)i = 8.3 \times 10^{-3} + 7.1 \times 10^{-3}$ [Mn(II)] -----(18)

$k_1 = 3.88 \times 10^{-4} + 3.44 \times 10^{-5}$ [Mn(II)] -----(19)

In equation 5, 12 and 18, the values of intercepts and slope are in absorbance units.min^{-1} and absorbance unit $min^{-1}.ng^{-1}.ml$ respectively. These are in sec^{-1} and $sec^{-1}.ng^{-1}.ml$ respectively for equation 6, 13 and 19. The [Mn(II)] are in ng/ml.

Effect of interferrants:

Aromatic amines:

The method-I is not applicable in presence of 2,3- dimethylaniline, o-anisidine, o-phenetidine and 3 – chloro-2 -methylaniline, while method -II and III are not suitable in presence of N-ethylaniline, o-ethylaniline, p-ethylaniline, p-toluidine, o chloroaniline, p-chloroaniline, m-anisidine, p-anisidine, N,N-diethyl aniline and 2,4-diethylaniline as these aromatic amines interfere in these methods by getting oxidized by periodate ion and the reaction mixture showing λmax in the range in which it influences the absorbance in the proposed estimation methods. Most of the other aromatic amines/ anilines do not interfere in these methods.

Interferring ions:

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. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method. 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 o-TOL or p-TOL 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 $(dA/dt)_i$ at a desired time by plane mirror method or evaluating k_1 by Guggenheim's method as discussed above. After it, different calibration curves may be used for determination of [Mn(II)] in ng/ml.

Discussion:

The proposed method was 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, 2 and 3).

Method I : The value of slope of the calibration curves, molar absorptivity, and Sandell's sensitivity (table - 1) indicated that the sensitivity of the method is good. A change in absorbance by 0.001 unit is expected on changing the concentration of Mn(II) by 0.909-1.456 ng/ml. Further, a change in concentration by 1.0 ng/ml will change the rate of reaction by 3.860×10^{-3} absorbance units/minute. In addition, the value of k_1 will change by 2.67×10^{-5} in 1 second on changing [Mn(II)] by 1 ng/ml. The detection limits (52 ng/ml to 109.8 ng/ml) are also considerably low and these are good for the trace determination of Mn(II). The correlation coefficient (r) is in the range 0.988 to 0.999 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 97.6% to 99.8% change in the value of A_{10} or A_{20} or A_{30} or A_{40} or $(dA/dt)_i$ or k_1 is caused by Mn(II) and the

rest 2.4% to 0.2% is the effect of unknown factors. The value of 't' as calculated for the calibration curves, are in the range 9.93 to 22.17 which are much higher than the tabulated critical value at 5% significance level or 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 99.23% to 99.99%. Molar absorptivity is 37760 to 60500 L. $mol^{-1}.cm^{-1}$ for the curves 'A', 'B', 'C' and 'D' respectively. It is clear that curves 'A', 'B', 'C' and 'D' are the useful calibration curves. Curve 'E' and 'F' are also significant as the change in rate or rate constant values is reasonable.

Method II : The value of slope of the calibration curves, molar absorptivity, and Sandell's sensitivity (table-2) indicated that the sensitivity of the method is good. A change in absorbance by 0.001 unit is expected on changing the concentration of Mn(II) by 1.826 - 3.178 ng/ml. Further, a change in concentration by 1.0 ng/ml will change the rate of reaction by 1.83 x 10^{-4} absorbance units/minute. In addition, the value of k_1 will change by 4.1 x 10^{-6} in 1 second on changing [Mn(II)] by 1 ng/ml. The detection limits (109.8 ng/ml to 2635.2 ng/ml) are good for the trace determination of Mn(II) Actually, method I and method II can be coupled for determination of Mn(II) in the range 52.0 ng/ ml to 2635.2 ng/ml that shows a wide range of determination. The correlation coefficient (r) is in the range 0.996 to 0.999 indicates high precision involved. The value of coefficient of determination (r^2) suggests that 99.2% to 99.8% change in the value of A_2 or A_4 or A_6. or A_8 or A_{10} or $(dA/dt)_i$ or k_1 is caused by Mn(II) and the rest 0.8% to 0.2% is the effect of unknown factors. The value of t as calculated for the calibration curves, are in the range 6.530 to 7.610 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 and percentage recovery along with the high value of molar absorptivity suggest that curves 'A', 'B', 'C' 'D', 'E' , 'F' and 'G' are the useful calibration curves.

Method - III: Various characteristics of the calibration curves (table-3) indicate reasonable sensitivity, molar absorptivity, percentage recovery, and correlation the range of [Mn(II)] 0.5 ng/ml to 48 ng/ml. Although the limits of applicability of Beer's law are not as wide as in case of Method -I or II, the method is very well suited to estimation of Mn(II) in trace amounts.

A comparison of the proposed method with **twelve** reported methods is shown in table-4. It suggests that the proposed methods are better than a few reported methods based on the periodate oxidation of aromatic However, the simplicity involved in the procedure and the low cost of determination go in favor of the proposed methods. The proposed methods I to III offer better and wider range of concentration for the preparation of calibration curves. Much lower concentrations can be detected with reasonably good sensitivity.

The redox process involved in the method, may be mechanistically similar to our earlier report related to the Mn(II) catalyzed periodate oxidation of 4-chloro-2-methylaniline, 2,3 dimethylaniline and o-toluidine. It has also been given in the chart.

Conclusion:

The methods developed by us are cost effective and involve 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. These methods are better than some of the previously reported methods in terms of characteristics of calibration curves and the ease of the procedure involved. Further these methods are simple and less time consuming comparison to the other available methods for estimation of Mn(II) in aqueous /mixed media, as no pretreatment of the samples etc. are involved expect in cases where some rare in interferrants are present as already discussed. In general, the proposed methods are fairly suitable for estimation of Mn(II) at nanogram level.

Table – 1

Characteristics of various types of calibration curves for the proposed method
[o – TOL] x 10^3 = 1.0 M; [$NaIO_4$] x 10^2 = 1.0 M; pH = 5.5; Acetone = 10.0% (v/v); Temp. = 35 ± 0.1°C; λ_{max} = 525 nm.

Parameter	'A' plot	'B' Plot	'C' plot	'D' Plot	'E' plot	'F' Plot
Beer's law limits (ng/ml)	52.0-109.8	52.0-109.8	52.0-109.8	52.0-109.8	52.0-109.8	52.0-109.8
Molar absorptivity x 10^{-4} ($L.mol^{-1}.cm^{-1}$)	3.776	5.011	5.775	6.050	------	--------
Sandell's sensitivity (ng. cm^{-2})	1.456	1.098	0.952	0.909	-------	-------
Slope x 10^3 Absorbance units. $ng^{-1}.cm^3$ (from regression equation)	0.687	0.911	1.050	1.100	3.860min^{-1}	2.670 x 10^{-2} sec^{-1}
Intercept x 10^2 (abs. units) (from regression equation)	2.433	5.735	8.810	11.810	1.753x 10^{-2} min^{-1}	1.196 x 10^{-2} sec^{-1}
Correlation coefficient (r)	0.988	0.994	0.996	0.995	0.999	0.999
Coefficient of determination (r^2)	0.976	0.988	0.992	0.990	0.998	0.998
't' (at 0.05 significance level)	13.51	16.86	19.39	22.17	9.93	14.77
Standard deviation (%) (from six determinations)	0.500	0.645	0.736	0.957	0.204	0.102
Recovery (%)	99.99	99.62	99.90	99.23	99.90	99.95

Table – 2

Characteristics of various types of calibration curves for the proposed method
[o- TOL] x 10^4 = 5.0 M; [$NaIO_4$] x 10^3 = 5.0 M; pH = 6.5; Acetone = 5.0% (v/v); Temp = 35 ± 0.1° C; λmax = 475 nm

Parameter	'A' plot	'B' Plot	'C' plot	'D' Plot	'E' plot	'F' Plot	'G' Plot
Beer's law limits (ng/ml)	109.8-2635.2	109.8-2635.2	109.8-2635.2	109.8-2635.2	109.8 - 2635.2	109.8 – 2635.2	109.8-2635.2
Molar absorptivity x 10^{-4} ($L.mol^{-1}.cm^{-1}$)	1.732	2.294	0.294	2.448	3.013	---	---
Sandell's sensitivity (ng . cm^{-2})	3.178	2.685	2.398	2.247	1.826	---	---
Slope x 10^4 absorbance units $ng^{-1}.cm^3$ (from regression equation)	3.147	3.724	4.171	4.450	5.478	1.83 min^{-1}	4.100x10^{-2} sec^{-1}
Intercept x 10^2 (abs. units) (from regression equation)	2.670	6.854	10.240	11.860	12.320	-2.20x10^{-1} min^{-1}	7.360X 10^{-2} sec^{-1}
Correlation coefficient (r)	0.999	0.996	0.998	0.998	0.998	0.999	0.999
Coefficient of determination (r^2)	0.998	0.992	0.996	0.996	0.996	0.998	0.998
't' (at 0.05 significance level)	7.023	7.370	7.610	7.75	7.280	6.530	7.520
Standard deviation (%) (from six Determinations)	0.408	0.456	0.500	0.577	0.612	0.289	0.204
Recovery (%)	99.82	99.50	99.75	99.83	100.0	99.83	99.91

Table – 3

Characteristics of various types of calibration curves for the proposed method

[p – TOL] x 10^3 = 1.0 M; [$NaIO_4$] x 10^2 = 1.0 m; pH = 8.0; Acetone = 15.0% (v/v); Temp. = 35 ± 0.1°C; λ_{max} = 490 nm.

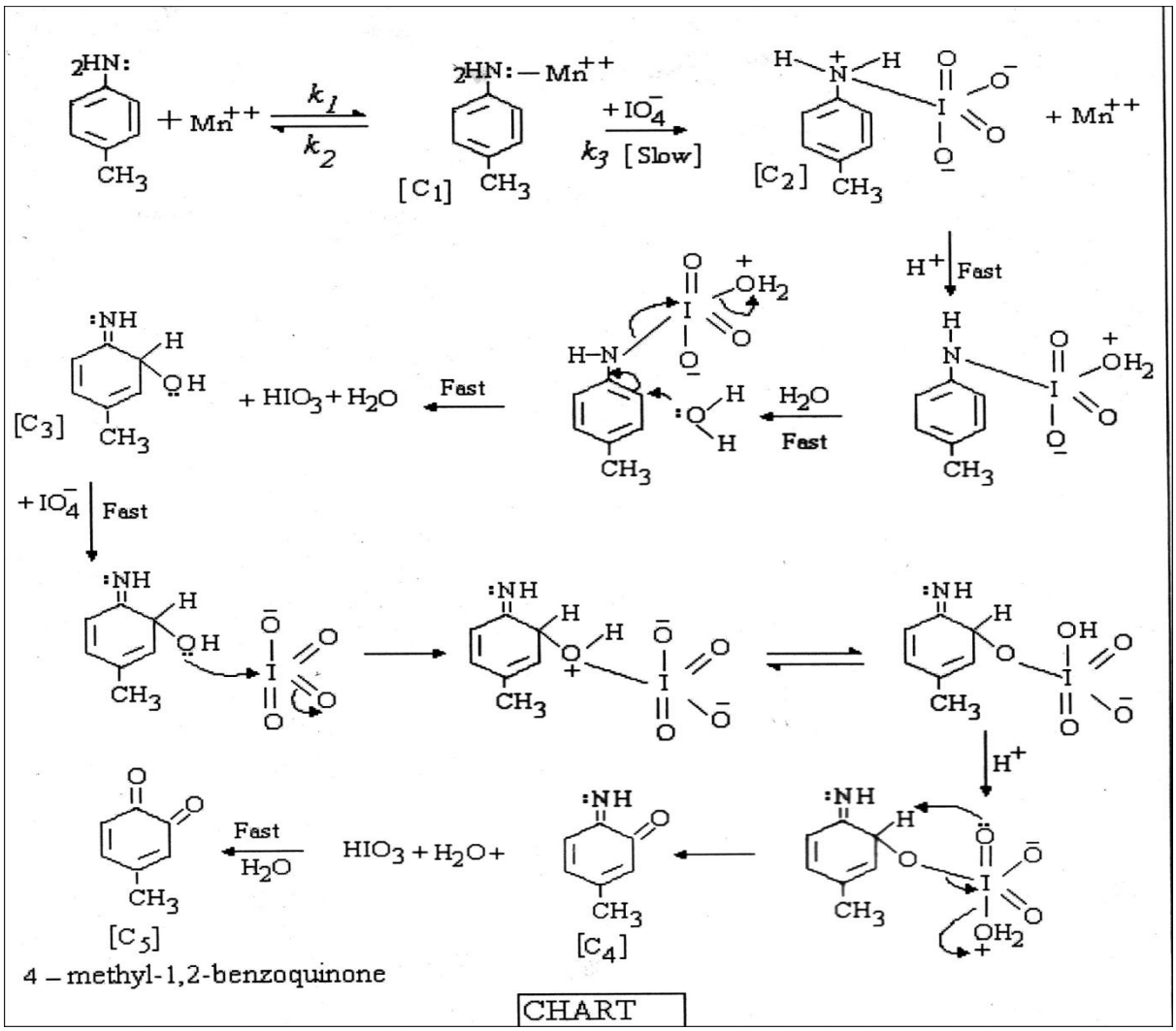
Parameter	'A' plot	'B' Plot	'C' plot	'D' Plot	'E' plot	'F' Plot
Beer's law limits (ng/ml)	0.5 – 48	0.5 – 48	0.5 – 48	0.5 – 48	0.5 – 48	0.5 – 48
Molar absorptivity x 10^{-5} ($L.mol^{-1}.cm^{-1}$)	2.019	3.410	4.180	5.060	----	----
Sandell's sensitivity (ng. cm^{-2})	0.272	0.161	0.132	0.109	----	----
Slope x 10^3 absorbance units. $ng^{-1}.cm^3$ (from regression equation)	3.670	6.200	7.600	9.200	7.100 min^{-1}	3.440x10^{-2} sec^{-1}
Intercept x 10^2 (abs. units) (from regression equation)	0.855	1.175	1.561	1.884	8.300x10^{-2} min^{-1}	3.880 x 10^{-1} sec^{-1}
Correlation coefficient (r)	0.996	0.999	0.998	0.999	0.999	0.999
Coefficient of determination (r^2)	0.992	0.998	0.996	0.998	0.998	0.999
't' (at 0.05 significance level)	8.460	7.590	7.890	7.900	3.75	5.910
Standard deviation (%)	0.135	0.158	0.073	0.238	0.147	0.224
(from six determinations)						
Recovery (%)	99.5	99.5	99.5	98.666	100.0	100.0

Table – 4. Comparison with reported methods**

[I,II,III…XII are the numbers assigned to methods for which the references are given at the end of the table.]

Parameter	I*	II*	III*	IV*	V*	VI*	VII*	VIII*	IX*	X*	XI*	XII*
Beer's law limits (ng/ml)	1000 - 25000	---	740- 10320	0.05 - 5.0	0.08-4.0	1-120	0.00 - 3520	5-50	5-50	32-200	2-120	11-440
Molar absorptivity x 10^{-3} ($L.mol^{-1}.cm^{-1}$)	---	---	4.972	---	---	99-165	5.842 - 7.240	54.945	197.8	79.2-180	21.99-57.75	37.5-65
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	0.952-2.5	0.845-1.465
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	0.997-0.999	0.998 0.9997
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	0.994-0.9984	0.996-0.9994
't' (at 0.01 significance level)	----	---	--	---	2.7	--	---	---	---	6.793 - 8.02	10.117-13.404	6.6467-9.2261
Relative standard deviation (%) (from 6 determinations) % error	---	---	0.73-1.4	--	1.7-3.3	0.353-0.885	0.27-0.50	1.509 -- ---	1.093	--	--	--
Standard deviation (%) (from six determinations)	---	---	---	---	--	0.37-0.929	0.37-0.524	--	---	0.506-1.655	0.089-0.328	0.0037-0.779
% Recovery	----	---	---	---	--	---	---	--	---	99.1-100.0	99.3-99.6	98.83-10

*while method I is persulphate; method II is based on periodate oxidation of p-phenetidine; III is based on complexation of Mn(II) with p-methylacetoacetanilide ; Method IV and V are also non aromatic amine oxidation based ones ; Method VI to XII are based on Mn(II) catalyzed periodate oxidation of m- ansidine, m-chloroaniline, 2,4- dimethylaniline , p-phenetidine , 2,3- dimethylaniline , 2,5- dimethylaniline and 5-chloro, 2methylanline respectively.



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