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NANOGRAM DETERMINATION OF MN^{II} CATALYST IN THE DEGRADATION OF *P*-BROMOANILINE BY PERIODATE ION

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ABSTRACT

A procedure has been developed for the specific estimation of Mn^{II} by determining its catalytic consequence on the deterioration of *p*-bromoaniline by periodate ion spectrophotometrically in the acetone water medium. The calibration curves for Mn^{II} in aqueous solutions were found to be linear over the concentration range of 1.06ng/mL to1254ng/mL at pH 5.5with detection limits in the range of 1.04-1.72ngcm^{-2}. The calculated RSDs of the method (n = 6) were 0.34–1.12 % for the concentration interval of Mn^{II} from 1.06 to 1254ng/mL. The alter in the reaction mixture's absorbance was spectrophotometrically recorded at 456nm in periodic intervals. For the estimation of Mn^{II} in aqueous solutions, this process was referred to and simultaneously compared with the reported various methods. Various parameters related to the determination of Mn^{II} as initial rates of the reaction, rate constant, molar extinction coefficient, Sandell's sensitivity, percentage recovery, correlation coefficient and the effect of interferants, etc. are being presented and discussed in this communication.

Keywords: Nanogram Determination, Sodium Metaperiodate, *p*-Bromoaniline, Mn^{II} Catalysed, 4-Methyl-1,2-benzoquinone.

INTRODUCTION

Manganese a component of enzymes, such as superoxide dismutase, glutamine synthetase and arginase[1], is broadly radiated atmospherically from metallurgic and chemical industries. The prolonged vulnerability to a minute quantity of manganese may augment the onset of Parkinsonian disturbances.[2] For a better interpretation of its pharmacokinetic behavior in the human body as well as the environment, an exceptionally precise and discriminatory course for the manganese estimation is necessarily required. On the ground of catalytic action of Mn^{II} on the oxidation of organic compounds, numerous kinetic methods have been detailed. Whereas, the commonly used oxidants include potassium periodate, hydrogen peroxide and triphenylmethane dyes[3], azo dyes[4, 5]and Schiff bases[6-12] were used as organic reagents. There are a few reports accessible within the literature concerning the kinetic spectrophotometric estimation of Mn^{II}, based on reduction of periodate ion by some substrates.[13-17] The Periodate degradation of aromatic amines has not been investigated broadly for kinetic spectrophotometric determination of Mn^{II} and only a few attempts have been made in this direction.[18-23] Manganese is a conventional trace element for human beings.[40] The kinetic point of view of the catalytic effect of Mn^{II} on the oxidation of *p*-bromoaniline with sodium metaperiodate was investigated.[24] To improve detection limits; *p*-bromoaniline is employed for the first time in the spectrophotometric kinetic system for the determination of Mn^{II} at the nanogram level.

EXPERIMENTAL

The analytical-reagent grade chemicals were used. Sodium metaperiodate (LobaChemie), manganese sulphate monohydrate (Aldrich), *p*-bromoaniline(PBA) (LobaChemie), acetone (E. Merck) were used after redistillation/ recrystallization. The usage of triple distilled water was done for the preparation of solutions. Thiel, Schultz and Koch buffer[25] were utilized for keeping up the pH of the reaction mixture.

General Procedure for Estimation

The determination of Mn^{II} in aqueous solutions was carried out by using the Shimadzu double beam spectrophotometer (UV-2550). The reaction mixture was completely mixed and rapidly redirected to an

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absorption cell which is equilibrated at 35 ±0.1^{0}C by the assistance of an incorporated temperature control unit (Shimadzu TCC-240). Under similar experimental requisites, the reaction mixture's wavelength maxima were recorded at 456 nm (Fig.-1).

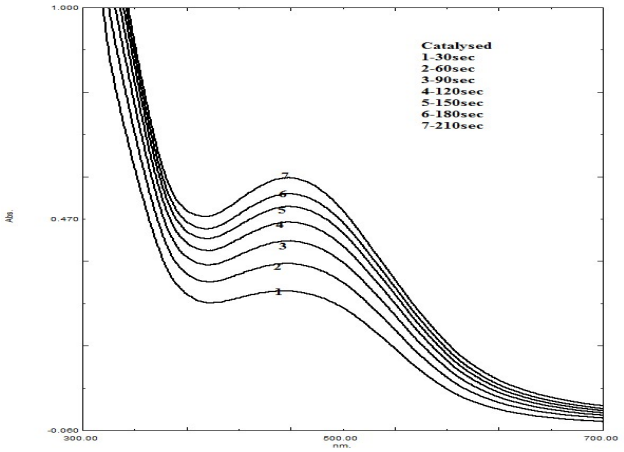

Fig.-1: Determination of Wavelength Maxima for PBA-$NaIO_4$ Reaction Catalyzed by Mn(II) at [PBA] × 10^5= 2.0 mol dm^{-3}, [$NaIO_4$]× 10^4 = 2.0 mol dm^{-3}, λ_{max} = 456 nm, [Mn(II)] × 10^6=7.28 mol dm^{-3}, Acetone = 5.0% (v/v), Temp. = 35 ± 0.1°C, pH = 5.5.

The reaction mixture shows the origin of light yellow color turning into wine red color and then orange succeeded by precipitation in around 24 hours.

The conditions worked out for spectrophotometric estimation of Mn^{II} in mixed(acetone-water) medium based on the periodate oxidation of PBA were: [$NaIO_4$] × 10^4= 7.0 moldm^{-3}, [PBA] × 10^5 = 8.0 moldm^{-3}, Acetone = 5.0 % (v/v), pH = 5.5, λ_{max} = 456 nm, Temp.= 35.0 ± 0.1°C,[Mn^{II}] = unknown in the range of 1.06ng/mL to 1254ng/mL.

Procedure for Calibration Curves

The calculated volume of reaction mixture containing PBA, water and acetone was blended with the particular proportion of stock solution of Mn^{II} in water. The solutions prepared were equilibrated thermostatically at 35 ± 0.1^{0}C temperature before starting the reaction. The further measured volume of periodate solution was added to the reaction mixture within 10 minutes. Diverse sets were worked out in a comparative way with differing [Mn^{II}]. The absorbance of the reaction was quickly recorded by Shimadzu double beam spectrophotometer (UV-2550) at periodic intervals of 30 seconds. Finally, the absorbance vs time plots was obtained, which are given in Fig.-2.

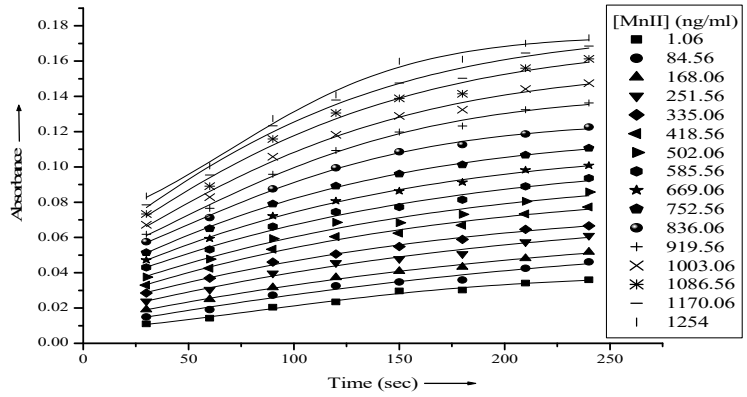

Fig.-2: Dependence of Absorbance on Time at Different Concentration of [Mn^{II}] at [$NaIO_4$] × 10^4 = 7.0 mol dm^{-3}, [PBA] × 10^5= 8.0 mol dm^{-3}, Acetone =5.0 % (v/v), Temp. = 35.0 ± 0.1^{0}C, pH =5.5, λ_{max}= 456 nm.

The Guggenheim's method[16] was employed for the calculations of pseudo-first-order rate constants (k_{obs}) and initial rates for the reaction evaluated by using a plane mirror method. Linear calibration curves were prepared by using the least-squares method and different plots were obtained as given in Fig.-3 and Fig.-4.

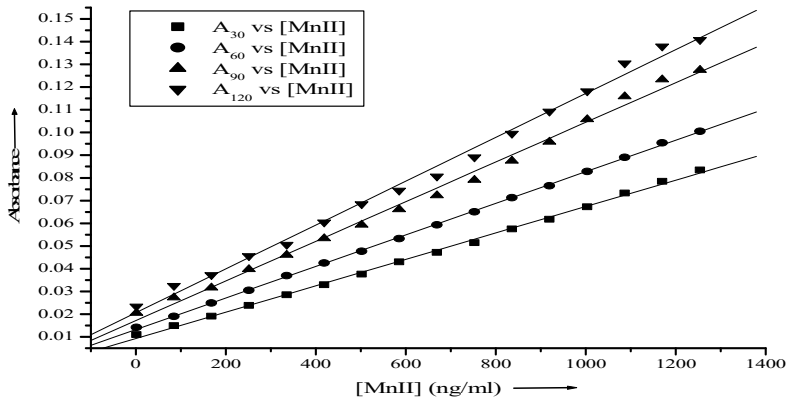

Fig.-3: Dependence of Absorbance on [Mn^{II}] at [$NaIO_4$] × 10^4 = 7.0 mol dm^{-3}, [PBA] × 10^5= 8.0 mol dm^{-3}, Acetone =5.0 % (v/v), Temp. = 35.0 ± 0.1^0C, pH =5.5, λ_{max}= 456 nm.

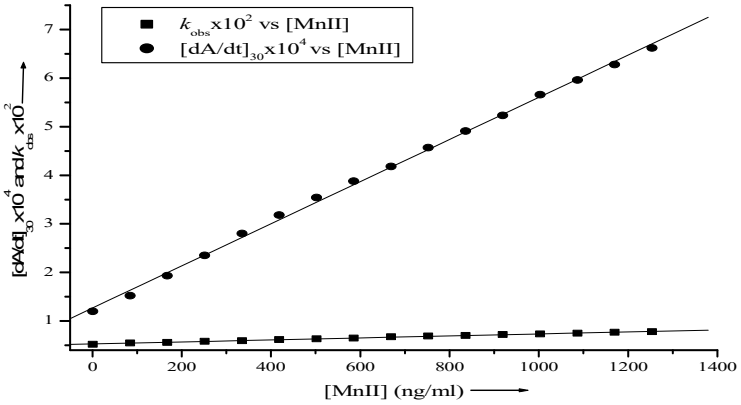

Fig.-4: Dependence of Initial Rate and Pseudo First Order Rate Constant on [Mn^{II}] at: [$NaIO_4$]× 10^4 = 7.0 mol dm^{-3}, [PBA] × 10^5 = 8.0mol dm^{-3}, Acetone =5.0 % (v/v),Temp. = 35.0 ± 0.1^0C, pH = 5.5, λ_{max}= 456 nm.

Procedure for Estimation of Mn^{II}

The absorbance of an aqueous solution with calculation proportions of PBA, acetone and $NaIO_4$ was spectrometrically recorded for the determination of [Mn^{II}] at different time interims. The initial rates in terms of $(dA/dt)_{30}$ were evaluated by applying a plane mirror method, k_{obs} by Guggenheim's method and [Mn^{II}] by varied calibration curves. The detailed process has been tried out for determining known amounts of [Mn^{II}] for many water samples within the range of reported detection limits.

RESULTS AND DISCUSSION

Validity of Beer's Law and Other Characteristics of The Method

The extent of Mn^{II} concentrations obeying Beer's law, molar absorptivity, Sandell's sensitivity, relative standard deviation, the correlation coefficient of determination and value of 't'(at 0.05 significance level) for diverse calibration curves are given in Table-1. Following are equations of the straight line depicting peculiarity of varied calibration curves:

$A_{30}= 9.2 \times 10^{-3} + 0.58 \times 10^{-4}$ [Mn^{II}] (1)
$A_{60} = 13.0\times 10^{-3} + 0.69 \times 10^{-4}$[$Mn^{II}$] (2)
$A_{90} = 17.0 \times 10^{-3}+ 0.87 \times 10^{-4}$ [Mn^{II}] (3)
$A_{120}= 21.0 \times 10^{-3} + 0.96 \times 10^{-4}$ [Mn^{II}] (4)
$(dA/dt)_{30} = 5.3\times10^{-1}+ 2.07\times 10^{-4}$ [Mn^{II}] (5)
$k_{obs} = 12.7\times10^{-1}+ 43.4\times 10^{-4}$ [Mn^{II}] (6)

Where A_{30}, $A_{60,}$ A_{90}, A_{120} are the absorbance recorded at 30, 60, 90 or 120 seconds respectively and k_{obs} is pseudo first-order rate constant. The values of intercept and slope given in equation 1-4, are in absorbance units and absorbance units ng^{-1} mL respectively, whereas in equation 5-6, intercept and slope are in absorbance $units^{-1}$ and mL ng^{-1} s^{-1}respectively. The concentration of $Mn^{II}$is in ng/mL.

Effect of Interferrants

Some interfering ions like Na^+, K^+, NO_2^-, ClO_4^{-2}, NO_3^-, and SO_4^{-2}do did not interfere in the reaction system for the estimation of Mn^{II} in trace amounts, so this method can be used in the presence of these ions. However, in some cases where some metals like Zn, Mo, Cd, Se, Hg, Ni, Ag, As, B, Co, Cr, Cu, Pb, Sb, U and Fe are anticipated to obstruct in the reaction system, a pre-treatment is required for the elimination of these metals from the reaction under consideration. For the elimination of these interferants from the reaction system Hydrogen sulfide gas should be passed in the presence of 0.3 M solution of H^+. After filtration and boiling of H_2S, a dilute alkaline solution of α-nitroso-β-naphthol should be added for the neutralization of the solution and all the metals are evacuated by filtration.[26] Presently, the suggested procedure can be applied for the determination of Mn^{II} in trace amounts in water samples. If Iron is present within the reaction system as an interferrant, it may be removed by precipitation using fundamental formate method.[14, 27]

Various calibration curves characteristically indicate that reasonable sensitivity, percentage recovery, and correlation are in the range of 1.06- 1254ng/mL as given in Table 1. Sandell's sensitivity recommends that change in absorbance by 0.001 units is expected on varying the concentration of Mn^{II} from 1.04to1.72 ng/mL. The correlation coefficient (r) is in the range of 0.9973-0.9998 which depicts high accuracy involved in the determination of Mn^{II} and almost perfect correlation of the data. The coefficient of determination (r^2) is evaluated in the range of 0.9946 to 0.9996, suggesting that 99.46% to 99.96% shift in the value of absorbance or $(dA/dt)_i$ or k_{obs} is induced by $Mn^{II}$and the rest 0.54% to 0.04% is due to the unknown factors. The value of 't' at 0.05 significance level, as calculated for the calibration curves, are in the range of 7.9017 to 31.96 which are much higher than the tabulated critical value at 0.05 significance level suggesting that there are fewer chances of error in delineating the conclusions. All the results obtained from the above method lies within reasonable limits (Table 1).

Table-1: Parameters of Calibration Curves, for the Determination of [MnII] in Aqueous mixed $[NaIO_4]\times10^4$ = 7.0 $moldm^{-3}$; [PBA] $\times10^5$ = 8.0 $moldm^{-3}$; pH=5.5, Acetone = 5 %(v/v); λ_{max}=456nm;Temp. =35±0.1^{0}C

Parameters	A plot (60 s)	B plot (120 s)	C plot (180 s)	D plot (240 s)	E plot (k_{obs})	F plot (*rate*)
Liner range of [Mn(II)](ng/ml)	1.06-1254	1.06-1254	1.06-1254	1.06-1254	1.06-1254	1.06-1254
Molar absorptivity$\times10^2$($L.mol^{-1}.cm^{-1}$)	982.84	1174.11	1475.86	1632.103	---	---
Sandal's sensitivity ($ng.cm^{-2}$)	17.2	14.4	11.45	10.35	---	---
Slope$\times10^4$ absorbance units. $ng^{-1}cm^3$(from regression equation)	0.582	0.695	0.873	0.965	43.4	2.07
Intercept (abs. units)(from regression equation)	0.0092	0.013	0.017	0.021	1.27	0.53
Correlation coefficient(r)	0.9992	0.9998	0.9974	0.9973	0.9992	0.9982
Coefficient of determination (r^2)	0.9984	0.9996	0.9948	0.9946	0.9984	0.9964

't'(at 0.05 significance level)	7.9017	8.2254	8.2654	8.4357	9.2418	31.96
Relative Standard Deviation(%)(for six determinations)	0.337	0.500	0.413	0.589	1.1167	1.0503
Recovery (%)	98.55	99.21	98.96	98.64	99.13	99.53

Other methods are also reported for the determination of [Mn^{II}] using or not using periodate as an oxidant and lower detection limits are also available[20-26], but these methods require prolonged pre-concentration and pre-treatment of the samples counting numerous complex reactions of the sample with oxidants and chromogenic substances. Further, most of these methods require rarely available facilities like GC-ECD, GC-MS, solid-phase extraction coupled with HPLC, differential pulse voltammetry and adsorptive stripping voltammetry, flow injection method, etc. The method reported by Mutaftchiev[15, 17]involves low detection limits in the range 0.015-0.025 ng/mL but this method is more complexed than the method proposed in this communication. Hence, the suggested method for the determination of [Mn^{II}] is characterized by higher selectivity and sensitivity compared to other spectrophotometric methods (Table-2).

The method advanced by us is cost-effective involving usage of basic equipment, frequently available chemicals and laboratory set up. The linear range of concentration in which Beer's law is being obeyed; detection limits in terms of Sandell's sensitivity, reproducibility of results and % recovery are good enough to make this method proficient for general analysis. The ease of manganese determination makes this method an enhanced model of some of the early reported methods. Moreover, the process can be effortlessly done without much time consumption 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 with rare involved of interferants.

Table-2: Comparison of the Method Proposed by Us with Other Reported Methods

Parameters	I [28]	II [36]	III [14]	IV [15]	V [35]	VI [19]	VII [30]
Beer's Law Limits (ng cm^{-3})	1000 - 25000	--	740-10320	0.05 - 5.0	0.08- 4.0	1-120	0.00 - 3520
Molar Absorptivity x10 $^{-3}$ (L mol^{-1} cm^{-1})	--	--	4.972	--		99-165	5.84-7.24
Sandell's Sensitivity (ng cm^{-2})	50	$1x10^4$	11	0.015	0.025	0.333-0.556	7.3-9.2
Correlation Coefficient (r)	--	--	--	--	0.998	0.998-1.000	0.998 - 0.999
Coefficient of Determination (r^2)	--	-	--	--	0.996	0.9996-1.000	0.996 - 0.9984
't' (at 0.01 Significance Level)	--	--	--	--	-	--	--
Relative Standard Deviation (%)(From 6 Determinations)	--	--	0.73-1.4	--	2.7	0.353- 0.885	0.27-0.50
% Error	--	--	-	-	1.7-3.3	0.37- 0.929	0.37-0.524
Standard Deviation (%) (From six Determinations)	-	--	--	--	--	--	--
% Recovery	--	--	--	--	---	--	--

Parameters	VIII [31]	IX [32]	X [33]	XI [37]	XII [38]	XIII*
Beer's Law Limits (ng cm^{-3})	5 -50	5 -50	32-200	0.54-345.22	1.23-190.98	1.06-1254
Molar Absorptivity x10 $^{-3}$ (L mol^{-1} cm^{-1})	54.945	197. 8	79.2-180	94.15-148.24	55.60-72.34	0.0098-0.016-
Sandell's Sensitivity (ng cm^{-2})	1.0	0.278	0.306-0.694	0.82-1.3	2.34-3.04	17.2-10.35
Correlation Coefficient (r)	0.9333-1.003	0.999 - 1.002	0.9951-0.9987	0.9981-0.9998	0.9934-0.9988	0.9973-0.9998
Coefficient of Determination (r^2)	0.870 - 1.006	0.998 - 1.004	0.9902-0.9974	0.9962-0.9996	0.9868-0.9976	0.9946-0.9996
't' (at 0.01 Significance Level)	--	--	6.793 -8.02	7.6033-14.4226	7.8700-9.7166	7.9017-31.96**
Relative Standard Deviation (%)(From 6 Determinations)	1.509	1.093	--	0.1417-0.4048	0.322-0.670	0.337-1.1167
% Error	--	--	--	--	--	--
Standard Deviation (%) (From Six Determinations)	--	--	0.506-1.655	--	--	--
% Recovery	--	--	99.1-100.0	98.72-99.91	97.32-99.97	98.55-99.53

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