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Simple Kinetic-Spectrophotometric Method for the Determination of Mn(II) in Water

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A new kinetic-spectrophotometric method based on the Mn(II) catalyzed periodate oxidation of *m*-anisidine (MMA) in acetone-water medium has been developed for 1.0 nanogram/mL to 120.0 nanogram/mL determination of Mn(II) in water samples. Molar absorptivity (99.0099×10^3-165.0165×10^3 L mol^{-1} cm^{-1}), Sandell's sensitivity (0.556–0.333 ng/cm^2), correlation coefficient (0.9998–1.000) and effect of few interferrants have been worked out for developing the calibration curves in terms of absorbance or initial rate or pseudo first order rate constant *vs.* [Mn(II)] plot. The method is simpler, more sensitive with improved detection limits in comparison to the reported methods and especially useful in absence of the expected interferrants.

Key Words: Nanogram determination, Mn(II), Periodate oxidation, *m*-Anisidine.

INTRODUCTION

The commonly used method for the spectrophotometric determination of Mn(II) in water is the persulphate method with detection limit 0.05 mg/L.[1] 4-(2-Pyridylazo)-resorcinol, 2-(5-bromopyridylazo)-5-(diethylaminophenol), chromeazurol-S, bis(2,4,4-trimethylpentyl) monothiophosphinic acid, 5,8-dihydroxy-1,4-napthaquinone and *p*-methylacetoacetanilide have been used for spectrophotometric estimation of Mn based on complexation, besides its estimation in effluents and tea leaves by its oxidation with sodium bismuthate[2]. However, the reports on kinetic-spectrophotometric estimation of Mn(II) based on periodate oxidation of aromatic amines are comparatively few[3–5]. The present paper deals with kinetic-spectrophotometric studies on the nanogram estimation of Mn(II) while it catalyses the *m*-anisidine-periodate redox system in acetone-water medium.

EXPERIMENTAL

All chemicals used were of E. Merck/Aldrich (AR) grade. Sodium metaperiodate and *m*-anisidine (MMA) were used after recrystallization and Zn dust distillation respectively. All solutions and reaction mixtures were prepared by using triply distilled water. Absorbance was recorded on Shimadzu double beam spectrophotometer, UV-150-02. λ_{max} for MMA and sodium metaperiodate were

found to differ widely from the λ_{max} of the reaction mixture 470 nm) at which the absorbance was noted only in the period in which the λ_{max} did not change and no precipitate/turbidity appeared. $MnSO_4 \cdot H_2O$ (E. Merck AR grade) was used for the preparation of aqueous solutions of different [Mn(II)] (being expressed in micrograms per mL). Following were the finally worked out conditions for running the kinetic sets for the purpose of determination of Mn(II) in aqueous medium: [MMA] = 0.01 M; [$NaIO_4$] = 0.001 M; Acetone = 5% (v/v); λ_{max} = 470 nm; Temp. = 35 ± 0.1°C. The reaction was found to follow second order kinetics with order being one in each reactant. Following procedure was adopted for preparation of the calibration curves.

A definite volume of stock solution of MMA in acetone was mixed with calculated volume of a stock solution of Mn(II), acetone and water and stirred a little with the help of the pipette. This mixture and stock solution of $NaIO_4$ was then clamped in a thermostat at 35 ± 0.1°C. After 30 min, 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 2 min and the absorbance was recorded and absorbance *vs.* time plots were made for different sets. Initial rates [$(dA/dt)_2$] were evaluated after 2 min from the start of the reaction by using plane mirror method. The pseudo first order rate constants (k_1) were found by Guggenheim's method[4]. Linear calibration curves were obtained in terms of type 'A', type 'B', type 'C', type 'D' and type 'E' plot, *i.e.*, A_2 or A_4 or A_6 or $(dA/dt)_2$ or k_1 *vs.* [Mn(II)] plots respectively (where A_2, A_4 and A_6 are the absorbance values after 2, 4 and 6 min from the start of reaction respectively).

RESULTS AND DISCUSSION

[Mn(II)] may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity MMA, acetone and starting the reaction by adding $NaIO_4$ followed by noting the A_2 or A_4 or A_6, evaluatimg $(dA/dt)_2$ and k_1 by the methods discussed above. After this, different calibration curves may be used for determination of [Mn(II)] in nanograms/mL (ng/mL). Method of least squares was used for obtaining the linear calibration curves with characteristics as given in Table-1.

The values of the slope of calibration curves, molar absorptivity and Sandell's sensitivity indicate that the sensitivity of the method is very good. A change in absorbance by 0.001 unit is expected on changing the concentration of Mn(II) by 0.333–0.556 ng/mL. Further, a change in concentration by 1.0 ng/mL will change the rate of reaction by 0.035 absorbance units/minute. In addition, the value of k_1 will change by 0.00063 sec^{-1} on changing [Mn(II)] by 1 ng/mL, *i.e.*, a change sufficient enough to be observed easily. The detection limits (1.0 ng/mL to 120 ng/mL) are also considerably low and these are very good for the trace determination of Mn(II). The correlation coefficient and the coefficient of determination indicate the high precision involved in the determination and good

correlation of the data. It should also be noted that the proposed method is far better than the reported ones[1-5] as far as the sensitivity and detection limits are concerned.

TABLE-1
CHARACTERISTICS OF VARIOUS TYPES OF CALIBRATION CURVES FOR THE PROPOSED METHOD

[MMA] = 0.01 M; [$NaIO_4$] = 0.001 M; Acetone = 5% (v/v); λ_{max} = 470 nm; Temp. = 35 ± 0.1°C; Dielectric Constant = 72.4

Parameters	'A' plot	'B' plot	'C' plot	'D' plot	'E' plot
Beer's law limits (ng/mL)	1–120	1–120	1–120	1–120	1–120
Molar absorptivity × 10^{-3} (L $mol^{-1}cm^{-1}$)	99.0099	132.0132	165.0165	—	—
Sandell's sensitivity (ng cm^{-2})	0.5560	0.4167	0.3330	—	—
Slope × 10^3 absorbance units ng^{-1} cm^3 (from regression equation)	1.8	2.4	3.0	35.0 min^{-1}	1.055 × 10^{-2} sec^{-1}
Intercept × 10^2 (abs. units) (from regression equation)	4.0	4.6	4.8	0.36 min^{-1}	0.04 sec^{-1}
Correlation coefficient (r)	0.9999	0.9999	0.9998	1.0000	0.9998
Coefficient of determination (r^2)	0.9998	0.9998	0.9996	1.0000	0.9996
't' (at 0.05 significance level)	5.0500	4.6734	4.4242	3.8700	6.3500
Relative standard deviation (%) (from 6 determinations)	0.7540	0.8090	0.4670	0.8850	0.3530
% error (95% confidence limit)	0.7910	0.8490	0.4910	0.9290	0.3700

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 good relative standard deviation and reasonable range of errors calculated on the basis of six determinations (Table-1).

The effect of various expected interferrants was also studied. The method is not applicable in presence of a few aromatic amines like N-ethylaniline, *o*-ethylaniline, *p*-ethyl aniline, *p*-toluidine, *o*-chloroaniline, *p*-chloroaniline, *p*-bromoaniline, *p*-anisidine, N,N-diethylaniline, N,N-dimethylaniline (when present in the amounts >120 μg/mL), *p*-phenetidine, 3,5-dimethylaniline and 4-chloro-2-methylaniline as they interfere in this method by getting oxidized by periodate ion and the reaction mixture showing λ_{max} in the range in which it influences the absorbance in the present estimation method. Further, aniline, N-methylaniline, *o*-toluidine, *m*-chloroaniline, *o*-anisidine, *m*-anisidine, *o*-p-henetidine, *m*-phenetidine, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, N,N-dimethylaniline (when present in the amounts 120 μg/mL), 2,6-dimethylaniline, 2,6-diethylaniline, 3,4-dimethylaniline, 2,5-dimethylaniline, 2,3-dimethylaniline, 2,6-dichloroaniline, 2,5-dichloro-aniline, 3-chloro-2-methylaniline, 3-chloro-4-methylaniline, *o*-amino-benzoic acid, and *p*-aminobenzoic acid have been found to have no interference in the proposed method. The method may be used in

presence of the ions like Na^+, K^+, NO_2^-, ClO_4^-, NO_3^- and SO_4^{-2} as they do not interfere in the 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 this, a dilute alkaline solution of α-nitroso-β-naphthol should be added and again the solution should be filtered[6]. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method[7]. In absence of the interferrants reported above, the proposed method may be successfully used for the determination of nanogram quantities of Mn(II) in water samples.

The involved redox process may be mechanistically similar to our earlier reports related to other aromatic amines[8–10] in which a charged intermediate formation between the active species of periodate (*i.e.* IO_4^-) and aromatic amines has been established. This intermediate is attacked by H_2O molecule and then reacts with another molecule of IO_4^- to form quinoneimine, which subsequently gets hydrolyzed to form the benzoquinones which are the expected main products of such reactions. The catalytic effect of Mn^{2+} may be attributed to the formation of an intermediate complex between Mn(II) and MMA. In comparison to MMA itself, this intermediate may be more reactive towards periodate leading to an enhanced reaction rate, probably due to the catalytic effect of Mn(II)[11].

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