KINETIC-SPECTROPHOTOMETRIC DETERMINATION OF *p*-BROMOANILINE AT THE MICROGRAM LEVEL

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ABSTRACT

The determination of *p*-Bromoaniline (PBA) was investigated by kinetic-spectrophotometric method followed by the progress of Mn^{II} catalyzed reduction of periodate ion in the acetone-water medium. The reaction was found to be first order with respect to the catalyst, substrate, and oxidant each. The reaction was followed by monitoring the increase in the absorbance of the reaction intermediate. The main reaction product characterized on the basis of melting point and spectroscopic studies is 4-methyl-1,2-benzoquinone. The effect of pH, dielectric constant of medium and free radical scavengers were studied to develop the best-fit conditions for developing a new and simple kinetic-spectrophotometric method for microgram determination of *p*-Bromoaniline in the range $0.52 \mu g/cm^3$ to $48.37 \mu g/cm^3$. The characteristics of various calibration curves, detection limits, percentage recovery, and effect of interferants, correlation coefficient and comparison of the proposed methods with other reported methods are presented in this article.

Keywords: Microgram Estimation, periodate ion, Mn^{II} catalyzed, *p*-Bromoaniline, 4-Bromo-1,2-Benzoquinone.

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INTRODUCTION

Aromatic amines are highly polar organic compounds that are widely used as intermediates or produced in various fields such as drugs, dyes, tobacco smoke, pesticides and pharmaceutical industries and as antioxidants in the polymer industries.^{1,2} Aromatic amines are suspected to be carcinogenic and highly toxic to the human body, aquatic organisms and environment, therefore de-contamination of aromatic amines from industrial wastewater is necessary. In order to understand the behavior of aromatic amines and fate in human body and environment, highly sensitive and selective methods for the determination of aromatic amines is necessary.

Many workers have reported the estimation of some aromatic amines in smaller amounts in different media and using various complex reaction systems involving complicated pre-treatment and employing various techniques like NMR, IR Spectroscopy, Spectrophotometry, Polarography, Flow injection analysis, Solvent extraction, Raman spectroscopy, and various chromatographic techniques including TLC, gas chromatography, HPLC, reversed phase HPLC, GC-MS, GC/LC, GC-ECD, ion exchange chromatography and electrochemical detection.³⁻¹² The only report available in the literature regarding the kinetic-spectrophotometric estimation of some anilines is based on their oxidation by periodate ion in aqueous/ mixed media.¹³⁻¹⁴ Earlier reports have proposed that Periodate oxidation of aromatic amines has not been explored widely for kinetic spectrophotometric determination of amines and only a few attempts have been made in this direction.¹⁵⁻²⁴ Some reports are available on Evaluation of stability constant of ternary intermediate complex formation in Mn^{II} catalyzed periodate oxidation of 2,5-xylidine by stopped flow method.³¹ Some aniline was investigated as fabrication of polyaniline nanofiber modified carbon paste electrodes (GOx/MCPE)³².

The detailed kinetic-mechanistic studies on Mn^{II} catalyzed the reduction of periodate by *p*-Bromoaniline has also been reported.²⁵ This reaction has not been explored for estimation of *p*-Bromoaniline (PBA). Present paper deals with a new and simple kinetic-spectrophotometric method

developed by us for microgram determination of PBA based on its oxidation by periodate ion catalyzed by Mn^{II} .

EXPERIMENTAL

Materials and Methods

Sodium metaperiodate (Loba Chemie), *p*-Bromoaniline (Loba Chemie), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. Triple distilled water was used for the preparation of the solutions. Thiel, Schultz and Koch buffer²⁶ was used for maintaining the pH of the reaction medium.

Effect of Interferents

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 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 it, a dilute alkaline solution of α -nitroso- β -naphthol should be added and again the solution should be filtered²⁸. Thereafter, the solution should be neutralized and the present method may be applied. 'Fe' may be removed by precipitation using basic formate method²⁹⁻³⁰. In absence of the above-given interferants, the proposed method may successfully be used for the determination of microgram quantities of [PBA] in water samples.

General Procedure

The reaction mixture containing PBA, Mn^{II} and the buffer were left overnight to ensure completion of the reaction, initially, the solution turned light yellow color, thereafter wine red color and then orange followed by precipitation in about 24 hours. The spectrophotometric cell was used to study the reaction and the reaction initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture. The temperature of the reaction mixture was maintained with the help of Shimadzu TCC-240- an inbuilt temperature control unit with an accuracy of $\pm 0.1^\circ C$ which is connected with the Shimadzu double beam spectrophotometer (UV-2550). The absorbance maxima for the reaction mixture was recorded at 456 nm i.e., the λ_{max} of the reaction mixture. λ_{max} was not found to change with a change in time under experimental conditions (Fig.-1).

Fig.-1: Rapid UV-VIS Scans of Reaction Mixture at Different Time
 $[NaIO_4] \times 10^3 = 2.0 \text{ mol dm}^{-3}$, $[PBA] \times 10^4 = 2.0 \text{ mol dm}^{-3}$, $[Mn^{II}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$,
 Acetone = 5.0 % (v/v), Temp = $30.0 \pm 0.1^\circ C$, pH = 5.5.

Following are the finally worked out conditions for running the kinetic sets for the purpose of determination of PBA in mixed (acetone-water) medium based upon the reduction of periodate ion: $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, $[\text{NaIO}_4] \times 10^4 = 7.0 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$, Temp. = $35.0 \pm 0.1^\circ\text{C}$, $[\text{PBA}] = \text{unknown in the range of } 0.52 \mu\text{g/cm}^3 \text{ to } 48.37 \mu\text{g/cm}^3$.

A definite volume of stock solution of Mn^{II} in water was mixed with calculated volumes of the stock solution of PBA, water, acetone, and stirred. This mixture and a stock solution of NaIO_4 were then clamped in a thermostat at $30.0 \pm 0.1^\circ\text{C}$. After 25 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 $[\text{PBA}]$ and the desired temperature was maintained in the spectrophotometer cell also. The absorbance of the reaction mixture was recorded at a definite repeated time interval 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 a plane mirror method on the absorbance vs. time plots. The pseudo-first-order rate constants (k_{obs}) were found by Guggenheim's method²⁷. Using least square methods, 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. $[\text{PBA}]$ plots respectively (Fig.-2 and 3).

Fig.-2: Calibration Curve in Terms of Absorbance vs. $[\text{PBA}]$ Plots at Following Conditions: $[\text{NaIO}_4] \times 10^4 = 7.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0% (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$.

Fig.-3: Calibration Curve in Terms of Initial Rate or Pseudo First Order Rate Constant vs. $[\text{PBA}]$ Plots at The Following Conditions: $[\text{NaIO}_4] \times 10^4 = 7.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$.

Table-1: Characteristic of Various Types of Calibration Curves for the Proposed Methods $[\text{NaIO}_4] \times 10^4 = 7.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), Temperature = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$.

Parameters	A plot(30s)	B plot(60s)	C plot(90s)	D plot(120s)	E plot(k_{obs})	F plot(rate)
Liner range of [PBA]($\mu\text{g}/\text{cm}^3$)	0.52-48.37	0.52-48.37	0.52-48.37	0.52-48.37	0.52-48.37	0.52-48.37
Molar absorption coefficient $\times 10^{-6}$ ($\text{cm}^2\mu\text{g}^{-1}\text{cm}^{-1}$)	3.85	4.85	5.42	6.01	---	---
Sandell's Sensitivity ($\mu\text{g}/\text{cm}^2$)	0.2597	0.2062	0.1845	0.1664	---	---
Slope $\times 10^3$ ($\mu\text{g}^{-1}\text{cm}^3$ (from regression equations))	3.85	4.85	5.42	6.01	342.65	148.11
Intercept $\times 10^3$ (from regression equation)	0.586	1.56	2.61	3.23	356.7	303.18
Correlation coefficient (r)	0.9985	0.9993	0.99961	0.99968	0.99946	0.99711
Coefficient of determination (r^2)	0.9970	0.9986	0.9992	0.9994	0.9990	0.9942
't' (at 0.05 significance level)	6.8283	7.2789	7.7031	7.8514	9.1742	11.794
Relative standard deviation (%) (for six determinations)	0.2409	0.2670	0.0841	0.1681	5.739	0.0553
Recovery (%)	99.60	98.90	99.13	99.50	99.45	98.92

The Validity of Beer's Law and Other Characteristics of the Methods

The range of [PBA] in which the Beer's law is obeyed, molar absorption coefficient, Sandell's sensitivity, the correlation coefficient of determination, the value of 't' (at 0.05 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:

$$A_{60} = 0.59 \times 10^{-2} + 3.85 \times 10^{-3} [\text{PBA}] \quad (1)$$

$$A_{120} = 1.56 \times 10^{-2} + 4.85 \times 10^{-3} [\text{PBA}] \quad (2)$$

$$A_{180} = 2.61 \times 10^{-2} + 5.42 \times 10^{-3} [\text{PBA}] \quad (3)$$

$$A_{240} = 3.23 \times 10^{-2} + 6.01 \times 10^{-3} [\text{PBA}] \quad (4)$$

$$(dA/dt)_{30} = 303.2 \times 10^{-2} + 148 \times 10^{-3} [\text{PBA}] \quad (5)$$

$$k_{\text{obs}} = 356.7 \times 10^{-2} + 342.65 \times 10^{-3} [\text{PBA}] \quad (6)$$

In equations(1-4), the values of intercepts and slopes are in unitless and $\mu\text{g}^{-1}\text{cm}^3$ respectively, while these are s^{-1} and $\text{cm}^3\mu\text{g}^{-1}\text{s}^{-1}$ in equation (5-6) respectively and the [PBA] is given in $\mu\text{g}/\text{cm}^3$.

Here A_{30} or A_{60} or A_{90} or A_{120} are the absorbance values after 30, 60, 90 and 120 seconds from the start of reaction respectively.

[PBA] may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of PBA, acetone and starting the reaction by adding NaIO_4 followed by noting the absorbance of reaction mixture at different desired times as described above and evaluating initial rates in terms of $(dA/dt)_{30}$ at a desired time by plane mirror methods discussed above. After it, different calibration curves may be used for determination of [PBA] in $\mu\text{g}/\text{cm}^3$.

RESULTS AND DISCUSSION

Various characteristics of the calibration curves indicate (Table-1):

1. The reasonable sensitivity, percentage recovery, and correlation are in the range of 0.52-48.37 $\mu\text{g}/\text{cm}^3$.

- The value of Sandell's sensitivity suggests that change in absorbance by 0.001 units is expected on changing the concentration of PBA by $0.2597\text{--}0.1664\mu\text{g}/\text{cm}^3$. Further, a change in [PBA] by $1\mu\text{g}/\text{cm}^3$ will change the value of k_{obs} by 5.79×10^{-3} .
- The correlation coefficient (r) is in the range 0.9985-0.9971 which indicates the high precision involved in the determination and almost perfect correlation of the data.
- The value of the coefficient of determination (r^2) suggests that 99.42% to 99.94% change in the value of absorbance or $(dA/dt)_i$ or k_{obs} is caused by PBA and the rest 0.58% to 0.06% due to unknown factors.
- The value of 't' at 0.05 significance level, as calculated for the calibration curves, are in the range 6.8283 to 11.794 which are much higher than the tabulated critical value at 0.05 significance level. This suggests that there is less than 1% chance of error in drawing conclusions.
- The standard deviation is within reasonable limits.
- Percentage recovery on the basis of six parallel determinations is 99.60% to 98.92%. In general, the proposed methods are fairly suitable for estimation of PBA at microgram level.

CONCLUSION

The methods developed by us are cost effective and involve the use of simple equipment (like a VIS-spectrophotometer) and easily available chemicals. 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 these methods competent for general analysis. These methods are better than some of the previously reported methods in terms of the ease of the procedure involved. Further, these methods are less time-consuming in comparison to the other available methods for estimation of PBA in aqueous/ mixed media, as no pretreatment of the samples etc. are involved except in cases where some rare interferants are present as already discussed. As a result, these methods have tremendous potential in trace analysis of PBA in polluted water.

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