

Determination of Some Aromatic Amines in Micrograms by Kinetic Spectrophotometric Method based upon Periodate Oxidation in Aqueous/Mixed Medium

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A kinetic-spectrophotometric method has been developed for the microgram determination of five aromatic amines in aqueous/mixed medium. Best suitable conditions in terms of pH, temperature, concentration etc. have been worked out. Calibration curve, validity of Beer's law, sensitivity, correlation coefficient and the effect of interferants have been discussed.

INTRODUCTION

The exposure of some aromatic amines causes skin eruption, nervousness, dimness of vision, weakness, nausea and cyanosis etc.¹ The chances of presence of substituted aromatic amines in water containing the chemical industry effluents cannot be ruled out.² A limited work has been done for developing the methods for determination of substituted anilines in aqueous or mixed medium.³⁻¹⁰ In our earlier work, we have reported the kinetic-mechanistic studies on periodate oxidation of some aromatic amines.¹¹⁻¹³ In the present paper we have used non-malaparadian periodate oxidation of aromatic amines as the basis for developing the kinetic-spectrophotometric methods for determination of N,N-dimethyl-*p*-toluidine (DMT) in the range of 9.37 $\mu\text{g mL}^{-1}$ to 74.96 $\mu\text{g mL}^{-1}$, *m*-toluidine (*m*-tol.) in the range of 50 $\mu\text{g mL}^{-1}$ to 100 $\mu\text{g mL}^{-1}$, *p*-toluidine (*p*-tol.) in the range of 10 $\mu\text{g mL}^{-1}$ to 150 $\mu\text{g mL}^{-1}$, N-ethylaniline (EA) in the range of 10 $\mu\text{g mL}^{-1}$ to 120 $\mu\text{g mL}^{-1}$ and N-methylaniline (MA) in the range of 71.2 $\mu\text{g mL}^{-1}$ to 178.0 $\mu\text{g mL}^{-1}$ in aqueous/mixed medium.

EXPERIMENTAL

All chemicals used were of E. Merck/Loba (G.R.) grade. Aromatic amines were used after redistillation/recrystallization. Solutions and reaction mixtures were prepared by using doubly distilled water. The absorbances of reaction mixtures were recorded on Shimadzu double beam spectrophotometer. The pH of reaction mixtures was maintained by using Thiele, Schultz and Coch buffer.¹²

The reactions were studied by recording the absorbance of reaction mixtures after different time intervals and the best suitable conditions *i.e.* pH, concentration

range, temperature, etc. were worked out. λ_{\max} for these aromatic amines and sodium metaperiodate were found to be in UV region. These differ widely from the λ_{\max} of the respective reaction mixtures under study (i.e. 560, 540, 470, 555 and 540 nm in case of DMT, *m*-tol., *p*-tol., EA and MA respectively). The λ_{\max} did not change during the period of study and no precipitation took place.

Rate of reaction was found in terms of $(dA/dt)_i$. For this purpose the tangent was drawn at *i* time (in minutes) on the curve obtained by plotting A against time, where A is the absorbance of the reaction mixture noted at different times.

RESULTS AND DISCUSSION

Determination of N,N-dimethyl *p*-toluidine (DMT) in acetone-water medium

A definite volume of stock solution of DMT in acetone was mixed with buffer solution of pH 7.0 and clamped in a thermostat at $40 \pm 0.1^\circ\text{C}$. Stock solution of periodate was also clamped in the same thermostat. After 40 minutes, a required amount of periodate was mixed with the DMT-buffer mixture so as to start the reaction. Different sets were prepared in which the initial concentration of periodate and acetone was kept 0.01 M and 20% (v/v) respectively. The $(dA/dt)_2$ values corresponding to different concentration of DMT used are given in Table-1. The calibration curve was obtained in terms of a plot between $(dA/dt)_2$ and [DMT] in the range $9.37 \mu\text{g mL}^{-1}$ to $74.96 \mu\text{g mL}^{-1}$. The correlation coefficient and coefficient of determination values for calibration curve were found to be 0.994 and 0.988 respectively which indicate a good correlation of data. The slope of the calibration curve ($70.308 \text{ lit. mol}^{-1}$) indicates a good sensitivity of the method. If other anilines are also present in the sample under consideration, these may also get oxidized by periodate and their colored products may interfere in the present method. It was found that the following anilines will interfere in the present method:

N,N-dimethylaniline (if present in the range 30 to $121 \mu\text{g mL}^{-1}$), *m*-toluidine (if present in amount 50 – $130 \mu\text{g mL}^{-1}$) and N-ethylaniline (if present in amount greater than $20 \mu\text{g mL}^{-1}$).

The proposed method was tested for many samples containing a known amount of DMT (in the range $9.37 \mu\text{g mL}^{-1}$ to $74.96 \mu\text{g mL}^{-1}$).

TABLE-1

DETERMINATION OF [DMT] IN ACETONE-WATER MEDIUM

[NaIO₄] = 0.01 M, Acetone = 20.0% (v/v), pH = 7.0, λ_{\max} = 560 nm, Temp. = $40 \pm 0.1^\circ\text{C}$

[DMT] $\mu\text{g mL}^{-1}$	9.37	18.74	28.11	37.48	46.85	56.22	65.59	74.96
$(dA/dt)_2 \times 10^3 \text{ (min}^{-1}\text{)}$	2.75	7.12	11.50	15.00	23.00	26.00	30.00	38.00

Determination of *m*-toluidine (*m*-tol) in aqueous medium

A definite volume of stock solution of *m*-tol was mixed with buffer solution of pH 5.0 and clamped in a thermostat with periodate solution at $40 \pm 0.1^\circ\text{C}$. After 40 min a required amount of periodate solution was mixed with *m*-tol.-buffer mixture to start the reaction. The calibration curve was obtained in terms of a plot

between $(dA/dt)_{2.5}$ and $[m\text{-tol.}]$ in the range $50 \mu\text{g mL}^{-1}$ to $100 \mu\text{g mL}^{-1}$. The $(dA/dt)_{2.5}$ values corresponding to different concentrations of *m*-touldine used are given in Table-2. The values of correlation coefficient and coefficient of determination were found to be 0.967 and 0.935 respectively which indicate a good correlation of data. The slope of the calibration curve (42 lit. mol^{-1}) indicates a good sensitivity of the method.

TABLE-2
DETERMINATION OF $[m\text{-TOL}]$ IN AQUEOUS MEDIUM
 $[\text{NaIO}_4] = 0.01 \text{ M}$, $\text{pH} = 5.0$, $\lambda_{\text{max}} = 462 \text{ nm}$, $\text{Temp.} = 40 \pm 0.1^\circ\text{C}$

$[m\text{-tol.}] \mu\text{g mL}^{-1}$	49.45	59.34	69.23	79.12	89.01	98.90
$(dA/dt)_{2.5} \times 10^3 (\text{min}^{-1})$	9.6	13.9	15.0	19.4	23.4	27.0

N,N-diethylaniline (if present in the range 1.5 to $29.8 \mu\text{g mL}^{-1}$), *p*-anisidine (if present in amount more than $12 \mu\text{g mL}^{-1}$) and *p*-toluidine (if present in the range $10 \mu\text{g mL}^{-1}$ to $214 \mu\text{g mL}^{-1}$), interfere in the present method.

The proposed method is suitable only when $[m\text{-toluidine}]$ is between $50 \mu\text{g mL}^{-1}$ to $100 \mu\text{g mL}^{-1}$. If *m*-toluidine is present in amount more than $100 \mu\text{g mL}^{-1}$, the reaction mixture shows a shift of λ_{max} from 462 to 540 nm . This is probably due to formation of another product at higher concentration. The proposed method was tested for many samples containing a known amount of *m*-toluidine (in the range $50 \mu\text{g mL}^{-1}$ to $100 \mu\text{g mL}^{-1}$).

Determination of *p*-toluidine (*p*-tol) in aqueous medium

A definite volume of stock solution of *p*-toluidine was mixed with buffer solution of $\text{pH} 5.0$ and clamped in a thermostat at $35 \pm 0.1^\circ\text{C}$. Stock solution of periodate was also clamped in the same thermostat. The reaction was started by mixing a suitable volume of periodate in *p*-tol.-buffer mixture. The $(dA/dt)_2$ values corresponding to different concentration of *p*-toluidine are presented in Table-3. The calibration curve was obtained in terms of plot between $(dA/dt)_2$ and $[p\text{-toluidine}]$ in the range $10 \mu\text{g mL}^{-1}$ to $150 \mu\text{g mL}^{-1}$. The correlation coefficient and coefficient of determination values for calibration curve were found to be 0.993 and 0.986 respectively which indicate a good correlation of data. The slope of calibration curve ($78.49 \text{ lit. mol}^{-1}$) indicates a reasonably good sensitivity of the method.

TABLE-3
DETERMINATION OF $[p\text{-tol}]$ IN AQUEOUS MEDIUM
 $[\text{NaIO}_4] = 0.01 \text{ M}$, $\text{pH} = 5.0$, $\lambda_{\text{max}} = 470 \text{ nm}$, $\text{Temp.} = 35 \pm 0.1^\circ\text{C}$

$[p\text{-tol.}] \mu\text{g mL}^{-1}$	10.0	30.0	50.0	80.0	100.0	120.0	135.0	150.0
$(dA/dt)_2 \times 10^2 (\text{min}^{-1})$	0.60	2.45	3.50	5.10	7.30	8.00	8.90	10.00

It has been found that *N,N*-dimethylaniline interferes if present in amount more than $120 \mu\text{g mL}^{-1}$, *N,N*-diethylaniline will interfere if present in the range 1.5 to $29.8 \mu\text{g mL}^{-1}$, *p*-methoxyaniline and *p*-ethoxyaniline interfere if present in amount more than $12 \mu\text{g mL}^{-1}$. Also *m*-toluidine (if less than $100 \mu\text{g mL}^{-1}$)

interferes in the present method. The proposed method was tested for many samples containing a known amount of *p*-toluidine (in the range of 10 $\mu\text{g mL}^{-1}$ to 150 $\mu\text{g mL}^{-1}$).

Determination of N-ethylaniline (EA) in acetone-water medium

A definite volume of stock solutions of N-ethylaniline in acetone was mixed with buffer solution of pH 6.0 and clamped in a thermostat at $40 \pm 0.1^\circ\text{C}$. Stock solution of sodium metaperiodate was also clamped in the same thermostat. After 30 min, a required amount of periodate solution was mixed with the N-ethylaniline-buffer mixture so as to start the reaction. The $(dA/dt)_5$ values corresponding to different concentrations of N-ethylaniline used are given in Table-4. The calibration curve was obtained in terms of a plot between $(dA/dt)_5$ and [EA] in the range 10 $\mu\text{g mL}^{-1}$ to 120 $\mu\text{g mL}^{-1}$. The correlation coefficient and coefficient of determination values for calibration curve were found to be 0.972 and 0.986 respectively which indicate a good correlation of data. The slope of calibration curve is 48 lit. mol^{-1} which indicate a good sensitivity of data.

TABLE 4
DETERMINATION OF [EA] IN ACETONE-WATER MEDIUM
[NaIO₄] = 0.01 M, Acetone = 10.0%, pH = 6.0, λ_{max} = 555 nm, Temp. = $40 \pm 0.1^\circ\text{C}$

[EA] $\mu\text{g mL}^{-1}$	10.0	30.0	50.0	80.0	100.0	120.0
$(dA/dt)_5 \times 10^2$ (min^{-1})	0.26	1.00	1.60	2.72	3.60	4.60

It was found that the following anilines interfere in the proposed method: N,N-dimethylaniline (if present in amount less than 120 $\mu\text{g mL}^{-1}$), *m*-toluidine (if present in amount more than 100 $\mu\text{g mL}^{-1}$) and N,N-dimethyl-*p*-toluidine (if present in amount more than 75 $\mu\text{g mL}^{-1}$). The proposed method was tested for many samples containing a known amount of N-ethylaniline (in the range 10 $\mu\text{g mL}^{-1}$ to 120 $\mu\text{g mL}^{-1}$).

Determination of N-methylaniline (MA) in acetone-water medium

Stock solution of N-methylaniline in acetone was mixed with buffer solution of pH 7.0 and clamped in a thermostat at $35 \pm 0.1^\circ\text{C}$. Stock solution of sodium metaperiodate was also clamped in the same thermostat. After 30 minute, a required amount of periodate solution was mixed with N-methylaniline-buffer mixture so as to start the reaction. The $(dA/dt)_5$ values corresponding to different concentration of N-methylaniline used are given in Table-5. The calibration curve was obtained in terms of a plot between $(dA/dt)_5$ and [MA] in the range of 71.2 $\mu\text{g mL}^{-1}$ to 178.0 $\mu\text{g mL}^{-1}$. The correlation coefficient and coefficient of determination values for calibration curve were found to be 0.999 and 0.998 respectively, which indicate a good correlation of data. The slope of calibration curve (43.13 lit. mol^{-1}) indicates a good sensitivity of data.

Following anilines interfere in this method: *m*-toluidine when present in amount more than 100 $\mu\text{g mL}^{-1}$, N-ethylaniline if present in the range 10 $\mu\text{g mL}^{-1}$ to 120 $\mu\text{g mL}^{-1}$, N,N-dimethylaniline if present in amount less than 120 $\mu\text{g mL}^{-1}$ and N,N-dimethyl-*p*-toluidine if present in the range 10 $\mu\text{g mL}^{-1}$ to 75 $\mu\text{g mL}^{-1}$.

mL⁻¹. The proposed method was tested for many samples containing a known amount of N-methylaniline (in the range of 71.2 µg mL⁻¹ to 178.0 µg mL⁻¹).

TABLE-5
DETERMINATION OF [MA] IN ACETONE-WATER MEDIUM
[NaIO₄] = 0.01 M, Acetone = 20.0% (v/v), pH = 7.0, λ_{max} = 540 nm, Temp. = 35 ± 0.1°C

[MA] µg mL ⁻¹	71.2	89.0	115.7	142.4	178.0
(dA/dt) ₅ × 10 ² (min ⁻¹)	0.27	1.15	1.90	2.80	4.00

Mn⁺² is expected to catalyse the oxidation of aromatic amines¹³ and so it also interferes in all of the methods discussed above.

The results obtained from the above given methods were found to be reproducible and the maximum deviation noted was between ± 1 to 2 per cent.

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