

Estimation of Periodate Ion Based on its Reduction with *p*-bromoaniline by Kinetic Spectrophotometric Method

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ABSTRACT

The determination of periodate by kinetic spectrophotometric method has been a practical and simple method for the rapid determination of trace amounts of periodate in aqueous mixed medium using its reduction by *p*-bromoaniline. Periodate was determined with linear calibration graphs in the range of 0.72 to 50.22 µg/mL. The detection limits in terms of Sandell's sensitivity for periodate in aqueous solutions at pH 5.5 are in the range of 0.12 to 1.19 µgcm⁻² at optimized conditions. The RSD for six replicate determinations were 0.27% to 1.82% for the linear range of concentration 0.72 to 50.22 µg/mL. The absorbance maximum of the reaction mixture was recorded spectrophotometrically at 456nm. The method used for the determination of periodate in aqueous solutions was compared with the reported spectrophotometric methods. Various parameters related to the trace amount determination of periodate as molar absorptivity, Sandell's sensitivity, initial rates of the reaction, percentage recovery and effect of interferrants etc. are being presented in this article.

Keywords: Microgram determination, Sodium metaperiodate, Mn^{II} catalyzed, Spectrophotometry.

INTRODUCTION

Periodate and iodates are powerful oxidizing agent active on many organic and inorganic compounds and can cause some damage to protein structure. Drinking water is the major route of environmental exposure to these oxyhailides¹. Therefore the determination of

periodate and iodate is required for environmental protection and important in biology, organic chemistry and life science. Extensive survey of literature reveals that several methods has been reported for the simultaneous determination of iodate ion (IO_3^-) and periodate ion (IO_4^-) in various media including complexation, masking agents and pre-treatment of samples, different reaction systems, include those based on the consecutive titration, spectrophotometric, electrosorption, chromatography, polarography, capillary electrophoresis, potentiometric titration against Hg(II), pulse polarography, spectro- electrochemical method, kinetic-spectrophotometric methods, sequential flow injection spectrophotometric determination, and capillary zone electrophoresis²⁻¹⁸.

Many methods have been reported for the determination of periodate ion in various media including IR spectroscopy, flow injection analysis coupled with chemiluminescence measurement, kinetic spectrophotometric methods, spectrophotometry, flow injection voltammetry, volumetric methods, static and spectrofluorimetric, SDME (single drop micro extraction under solution immersion) or HS-SDME (head space SDME) methods¹⁸⁻³¹. Most of these methods for the determination of periodate in various media tended to be expensive and complicated to be applying, and preliminary investigations revealed that the reported methods show much scope for the improvement in detection limits as well as the sensitivity³²⁻³⁶. Therefore, there is always a need to develop newer, simpler and cost effective techniques in this regard and determination of periodate was carried out on the basis of detailed kinetic study of the Mn^{II} catalyzed periodate oxidation of *p*-bromoaniline³⁷.

MATERIALS AND METHODS

All chemicals were of analytical-reagent grade, Sodium metaperiodate (Loba Chemie), *p*-bromoaniline (Loba Chemie), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) used after redistillation/ recrystallization and the solutions were prepared with triply distilled water. Thiel, Schultz and Koch buffer³⁸ was used for maintaining the pH of the reaction mixture.

GENERAL PROCEDURE FOR PERIODATE DETERMINATION

Reaction mixture shows the development of light yellow color changing into wine red color and then orange followed by precipitation in about 24 hours. The reaction was studied in a spectrophotometric cell and all the solutions were equilibrated at $35 \pm 0.1^\circ\text{C}$ before the beginning of the reaction. The determination of $[\text{NaIO}_4]$ was carried out by using Shimadzu double beam spectrophotometer (UV-2550). The reaction mixture was thoroughly mixed and quickly transferred to an absorption cell which is also equilibrated at $35 \pm 0.1^\circ\text{C}$ with the help of an in-built temperature control unit (Shimadzu TCC-240). The wavelength maximum of the reaction was recorded at 456 nm which does not change throughout the course of the study under experimental conditions (Fig.1).

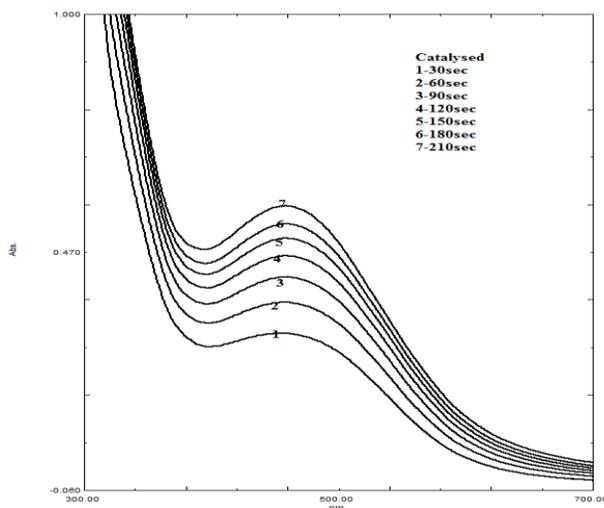


Fig 1: Wavelength maxima for PBA-NaIO₄ reaction mixture catalyzed by Mn^{II}

[PBA] $\times 10^5 = 2.0 \text{ mol dm}^{-3}$, [NaIO₄] $\times 10^4 = 2.0 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 456 \text{ nm}$, [Mn^{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

The conditions worked out for running the kinetic sets for the purpose of trace amount spectrophotometric determination of [NaIO₄] in mixed (acetone-water) medium based on its reduction with PBA: [PBA] $\times 10^5 = 2.0 \text{ mol dm}^{-3}$, [Mn^{II}] $\times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0% (v/v), pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$, Temp. = $35.0 \pm 0.1^\circ \text{C}$, [NaIO₄] = Unknown in the range of 0.72-50.22 $\mu\text{g/mL}$.

PREPARATION OF CALIBRATION CURVES

For the determination of [NaIO₄] in trace amounts, a definite volume of PBA, Mn^{II} and acetone was mixed with the calculated volume of buffer (pH 5.5) and stirred a little. This reaction mixture and periodate solution (oxidant) were separately clamped in a thermostat at $35 \pm 0.1^\circ \text{C}$ in order to maintain the desired temperature of the reaction mixture. Definite volume of periodate solution was added to the reaction mixture after 10 minutes. 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 [NaIO₄]. A portion of the reaction mixture was immediately transferred into the cuvette of Shimadzu double beam spectrophotometer (UV-2550) within few seconds and the temperature of spectrophotometer cell was also maintained at $35 \pm 0.1^\circ \text{C}$. After recording the absorbance of the reaction mixture in repeated time intervals of 30 seconds, the absorbance vs. time plots were made for different sets, which are given in fig.2. The pseudo first order rate constants (k_{obs}) were found by Guggenheim's method³⁹ and initial rates for the reaction were evaluated by using plane mirror method. Linear calibration curves were obtained by using least squares method and different plots were obtained as given in Fig. 3, 4.

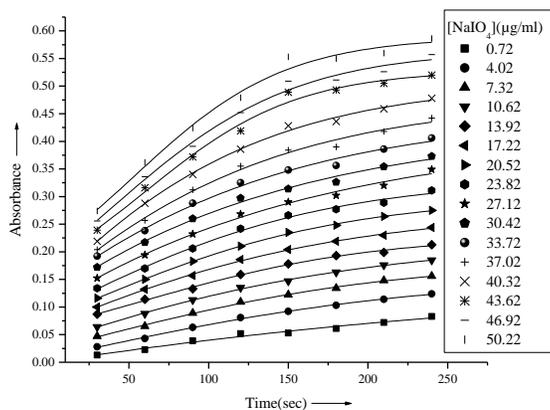


Fig 2: Absorbance vs time plots at different concentration of $[\text{NaIO}_4]$
 $[\text{PBA}] \times 10^5 = 2.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v),
 Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$, $[\text{NaIO}_4] =$ in the range of 0.72-50.22 $\mu\text{g/mL}$.

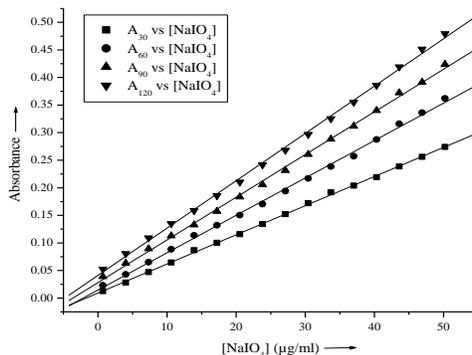


Fig 3: Calibration curve in terms of absorbance vs. $[\text{NaIO}_4]$ plots

$[\text{PBA}] \times 10^5 = 2.0 \times \text{mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$, $[\text{NaIO}_4] =$ in the range of 0.72-50.22 $\mu\text{g/mL}$.

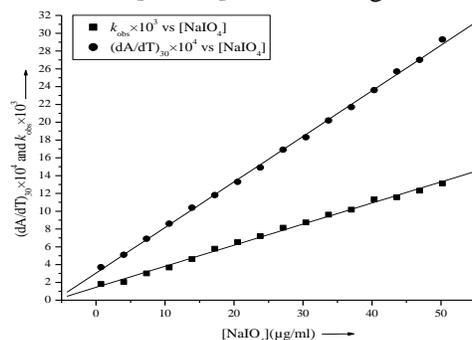


Fig. 4: Calibration curve in terms of initial rate or pseudo first order rate constant vs $[\text{NaIO}_4]$ plots

[PBA] $\times 10^5 = 2.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 \text{ mol dm}^{-3} = 7.28$, Acetone = 5.0 % (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$, $[\text{NaIO}_4] =$ in the range of 0.72-50.22 $\mu\text{g/mL}$.

Validity of beer's law and other characteristics of the method

The range of $[\text{NaIO}_4]$ in which the Beer's law is obeyed, molar absorptivity, Sandell's sensitivity, correlation coefficient of determination, value of 't' (at 0.05 significance level) and relative standard deviation for various calibration curves are given in table-1. Following are the characteristics of various calibration curves in the form of equations of straight line:

$$A_{30} = 3.77 \times 10^{-3} + 5.28 \times 10^{-3} [\text{IO}_4^-] \quad (1)$$

$$A_{60} = 7.68 \times 10^{-3} + 6.78 \times 10^{-3} [\text{IO}_4^-] \quad (2)$$

$$A_{90} = 2.038 \times 10^{-2} + 7.74 \times 10^{-3} [\text{IO}_4^-] \quad (3)$$

$$A_{120} = 3.27 \times 10^{-2} + 8.58 \times 10^{-3} [\text{IO}_4^-] \quad (4)$$

$$(\text{dA}/\text{dt})_{30} = 25.39 \times 10^{-1} + 5.12 \times 10^{-1} [\text{IO}_4^-] \quad (5)$$

$$k_{\text{obs}} = 12.07 \times 10^{-1} + 2.37 \times 10^{-1} [\text{IO}_4^-] \quad (6)$$

In equation 1-4, the values of intercept and slope are in absorbance units and absorbance units $\mu\text{g}^{-1} \text{ mL}$ respectively while these are absorbance units s^{-1} and $\text{mL } \mu\text{g}^{-1} \text{ s}^{-1}$ in equation 5-6. The $[\text{IO}_4^-]$ are in $\mu\text{g/mL}$.

Effect of interferrants

Some interfering ions like cations and anions do not interfere in the reaction system for the estimation of $[\text{NaIO}_4]$ in trace amounts, so this method may be used in the presence of these ions. However, in some cases where some metals like p-block elements and transition metal elements are expected to interfere in the reaction system, therefore a pre-treatment is required for the elimination of these metals from the reaction under consideration. For the elimination of these interferrants from the reaction system Hydrogen sulphide 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 removed by filtration⁴⁰. Now, proposed method may be applied for the determination of $[\text{NaIO}_4]$ in trace amounts in water samples. If 'Fe' metal present in the reaction system as an interferrant, it may be removed by precipitation using basic formate method^{41, 42}.

Procedure for estimation of $[\text{NaIO}_4]$

Determination of periodate ion in water samples and aqueous solutions was carried out by mixing the calculated quantity of PBA in acetone, Mn^{II} in water and acetone in a buffer solution of pH 5.5 and clamped this reaction mixture in a thermostat at $35 \pm 0.1^\circ\text{C}$ to maintained the reaction temperature. After maintaining the temperature, the calculated quantity of NaIO_4 solution was added in the reaction mixture to start the reaction followed by recording the absorbance of the reaction mixture for different sets at definite time interval. Plane mirror method and Guggenheim's method were used for the evaluation of k_{obs} and initial rates in terms of $(\text{dA}/\text{dt})_{30}$ as discussed earlier and different calibration curves under optimum conditions may be used for the determination of $[\text{IO}_4^-]$ in $\mu\text{g/mL}$.

RESULTS AND DISCUSSION

The results obtained from the proposed method were found to be reproducible within the range of the $[\text{IO}_4^-]$ limits with reasonable standard deviation, sandell's sensitivity and results lies within the experimental error as calculated from the six determinations and reported in table-1. Various parameters as molar absorptivity, percentage recovery, and correlation coefficient were evaluated from the characteristics of the calibration curves in the range of $[\text{IO}_4^-]$ i.e. 0.72-50.22 $\mu\text{g/mL}$ (table-1). The detection limits for various calibration curves are in the range of 0.12-0.19 μgcm^{-2} and high value of molar extinction coefficient indicates good correlation with the developed methods. 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. hence, from the above discussion it is clear that the proposed method for the determination of $[\text{NaIO}_4]$ is characterized by a higher selectivity and sensitivity compared to other photometric methods (Table-2).

Table 1: Parameters of calibration curves: for the determination of $[\text{NaIO}_4]$ in aqueous mixed media $[\text{PBA}] \times 10^5 = 2.0 \text{ mol dm}^{-3}$, $[\text{Mn}^{\text{II}}] \times 10^6 = 7.28 \text{ mol dm}^{-3}$, Acetone = 5.0 % (v/v), Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 5.5, $\lambda_{\text{max}} = 456 \text{ nm}$.

Parameters	A plot (30 s)	B plot (60 s)	C plot (90 s)	D plot (120 s)	E plot (k_{obs})	F plot (rate)
Linear range of $[\text{NaIO}_4]$ ($\mu\text{g/ml}$)	0.72- 50.22	0.72- 50.22	0.72- 50.22	0.72- 50.22	0.72- 50.22	0.72- 50.22
Molar absorptivity($\text{Lmol}^{-1} \text{ cm}^{-1}$)	1129.35	1450.187	1655.523	1835.192	---	---
Sandells sensitivity($\mu\text{g.cm}^{-2}$)	0.1894	0.1475	0.1292	0.1166	---	---
Slope $\times 10^3$ absorbance units. $\mu\text{g}^1\text{cm}^3$ (from regression equation)	5.28	6.78	7.74	8.58	236.84	511.85
Intercept $\times 10^2$ (abs. units) (from regression equation)	0.905	1.446	2.811	4.124	144.38	305.06
Correlation coefficient(r)	0.9997	0.99911	0.9993	0.9993	0.9981	0.9995
Coefficient of determination (r^2)	0.9994	0.9982	0.9986	0.9985	0.9961	0.9990
' t '(at 0.05 significance level)	6.9190	7.02139	7.40456	7.70286	8.02097	7.9979
Relative standard Deviation (%)	0.4028	0.3869	0.4310	0.6094	0.2698	1.8220
Recovery (%) (for six determinations)	99.05	98.71	98.96	98.94	98.43	99.74

Table 2: Comparison of the proposed method with other reported methods for the determination of Periodate

S.N.	Linear range of determination of periodate ($\mu\text{g/mL}$)	Detection Limit/Sensitivity	Technique used for the determination of periodate	Complex Pre-treatment- Yes(Y) or No(N)	Reference no.
1.	Macrograms	Not available	Volumetric titration	N	14
2.	0.4-45	Not available	---do---	Y	17
3.	1-10	Not available	---do---	Y	18
4.	10-60	Not available	---do---	Y	15
5.	Less than 95.5 μg	Accuracy 0.4%	Potentiometric titration	Y	14
6.	Not available	Not available	IR Spectroscopy	Y	15
7.	0.0382-3.82	Not available	Spectrophotometry	Y	16
8.	0.4-5.0	Not available	Kinetic Spectrophotometric	Y	23
9.	Not available	0.35 μg	Flow injection analysis & Chemiluminiscene	Y	19
10.	0.191-47.75	Not available	Chemiluminiscene	Y	20
11.	1.91-19.1	Not available	Static & Flow injection Voltammetry	Y	21
12.	0.25-0.50	0.08 $\mu\text{g/mL}$	Spectrofluorometric flow injection	Y	24
13.	0.09-1.07	0.0764 $\mu\text{g/mL}$	Fluorometry	Y	16
14.	0.764-1.91	0.0191 $\mu\text{g/mL}$	Fluorescence quenching	Y	17
15.	0.01-10	Better Detection limit and sensitivity for HS-SDME method	HS-SDME (Head space single drop micro extraction under solution immersion)	Y	25
16.	0.05-50	Compare to SDME method	SDME (single drop micro extraction under solution immersion)	Y	25
17.	0.0096-0.516	0.00069 $\mu\text{g/mL}$	Using L- cystine- CdTe/ZnAs quantum dots as selective fluorescent probes	Y	18
18.	1.53-27.3	0.037-0.052 $\mu\text{g/mL}$	Kinetic- Spectrophotometric	N	29
19.	3.82-101.72	0.17-0.24 $\mu\text{g/mL}$	Kinetic- Spetctrophotometric	N	30
20.	1.93-22.67	0.072-0.127 $\mu\text{g/mL}$	Kinetic- Spetctrophotometric	N	31
21.	0.72-50.22	0.12-0.19 $\mu\text{g.cm}^{-2}$	Kinetic- Spectrophotometric	N	\$

\$=Present method

The methods developed by us for the determination of NaIO_4 are cost effective and involve the use of simple equipments 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 better than some of the previously reported methods in terms of the ease of the procedure involved and are less time consuming in comparison to the other available methods for estimation of NaIO₄ in aqueous/ mixed media, as no pretreatment of the samples etc are involved in the proposed method except in cases where some rare interferrants are present as already discussed.

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