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Microgram Determination of Periodate: Application of Its Reduction By P-Phenetidine.

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ABSTRACT

The progress of Mn^{II} catalysed reduction of periodate by p-phenetidine in acetone-water medium was followed by monitoring the increase in the absorbance of reaction intermediate. The reaction was found to be first order with respect to catalyst, substrate and oxidant each. The main reaction product characterized on the basis of melting point and spectroscopic studies, is 4-ethoxy-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 periodate in the range 1.93 µg/mL to 22.67 µg/mL. The characteristics of various calibration curves, percentage recovery, effect of interferrants, correlation coefficient and comparison with other reported methods are presented.

Keywords: Microgram Estimation, periodate ion, p-phenetidine, Mn^{II} catalysed, 4-ethoxy-1, 2-benzoquinone

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INTRODUCTION

A perusal of literature reveals that many methods[1-16] that have been reported for determination of periodate ion alone or in combination with iodate are based on techniques such as spectrophotometry, pulse polarography, fluorometry, chemiluminescence measurement, chromatography, potentiometry, and I.R. Spectroscopy etc. and suffer from a complicated pre-treatment of samples, complex operation and use of costly equipments. Although there are some reports available in literature related to the Mn^{II} catalysed/uncatalysed periodate oxidation of aromatic amines[17-34,40], only two methods have been developed for estimation of periodate based on its Mn^{II} catalysed reduction by *N,N*-dimethylaniline[41] and *o*-anisidine[42]. In continuation to our reports on detailed kinetic-mechanistic studies on Mn^{II} catalysed periodate oxidation of *p*-phenetidine[43], the present paper deals with a new and simple kinetic-spectrophotometric method developed by us for microgram determination of periodate based on its Mn^{II} catalysed reduction by *p*-phenetidine (PEA).

EXPERIMENTAL

Reagents

Sodium metaperiodate (Loba Chemie), *p*-phenetidine (Aldrich), acetone (E. Merck), manganese sulphate monohydrate (Aldrich) and all other chemicals of analytical reagent/ guaranteed reagent grade were used after redistillation/ recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[35] was used for maintaining the pH.

Recommended Kinetic-spectrophotometric procedure

The reaction mixture turned light yellow to wine-red, thereafter brown followed by precipitation. The reaction was studied in a spectrophotometric cell and initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the PEA, Mn^{II} and buffer and maintained at the desired temperature ($\pm 0.1^\circ C$). The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV-2550), at 465 nm, i.e., the λ_{max} of the reaction mixture. λ_{max} was not found to change with change in time under experimental conditions (Fig.1). Desired temperature was maintained with the help of a high precision thermostatic control.

Following are the finally worked out conditions for running the kinetic sets for the purpose of determination of periodate in mixed (acetone-water) medium based upon the periodate oxidation of periodate ion: $[Mn^{II}] = 7.28 \times 10^{-7} \text{ mol dm}^{-3}$, $[PEA] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, Acetone = 5.0% (v/v), pH = 6.5, $\lambda_{max} = 465 \text{ nm}$, Temp. = $35.0 \pm 0.1^\circ C$, $[IO_4^-] = \text{unknown in the range of } 1.932 \mu\text{g/mL} - 22.67 \mu\text{g/mL}$.

A definite volume of stock solution of Mn^{II} in water was mixed with calculated volumes of the stock solution of PEA in acetone, acetone and water and stirred a little with the help of the pipette. This mixture and stock solution of $NaIO_4$ were then clamped in a thermostat at $35.0 \pm 0.1^\circ C$. After 30 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 $[IO_4^-]$. The reaction mixture was transferred to the cuvette of double beam spectrophotometer immediately after start of reaction. The desired temperature was maintained in spectrophotometer cell also with the help of an in built temperature control unit Shimadzu TCC-240 with an accuracy of $\pm 0.1^\circ C$. The absorbance was recorded after repeated intervals 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 plane mirror method on the absorbance vs time plots. The pseudo first order rate constants (k_{obs}) were found by Guggenheim's method[39]. Using the method of least squares, 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_{90} or A_{150} or A_{210} or initial rate or k_{obs} vs $[IO_4^-]$ plots respectively (Fig. 2-3). Here A_{30} or A_{90} or A_{150} or A_{210} are the absorbance values after 30, 90, 150 and 210 seconds from the start of reaction respectively.

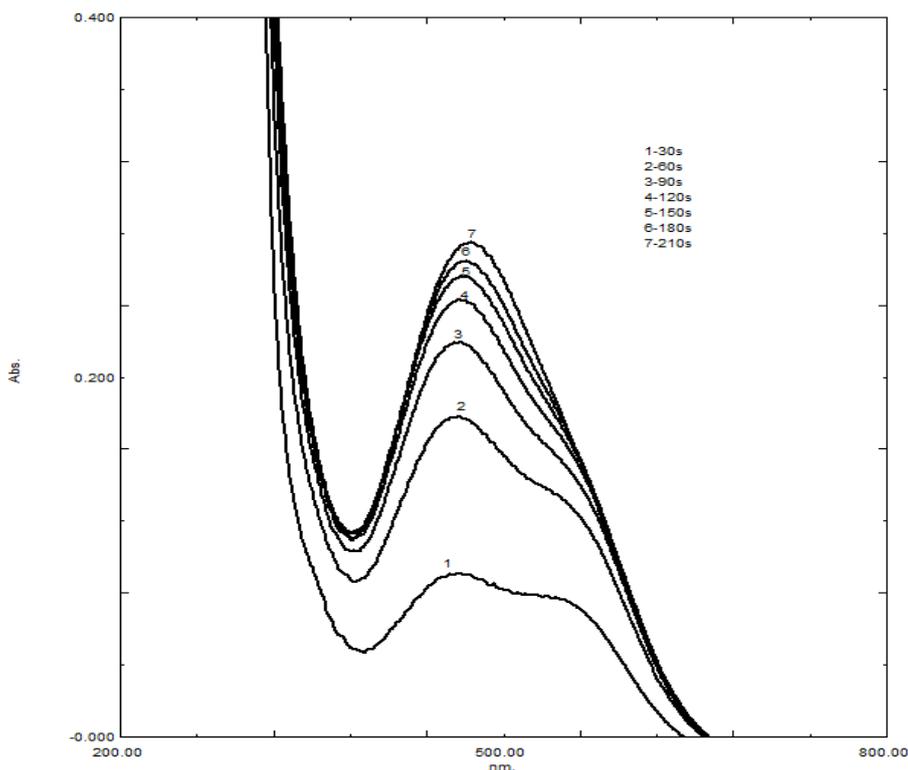


Fig 1: Determination of absorbance maxima for Mn(II) catalysed periodate oxidation of *p*-phenetidine

[PEA] = 8.0×10^{-5} mol dm⁻³, [NaIO₄] = 3.0×10^{-4} mol dm⁻³, λ_{max} = 465 nm
[Mn (II)] = 1.456×10^{-6} mol dm⁻³, Acetone = 5.0%, Temp. = 35 ± 0.1 C, pH = 6.5

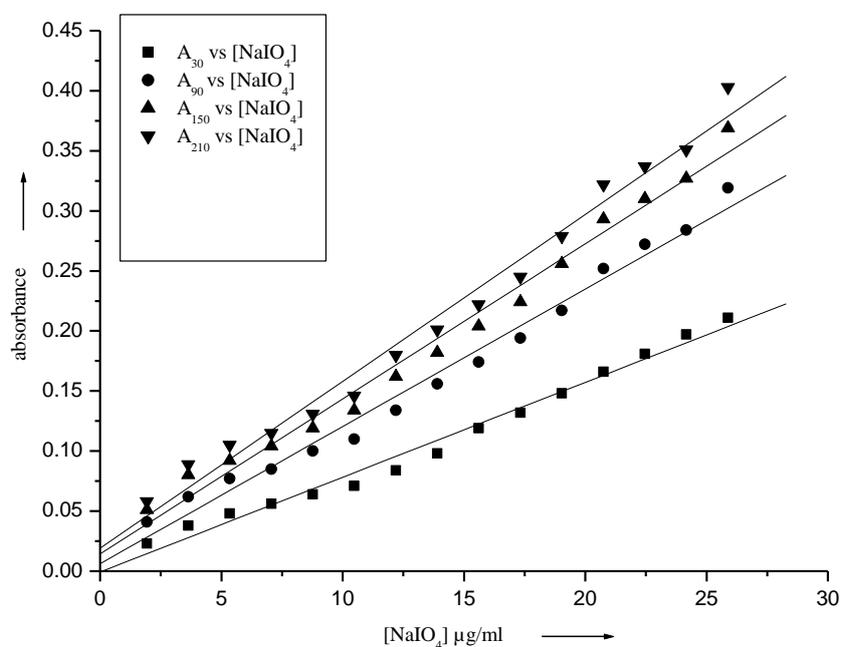


Fig 2: Estimation of [NaIO₄] by using the [PEA]
(Calibration curve in terms of absorbance vs. [NaIO₄] plots)
[PEA] = 1.0×10^{-4} mol dm⁻³, [Mn(II)] = 7.28×10^{-7} mol dm⁻³,
Acetone = 5.0 % (v/v), Temp. = 35 ± 0.1 C, pH = 6.5, λ_{max} = 465 nm.

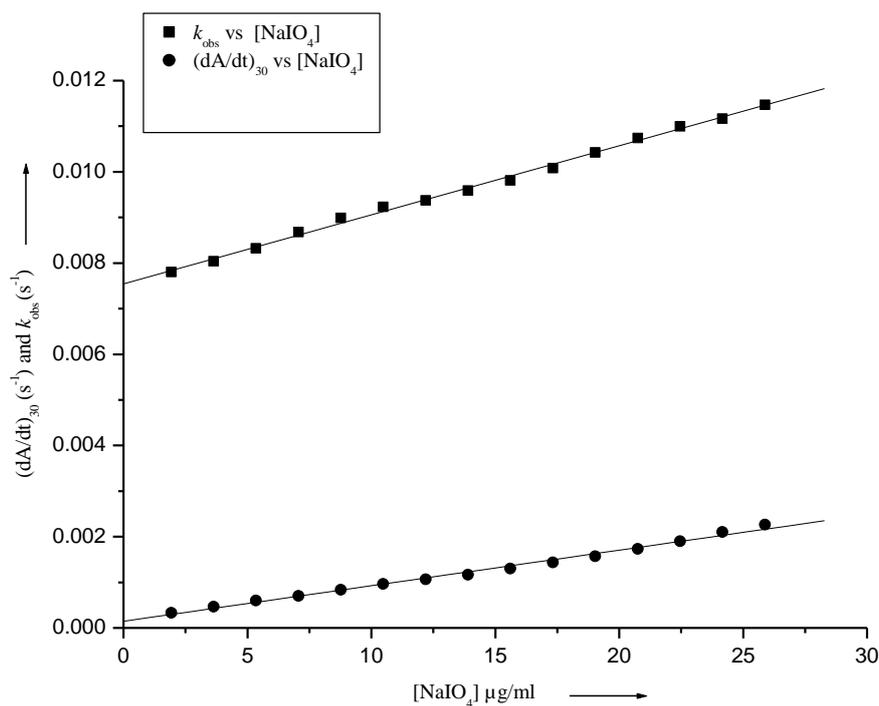


Fig 3: Estimation of [NaIO₄] by using the p-phenetidine as reductent (Calibration curve in terms of initial rate or pseudo first order rate constant vs [NaIO₄] plots)
 [PEA] = 1.0×10^{-4} mol dm⁻³, [Mn(II)] = 7.28×10^{-7} mol dm⁻³,
 Acetone = 5.0 % (v/v), Temp. = 35 ± 0.1 °C, pH = 6.5, λ_{max} = 465 nm.

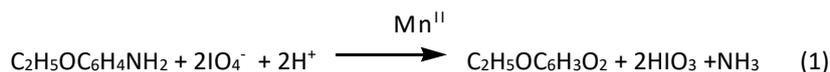
[IO₄⁻] may be determined in aqueous solutions and water samples by mixing the sample with calculated quantity of PEA and acetone and starting the reaction by adding NaIO₄ followed by noting the absorbance of reaction mixture at different desired times as described above, or evaluating initial rate in terms of $(dA/dt)_{30}$ at a desired time by plane mirror method as discussed above. After it, different calibration curves may be used for determination of [IO₄⁻] in µg/ml.

Effect of interferences

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⁺, NO₂⁻, ClO₄⁻², NO₃⁻, and SO₄⁻² as they do not interfere in 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, H₂S may be passed in presence of 0.3 M H⁺ solution, followed by filtration and boiling off H₂S. After it, a dilute alkaline solution of α -nitroso- β -naphthol should be added and again the solution should be filtered[36]. Thereafter, the solution should be neutralized and the present method be applied. Fe may be removed by precipitation using basic formate method[37-38]. In absence of the above given interferences, the proposed method may successfully be used for the determination of microgram quantities of [IO₄⁻] in water samples.

RESULTS AND DISCUSSION

The reaction under consideration is already reported[43] to be first order in each reactant and catalyst with rate-pH profile showing a maximum at pH = 7.0 and reaction rate decreasing with decrease in dielectric constant of the medium. The reaction is not influenced by free radical scavengers and the main product of the reaction is 4-ethoxy-1,2-benzoquinone. The stoichiometry is 1 mol PEA : 2 moles periodate for the initial part of reaction as given by the equation,

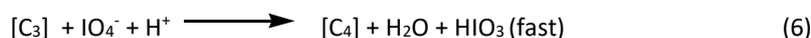
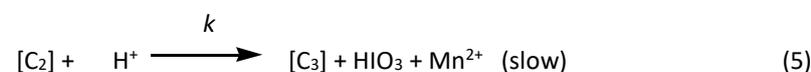
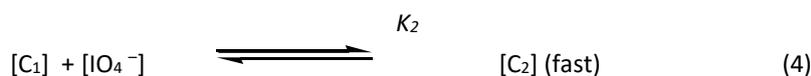
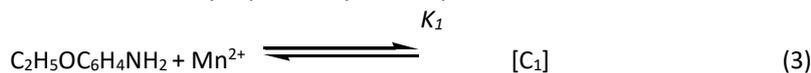


The rate law can be given by Eq. (1),

$$d[\text{C}]/dt = k_{cat} [\text{PEA}]_0 [\text{IO}_4^-]_0 [\text{Mn}^{\text{II}}] \quad (2)$$

Where, k_{cat} is the rate constant. $[\text{IO}_4^-]_0$ and $[\text{PEA}]_0$ represent respectively, the initial concentration of periodate and substrate.

As already reported by us, the probable mechanism based on kinetic and other studies, is as follows:



In steps (6 – 9), $[\text{C}_1]$, $[\text{C}_2]$, $[\text{C}_3]$ and $[\text{C}_4]$ are intermediates, out of which $[\text{C}_4]$ appears to undergo very slow reorganization/ hydrolysis to yield the reaction product, C_5 .



In the mechanism for simplicity, H_4IO_6^- has been written as IO_4^- . The formation of intermediates $[\text{C}_1]$ and $[\text{C}_2]$ in a rapid step having low values of equilibrium constants, K_1 and K_2 , is assumed in the proposed gross mechanism. The catalytic role of Mn^{2+} appears to be due to the formation of a ternary complex, $[(\text{PEA})\text{Mn}(\text{H}_4\text{IO}_6)]^+$, in which Mn acts as a conduit for electron transfer. High negative value of entropy of activation and the effect of dielectric constant on the reaction rate that support the solvation effects operating, as well as the formation of a charged intermediate complex C_2 by the attack of IO_4^- on the nitrogen of anilino group due to stabilization of positive charge on aniline nitrogen, have already been reported for the uncatalyzed/ catalyzed periodate oxidation of aromatic amines[32-33, 43].

Some of the characteristics of calibration curves can be presented in the form of equations of straight line as follows:

$$A_{30} = 0.758 \times 10^{-3} + 7.90 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(1)}$$

$$A_{90} = 6.08 \times 10^{-3} + 11.44 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(2)}$$

$$A_{150} = 14.23 \times 10^{-3} + 12.91 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(3)}$$

$$A_{210} = 19.00 \times 10^{-3} + 13.90 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(4)}$$

$$(dA/dt)_{30} = 0.15 \times 10^{-3} + 0.78 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(5)}$$

$$k_{obs} = 7.54 \times 10^{-3} + 0.15 \times 10^{-3} [\text{IO}_4^-] \quad \text{----(6)}$$

In equation 1-4, the values of intercept and slope are in absorbance units and absorbance units μg^{-1} 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 $\mu\text{g}/\text{mL}$.

Various characteristics of the calibration curves indicate reasonable sensitivity, percentage recovery, and correlation in the range of 1.93-22.67 $\mu\text{g}/\text{mL}$ as given in Table 1. Value of Sandell's sensitivity suggests that a change in absorbance by 0.001 units is expected on changing the concentration of IO_4^- by 0.072-0.127 $\mu\text{g}/\text{mL}$. Further, on changing concentration of IO_4^- by 1 $\mu\text{g}/\text{mL}$, the value of k_{obs} will change by 1.5×10^{-4} in 1 second. This change is quite satisfactory and can be easily detected by using the methods under consideration. The correlation coefficient (r) is in the range 0.9919 to 0.9983 which indicates the high precision involved in the determination and almost perfect correlation of the data. The value of coefficient of determination (r^2)

suggests that 98.39% to 99.66% change in the value of absorbance or $(dA/dt)_i$ or k_{obs} is caused by IO_4^- and the rest 0.33% to 1.61% is the effect of unknown factors. The value of 't' at 0.01 significance level, as calculated for the calibration curves, are in the range 6.9009 to 31.8605 which are much higher than the tabulated critical value at 1% significance level. This suggests that there are less than 1% chances of error in drawing conclusions. The standard deviation is within reasonable limits. Percentage recovery on the basis of six parallel determinations is 98.99% to 99.92%.

Table- 1: Characteristic of various types of calibration curves for the proposed method

Parameter	A plot (30s)	B plot (90 s)	C plot (150 s)	D plot (210 s)	E plot (k_{obs})	F plot (rate)
Linear range of $[NaIO_4](\mu\text{g/ml})$	1.93-22.67	1.93-22.67	1.93-22.67	1.93-22.67	1.93-22.67	1.93-22.67
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	1689.73	2446.90	2761.32	2973.07	---	---
Sandells sensitivity ($\mu\text{g}.cm^{-2}$)	0.1266	0.0874	0.0775	0.07194	---	---
Slope $\times 10^3$ absorbance units. $\mu\text{g}^{-1}cm^3$ (from regression equation)	7.90	11.44	12.91	13.90	0.15	0.78
Intercept $\times 10^3$ (abs. units) (from regression equation)	0.758	6.08	14.23	19.00	7.54	0.1454
Correlation coefficient(r)	0.9925	0.9922	0.9926	0.9919	0.9983	0.9962
Coefficient of determination (r^2)	0.9851	0.9845	0.9853	0.9839	0.9966	0.9926
t(at 0.01 significance level)	6.9009	7.2148	7.4997	7.6320	31.8605	7.8811
Relative standardDeviation (%) (for six determinations)	0.0785	0.0908	0.0796	0.0494	0.5279	6.374
Recovery (%)	99.87	99.83	99.92	99.75	99.81	98.99

$[PEA] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[Mn(II)] = 7.28 \times 10^{-7} \text{ mol dm}^{-3}$, Acetone = 5.0 %(v/v),
Temp. = $35 \pm 0.1^\circ\text{C}$, pH = 6.5, $\lambda_{max} = 465 \text{ nm}$

Table- 2: Percentage Recovery by using various developed methods

Plots	Added($\mu\text{g/ml}$)	Detected ($\mu\text{g/ml}$)	Recovery (%)
A	15.61	15.59	99.87
B	15.61	15.58	99.83
C	15.61	15.60	99.92
D	15.61	15.57	99.75
E(Rate)	15.61	15.45	98.99
F(k_{obs})	15.61	15.58	99.81

(Values shown are calculated from calibration curves and are mean of n=6 in each case)

Table-3: Comparison of the developed methods with the other reported methods for Determination of Periodate.

S.N.	Linear range of determination $\mu\text{g}/\text{mL}$	Detection limit/ Sensitivity	Technique used	Complex Pre-treatment- Yes (Y) or No (N)	Reference no.
1.	Macrograms	Not available	Volumetric titration	N	1
2.	0.4 – 45	Not available	---do---	Y	5
3.	1 – 10	Not available	---do---	Y	6
4.	10 – 60	Not available	---do---	Y	7
5.	Less than 95.5 μg	Accuracy 0.4%	Potentiometric titration	Y	2
6.	Not available	Not available	I.R. Spectroscopy	Y	3
7.	0.0382 – 3.82	Not available	Spectrophotometry	Y	4
8.	0.4 – 5.0	Not available	Kinetic-spectrophotometric	Y	11
9.	Not available	0.35 μg	Flow injection analysis & Chemiluminescence	Y	8
10.	0.191 – 47.75	Not available	Chemiluminescence	Y	9
11.	1.91 – 19.1	Not available	Static & Flow injection Voltammetry	Y	10
12.	0.25 – 0.50	0.08 $\mu\text{g}/\text{mL}$	Spectrofluorometric flow injection	Y	12
13.	0.09 – 1.07	0.0764 $\mu\text{g}/\text{mL}$	Fluorometry	Y	13
14.	0.764 – 1.91	0.0191 $\mu\text{g}/\text{mL}$	Fluorescence quenching	Y	14
15.	0.01 – 10	Better Detection limit and Sensitivity for HS-SDME method compared to SDME method	HS-SDME (Head space Single drop micro extraction under solution immersion)	Y	15
16.	0.05 – 50		SDME (Single drop micro extraction under solution immersion)	Y	15
17.	0.0096 – 0.516	0.00069 $\mu\text{g}/\text{mL}$	Using L-cysteine-CdTe/ZnAs quantum dots as selective fluorescent probes	Y	16
18.	1.53-27.3	0.037-0.052 $\mu\text{g}/\text{mL}$	Kinetic-spectrophotometric	N	41
19.	3.82-101.72	0.17-0.24 $\mu\text{g}/\text{mL}$	Kinetic-spectrophotometric	N	42
20.	1.93-22.67	0.072-0.127 $\mu\text{g}/\text{mL}$	Kinetic-spectrophotometric	N	§

§ - Methods in present paper

A perusal of literature given in the introduction part of this paper reveals that many methods that have been reported for determination of periodate ion alone or in combination with iodate ion and based on techniques such as spectrophotometry, pulse polarography, fluorometry, chemiluminescence, chromatography and capillary electrophoresis, suffer from lack of proper sensitivity, complicated pre-treatment of samples, complex operation and use of costly equipments [1-16].

Although lower detection limits and linear range of concentrations are available for estimation of periodate by using some of the already reported methods [2-4, 8-16], all of these methods require lengthy preconcentration and pretreatment of the samples including many complex reactions of the sample with other substances and chromogenic substances. Further, most of these methods require not-readily available facilities like flow injection analysis, chemiluminescence measurements, fluorometry, fluorescence quenching, solid phase extraction coupled with HPLC and static and flow injection voltammetry etc. However, the requirement of cumbersome pre-treatments makes these methods more complicated than the methods developed by us. A comparison of the characteristics of various reported methods with the methods developed by me in present paper is given in the table-3.

The volumetric titration based methods for periodate determination [1, 5-6], claim the applicable concentration range between 0.4 $\mu\text{g}/\text{mL}$ to micrograms and the detection limits as well as the sensitivity of the methods have not been worked out. The applicability of these methods is questionable as personnel errors are expected to occur in these methods. Less than 95.5 μg amounts of periodate are claimed to be determined by using potentiometric titrations [2]. There is no range available for periodate determination using I. R. Spectroscopy [3]. A perusal of the data given in table-1, shows that the methods developed by us for microgram determination of periodate are comparable and sometimes better in terms of wider linear range of concentration applicable and better sensitivity than other methods based on the techniques like flow injection, spectrofluorometric flow injection, chemiluminiscence, fluorescence measurements, static and flow injection voltammetry, SDME (Single drop micro extraction under solution immersion) and HS-SDME (Head space Single drop micro extraction under solution immersion) [8-10, 12-15]. A comparison with the kinetic-spectrophotometric methods developed by other workers [4, 11] reveals that the sensitivity is better in the methods developed by me and my methods have wider linear range of concentration applicable. The Sandell's sensitivity of 0.037 – 0.052 $\mu\text{g}/\text{mL}$ in the method developed by me based on the reduction of periodate by PEA, is better than all methods available except the method based on fluorescence quenching [14] and a method reported recently and based on the use of L-cysteine-CdTe/ZnAs quantum dots as selective fluorescent probes [16].

In general, my proposed methods are fairly suitable for estimation of IO_4^- at microgram level. The methods developed by me are cost effective and involve the use of simple equipments (like a VIS-spectrophotometer) and chemicals that are generally expected to be available in small centers of research or laboratories. 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 most 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 periodate ion in aqueous/ mixed media, as no pretreatment of the samples etc are involved except in cases where some rare interferrants are present as discussed earlier.

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