

## SHORT COMMUNICATION

### SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF IODATE USING METHYLENE BLUE AS A CHROMOGENIC REAGENT

B. Narayana\*, Chand Pasha, Tom Cherian and Mendalin Mathew

Department of Post Graduate Studies and Research in Chemistry, Mangalore University,  
Mangalagangothri – 574 199, Karnataka, India

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**ABSTRACT.** A simple, rapid and sensitive spectrophotometric method has been developed for the determination of iodate ( $\text{IO}_3^-$ ) in table salt and sea water. The proposed method is based on the reaction of iodate with potassium iodide in an acid medium to liberate iodine. The liberated iodine bleaches the blue color of methylene blue and is measured at 665.6 nm. This decrease in absorbance is directly proportional to the iodate concentration and obeys Beer's law in the range of 0.5-14  $\mu\text{g mL}^{-1}$  of  $\text{IO}_3^-$ . The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit of the method were found to be  $1.24 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ,  $1.41 \times 10^{-2} \mu\text{g cm}^{-2}$ , 0.048  $\mu\text{g mL}^{-1}$  and 0.145  $\mu\text{g mL}^{-1}$ , respectively. The optimum reaction conditions and other analytical conditions were evaluated. The effect of interfering ions on the determination has been described. The proposed method has been successfully applied to the determination of the iodate in the table salt and sea water.

**KEY WORDS:** Iodate determination, Methylene blue, Spectrophotometry, Table salt, Sea water

## INTRODUCTION

Iodine occurs naturally not only as iodide but also as iodate in the form of minerals such as lautarite [ $\text{Ca}(\text{IO}_3)_2$ ] and dietzeite [ $7[\text{Ca}(\text{IO}_3)_2] \cdot 8\text{CaCrO}_4$ ]. Iodine appears to be a trace element essential to animal and plants. Iodine is an essential part of the thyroid hormones that play an important role in the development of brain function and cell growth. Deficiency of iodine causes serious delay in neurological development. On the other hand an excess of iodine or iodide can cause goiter and hypothyroidism as well as hyperthyroidism [1]. Table salt is iodized by iodate as a source of iodine, in order to prevent iodine deficiency. The recommended concentration of the iodate in the salt is 40 ppm [2]. Iodate is also present in sea water and is in the range 0-60  $\mu\text{g L}^{-1}$  [3].

Several methods have been reported for the determination of iodate, such as GC-MS [4], ion-chromatography [5], chemiluminescence [6], flow injection-amperometry [7], potentiometric titrations [8], differential pulse-polarographic method [9], spectroflurometry [10], flow injection-spectrophotometry [11-12], coulometry [13], photometric analysis [14-16] and gravimetric method [17]. Some reported spectrophotometric methods for the determination of iodate are based on its reaction with excess iodide to liberate iodine which forms tri-iodide [18-21]. In other spectrophotometric methods iodate was determined after prior oxidation to periodate [22, 23]. Many spectrophotometric methods for the determination of iodate have been reported with chromogenic reagents, such as 2-oximinodimedonedithiosemicarbazone [24], 3,4-dihydroxybenzaldehyde-guanylhydrazine (3,4-DBGH) [25], 1,3-diphenyl-3-hydroxyamino-1-propanoneoxime [26], dithizone [27], blue indamine dye [28], isonicotinic acid hydrazide and 2,3,5-triphenyl tetrazoliumchloride [15] and  $\text{N,N}^1$ -di( $\beta$ -hydroxypropyl)-*o*-phenylene diamine [29]. Of these reagents, some have been reported to be carcinogenic [25, 15] while few others

\*Corresponding author. E-mail: Fax: 0091-824 2287367. Email : nbadiadka@yahoo.co.uk

are less selective such as Alizarin Navy Blue [18] (ions like Ba<sup>2+</sup>, Sr<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> are found to interfere) and tetramethylammonium iodide [22] method (the ions Mn<sup>2+</sup>, Cr<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>7+</sup> and Ru<sup>3+</sup> found to interfere seriously even at low concentrations). The need for a sensitive simple reliable method for the determination of iodate is therefore clearly recognized.

In the present investigation, a facile, sensitive and selective method has been reported for the determination of iodate with a new reagent methylene blue. The developed method has been successfully employed for the determination of iodate in table salt samples and sea water.

## EXPERIMENTAL

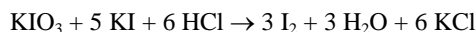
*Apparatus.* A Secoman Anthelie NUA 002 UV-Visible spectrophotometer with 1 cm quartz cell was used for the absorbance measurements and a WTW pH 330 pH meter was used for the pH measurements.

*Reagents.* All chemicals used were of analytical reagent or chemically pure grade and double distilled water was used throughout the study. A stock solution (1000 µg mL<sup>-1</sup>) of iodate was prepared by dissolving 1.2220 g of potassium iodate in 1000 mL of water and standardized using sodium thiosulphate solution [17]. The hydrochloric acid 2 M, sodium acetate 1 M and potassium iodide 2 % solution were used. A 0.01 % solution of methylene blue was prepared by dissolving 0.01 g of methylene blue in distilled water and made up to 100 mL with distilled water.

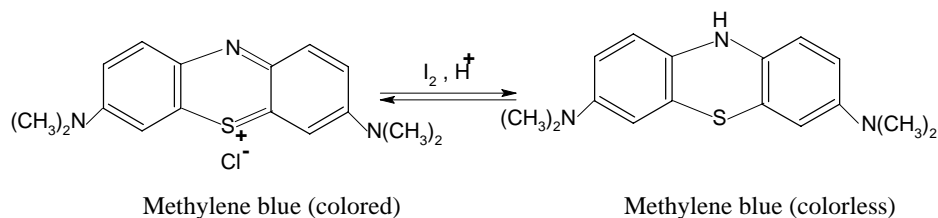
*Procedure.* An aliquot of a sample solution containing 0.5-14 mL of iodate was transferred into a series of 25 mL calibrated flasks. Potassium iodide (2 %, 1 mL) and hydrochloric acid (2 M, 1 mL) were added and the mixture was gently shaken until the appearance of yellow color, indicating the liberation of iodine. Methylene blue (0.01 %, 0.5 mL) was then added to it followed by the addition of sodium acetate (1 M, 2 mL) and the reaction mixture was shaken for 2 min. The contents were diluted up to 25 mL with distilled water and mixed well. The absorbance of the resulting solution was measured at 665.6 nm against distilled water. A reagent blank was prepared by replacing the analyte (iodate) solution with distilled water. The absorbance corresponding to the bleached color which in turn corresponds to the analyte (iodate) concentration was obtained by subtracting the absorbance of the blank solution from that of test solution. The amount of the iodate present in the volume taken was computed from the calibration graph.

## RESULTS AND DISCUSSION

This method involves the liberation of iodine by the reaction of iodate with potassium iodide in an acidic medium. The liberated iodine selectively bleaches the blue color of methylene blue and measured at 665.6 nm. This decrease in absorbance is directly proportional to the iodate (IO<sub>3</sub><sup>-</sup>) concentration and obeys Beer's law in the range of 0.5-14 µg mL<sup>-1</sup> of IO<sub>3</sub><sup>-</sup>. The reaction system is represented in Scheme 1 and Scheme 2.



Scheme 1



Scheme 2

#### *Effect of iodide concentration and acidity*

The effect of iodide concentration and acidity on the decolorisation development was studied with  $2.0 \mu\text{g mL}^{-1}$  of potassium iodate. The oxidation of iodide to iodine by iodate was effective in the pH range 1.0-1.5, which could be maintained by adding 1 mL of 2 M HCl in a final volume of 25 mL. The liberation of iodine from potassium iodide in an acidic medium was quantitative. The appearance of yellow color indicates the liberation of iodine. Although any excess of iodide in the solution will not interfere, it was found that 1 mL of 2 % KI and 1 mL of 2 M HCl were sufficient for the liberation of iodine from iodide by iodate and 0.5 mL of 0.01 % methylene blue was used for subsequent decolorization.

The variation of absorbance of known concentration of the iodate with pH of the medium was studied. A series of buffer solutions differing by pH 0.5 was prepared and using each of these buffers system was studied. The maximum absorbance value was found at  $\text{pH} = 4 \pm 0.2$ . Hence the pH was maintained at a  $\text{pH} 4 \pm 0.2$  throughout the study by using acetate buffer. The maximum absorbance was obtained instantaneously and required no heating under the reaction conditions. Under the optimum reaction conditions, the bleached color was found to be stable for more than a week.

#### *Analytical data*

The adherence to Beer's law was studied by measuring the absorbance values of solutions varying iodate concentration. A straight line graph was obtained by plotting absorbance against concentration of iodate. Beer's law was obeyed in the range of  $0.5\text{-}14 \mu\text{g mL}^{-1}$  of iodate. The molar absorptivity [30-32] and Sandell's sensitivity [33] for colored system were found to be  $1.24 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $1.41 \times 10^{-2} \mu\text{g cm}^{-2}$ , respectively. The detection limit ( $D_L = 3.3 \sigma/s$ ) [34] and quantitation limit ( $Q_L = 10 \sigma/s$ ) [34] where  $\sigma$  is the standard deviation of the reagent blank ( $n = 5$ ) and  $s$  is the slope of the calibration curve, for iodate determination were found to be  $0.048 \mu\text{g mL}^{-1}$  and  $0.145 \mu\text{g mL}^{-1}$ , respectively. The molar absorptivity of the reference method [37] is  $7.48 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$ . Ions like Cr(VI), Hg(II), and  $\text{S}_2\text{O}_3^{2-}$  interfered.

#### *Effect of diverse ions*

The effect of various diverse ions on the determination of iodate by the proposed procedure was examined. The tolerance limits of interfering species were established at the concentration required to cause not more than  $\pm 2 \%$  error in the recovery of iodate at  $1 \mu\text{g mL}^{-1}$ . The tolerance limits of diverse ions are listed in Table 1. The oxidising agents such as Fe(III), Ce(IV), V(V) and Cr(VI), interfere severely with the determination of iodate. The interference of chromium was removed by extracting with methyl isobutyl ketone [35]. However, the tolerance limit of iron, cerium and vanadium can be increased by the addition of appropriate (1 mL of 2 % NaF) amount of sodium fluoride [36].

Table 1. Effects of diverse ions in the determination of (1.0  $\mu\text{g mL}^{-1}$ ) of iodate.

Foreign ion	Tolerance limit in $\mu\text{g mL}^{-1}$
Hg <sup>2+</sup> , Ca <sup>2+</sup> , Br <sup>-</sup> , Cl <sup>-</sup>	2000
NO <sub>3</sub> <sup>-</sup> , Mn <sup>2+</sup> , Mg <sup>2+</sup> , Zn <sup>2+</sup>	1500
Gd <sup>3+</sup> , PO <sub>4</sub> <sup>3-</sup> , Yb <sup>3+</sup> , Sm <sup>3+</sup> , Eu <sup>3+</sup>	1000
Cr <sup>3+</sup> , NO <sub>2</sub> <sup>-</sup> , La <sup>3+</sup> , Al <sup>3+</sup> , SCN <sup>-</sup>	500
<sup>*</sup> Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , <sup>*</sup> Fe <sup>3+</sup> , <sup>*</sup> Ce <sup>4+</sup> , F <sup>-</sup> , <sup>*</sup> VO <sub>3</sub> <sup>-</sup> , oxalate, citrate, tartarate	≤ 1
MoO <sub>4</sub> <sup>2-</sup> , AsO <sub>4</sub> <sup>3-</sup> , Co <sup>2+</sup> , WO <sub>4</sub> <sup>2-</sup>	≤ 100

<sup>\*</sup>Masked with masking agents.

### Application

The method developed was applied to the quantitative determination of traces of iodate in table salt and sea water. The results, listed in the Table 2 and 3, compare favorably with those from a reference method [37], statistical analysis of the results by the use of F- and t-tests showed there was no significant difference between the accuracy and precision of the proposed and reference methods. The precision of the proposed method was evaluated by replicate analysis of 5 samples containing iodate at different concentrations.

Table 2. Determination of iodate in iodized table salts.

Table salt samples	Proposed method		Reference method [37]			
	Iodate found <sup>a</sup> mgkg <sup>-1</sup>	Standard deviation	Iodate found mgkg <sup>-1</sup>	Standard. deviation	<sup>b</sup> t-test	<sup>c</sup> F-test
1	25.67	0.02	25.69	0.01	2.00	4.00
2	29.09	0.02	29.11	0.02	2.00	4.00
3	34.23	0.01	34.24	0.01	1.67	1.00

a. Iodate concentration expressed in mgkg<sup>-1</sup>. b. Tabulated t-value for four degree of freedom at P (0.95) is 2.78. c. Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39.

Table 3. Determination of iodate in sea water.

Sea water samples	Proposed method			Reference method [37]			
	Iodate added $\mu\text{g mL}^{-1}$	Iodate found <sup>a</sup> $\mu\text{g mL}^{-1}$	Standard deviation	Iodate found $\mu\text{g mL}^{-1}$	Standard. deviation	<sup>b</sup> t-test	<sup>c</sup> F-test
1	2.00	2.00	0.02	2.01	0.04	0.50	4.00
2	4.00	4.02	0.03	4.04	0.05	0.77	2.78
3	8.00	8.04	0.05	8.05	0.07	0.26	1.96
4	12.00	12.02	0.10	12.04	0.14	0.26	1.96

a. Iodate concentration expressed in  $\mu\text{g mL}^{-1}$ . b. Tabulated t-value for four degree of freedom at P (0.95) is 2.78. c. Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39.

## CONCLUSION

For the first time, methylene blue has been used as a chromogenic reagent for the spectrophotometric determination of iodate. The proposed method, which is simple and rapid, offers the advantages of sensitivity and wide range of determinations without the need for extraction or heating. The method does not involve any stringent reaction conditions and the reaction system was found to be stable for 5 hours. The proposed method has been successfully applied to the determination of iodate in table salt samples and seawater.

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