Journal of Analytical Science and Technology
a SpringerOpen Journal

RESEARCH Open Access

A rapid assessment method for determination of iodate in table salt samples

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Abstract

Background: In the present work, a simple and rapid method for determination of iodate is described.

Methods: Iodometric reaction between iodate, excess iodide, and acid has been used, and the iodine liberated is allowed to react with variamine blue (VB) dye in the presence of sodium acetate to yield a violet-colored species.

Results: A calibration curve was obtained in the concentration range of 2 to 30 μg of iodate in a final equilibration volume of 10 mL. The effect of different interfering anions on determination of iodate was also studied.

Conclusions: The developed method was applied to iodate determination in various iodized salt samples obtained from local markets in and around Pune city, India. The amount of iodate in various table salt samples was in the range of 10 to 25 ppm.

Keywords: Iodate; Table salt; Variamine blue dye; Iodometric reaction; Spectrophotometry

Background

Iodine is an essential trace element for human nutrition. The safe dietary intake of iodine as recommended by the World Health Organization (WHO) is 100 μg day^{-1} for infants and 150 μg day^{-1} for adults (Hetzel 1983). Iodine is required by the thyroid gland for the synthesis of T_3 and T_4 hormones (Visser 2006). The storehouse of iodine in the human body is the thyroid gland. Inadequate intake of iodine leads to iodine deficiency symptoms and disorders like goiter, extreme fatigue, mental retardation, and depression which are collectively called as iodine deficiency disorders (IDDs). In India, about 71 million people suffer from iodine deficiency disorders. Statistics furnished by the Ministry of Health and Family Welfare in its report revealed that Uttar Pradesh, Bihar, Madhya Pradesh, Maharashtra, and Gujarat states contributing to almost 70% population have maximum IDD cases.

The natural dietary sources of iodine include milk, vegetables, fruits, cereals, eggs, meat, spinach, and sea foods (Zimmermann 2009). However, natural sources of iodine may not satisfy its requirement by the body as iodine from these sources may not be in bioavailable form and also the concentration of iodine may be less. Adequate intake of iodine can be achieved by consumption of iodized salt. Iodization of salt is done by addition of iodate to salt samples due to its good stability and bioavailability (Bürgi et al. 2001). Thus, determination of iodate in salt samples is of considerable importance as the amount of iodate in the salt samples may vary with environmental conditions, the nature of transport, packing conditions, and cooking methods (Bruchertseifer et al. 2003).

There are various analytical methods for determination of iodate in seawater and iodized salt samples. Some of the recent methods include kinetic spectrophotometric methods (Ni and Wang 2007), flow injection analysis (Shabani et al. 2011), microspectrophotometry after liquid-phase microextraction (Pereira et al. 2010), using cadmium sulfide quantum dots as fluorescence probes (Tang et al. 2010), liquid-liquid microextraction by high-performance liquid chromatography-diode array detection (Gupta et al. 2011), ion chromatography with integrated amperometric detection (Babulal et al. 2010), transient isotachophoresis-capillary zone electrophoresis (Wang et al. 2009), gas chromatography–mass spectrometry (Das et al. 2004), using polymer membrane selective for molecular iodine (Bhagat et al. 2008), and neutron activation analysis method (Bhagat et al. 2009). A non-suppressed ion chromatography with inductively coupled mass spectrometry (ICP-MS) has been

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developed for the simultaneous determination of iodate and iodide in seawater (Zul et al. 2007). Most of the techniques are complex and involve sophisticated instruments and complex procedures. It is also observed that application of these analytical methods for iodate determination in table salt is complicated due to the presence of huge excess of chloride, for example, in the case of anion exchange chromatography with conductometric detection which requires the removal of large excess of chloride from the sample matrix (Kumar et al. 2001). Hence, development of a method that is selective for iodate and sensitive and requires simple and inexpensive experimental setup is of considerable scientific interest. Also, accurate determination of the contribution of iodine from table salt to total dietary intake requires novel methods. With this objective in the present work, a simple and rapid method for determination of iodate is described. Iodometric reaction between iodate, excess iodide, and acid has been used, and the liberated iodine is allowed to react with variamine blue (VB) dye to yield a violet-colored species with absorbance maxima at 550 nm. The developed method was applied to determine the iodate concentration in table salt samples obtained from local markets in and around Pune city in India. The kinetics of the method is very fast, and a large number of table salt samples can be screened for their iodate content in a short time. The iodate content thus determined by the developed method was compared with the iodate content determined by conventional iodometric titration. The method developed in the present work has advantages over conventional methods, for example, it is free from losses of iodine and it is interference free.

Methods

Apparatus

A computer-based spectrophotometer (Systronics, Ahmedabad, India) was used for all the absorbance measurements. A pH meter (Labtronics, Panchkula, India) was used to monitor the pH of the equilibrating solutions. The pH meter was standardized using pH 4, 7, and 10 buffer solutions. A digital balance (Contech, Mumbai, India) was used for weighing all the reagents. Double-distilled water was used throughout all the work which was prepared using Equitron's instrument (Mumbai, India).

Reagents and solutions

All reagents used were of analytical reagent grade (A.R. grade) and used without further purification. Variamine blue (Merck, Mumbai, India), potassium iodate (S.M Chemicals, Mumbai, India), potassium iodide (Loba Chemie, Mumbai, India), sodium chloride (Qualigens, Mumbai, India), potassium bromate (Qualigens), ammonium oxalate (Qualigens), potassium chloride (Qualigens), sodium bicarbonate (Qualigens), potassium nitrate (Qualigens), zinc sulfate (Qualigens), methyl alcohol (Qualigens), and magnesium carbonate (Qualigens) were used. A variamine blue dye solution was prepared by dissolving 20 mg of the dye in methyl alcohol and diluting the solution to 50 mL using distilled water. A potassium iodate solution was prepared by dissolving 0.0122 g of KIO_3 in distilled water and diluting it to 100 mL [1 mL = 100 μg IO_3^-]. Sulfuric acid (1 M) was prepared by diluting 6.95 mL of stock H_2SO_4 to the mark in a 250-mL volumetric flask with distilled water. A solution of potassium iodide was prepared by dissolving 25 mg potassium iodide in water and diluting it up to 100 mL [1 mL = 250 μg]. A solution of sodium acetate (2 M) was prepared by dissolving 13.608 g of A.R. grade sodium acetate in distilled water and diluting the solution to 100 mL in a volumetric flask The different interfering ion solutions such as potassium chloride (KCl), sodium bicarbonate ($NaHCO_3$), potassium nitrate (KNO_3), zinc sulfate ($ZnSO_4$), potassium bromate ($KBrO_3$), etc. were prepared by dissolving and diluting suitable amounts of the respective salts in distilled water to make a concentration of 1 mL = 100 μg.

Samples for iodate determination

A total of 12 different brands of iodized salt samples were analyzed in the present work. The samples were purchased from local markets in and around Pune city. The samples were stored in cool and dry conditions. The contents of the packets were transferred immediately upon opening into an air tight container.

Optimization of parameters for the iodometric reaction

Various parameters associated with the iodometric reaction were optimized. The amount of potassium iodide and the concentration of acid were optimized in a similar manner as reported in our previous work (Bhagat et al. 2008) The concentration of iodate was fixed as 10 μg during the optimization experiments. Experiments were performed to optimize the dye concentration and pH of the reaction mixture. pH adjustments were done using either 2 M NaOH or 2 M HCl. The time required for the completion of the reaction was measured by studying the changes in absorbance as a function of time. The absorbance values were recorded in the intervals of 30 s till 30 min.

Measurement of iodate in the aqueous solution

An aliquot of iodate solution containing 2 to 30 μg of iodate was taken in 10-mL volumetric flasks. Excess of KI (250 μg) was added to each flask followed by 1 mL of H_2SO_4 (1 M). The solution turned yellow due to liberation of iodine. At this stage, 1 mL of dye solution was added followed by addition of 2 mL sodium acetate (2 M). The solutions were diluted to 10 mL with distilled water and kept for 5 min to allow the reaction to complete. After 5 min, the absorbances of all the solutions were recorded

at 550 nm against water as a reagent blank. A calibration plot of absorbance values of VB dye was plotted against the amount of iodate in solution.

Interference studies

The effect of common interfering anions like Cl^-, SO_4^{2-}, NO_3^-, Br^-, PO_4^{3-} HCO_3^-, $C_2O_4^{2-}$, and BrO_3^- on determination of iodate by the VB method was studied by the following procedure. The concentration of iodate in the reaction mixture was kept fixed as 5.72×10^{-8} M, and the concentration of interfering anions in the equilibrating solution was varied.

Application to table salt samples

Before application of the method to table salt samples, it was applied to A.R. grade laboratory reagent NaCl to study the effect of sodium chloride on the absorbance values. In the case of iodized table salt samples, a homogenous portion of 2 g of sample was weighed accurately on a balance and dissolved in distilled water. The final volume was made up to 25 mL, and the solution was used for further analysis. The concentration of iodate in the samples was calculated using a calibration curve. Each sample was analyzed five times, and the standard deviation was calculated. The iodate content in these salt samples was also analyzed by conventional iodometric titration using $Na_2S_2O_3$ with starch as an indicator.

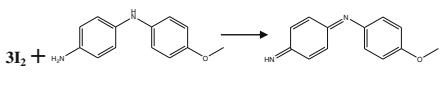
Results and discussion

Iodometric reaction

When an oxidizing agent (analyte) is added to excess iodide in an acidic medium to produce iodine which is determined by titration, the method is called iodometry. Iodometry provides a simple and rapid method of analysis. It also provides chemical amplification of signals (Zhang et al. 1998). However, conventional iodometric titrations suffer from several limitations like losses of iodine, titration error, lack of suitable indicators, and poor detection limits. These limitations can be overcome by converting the liberated iodine into an appropriate signal to prevent losses of iodine. Iodate is a good oxidizing reagent, hence oxidizes iodide to iodine in the presence of mineral acid (Pierce and Haenisch 1945). The reaction offers good signal enhancement as it can be seen from reaction 1 that the iodine content in the product side of the reaction is increased three times on a molar basis. This chemical amplification was conveniently used to determine the concentration of iodate in the present work.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2. \quad (1)$$

This modified iodometric reaction is selective towards iodate, and huge excess of chloride in the table salt samples does not interfere the determination of iodate as chloride cannot oxidize iodide to iodine. The common difficulty with the iodometric reaction for analytical purposes is the trapping of liberated iodine. In this work, the liberated iodine was allowed to react with the VB dye in the presence of sodium acetate (reaction 2). Variamine blue is known to be a suitable chromogenic reagent for iodine (Revansiddapa and Kumar 2001; Narayana and Cherian 2005; Coo and Martinez 2004). The liberated I_2 oxidizes the dye to a violet color whose absorbance maxima is at 550 nm. The visible spectrum of the oxidized variamine blue dye is shown in Figure 1. The use of this dye offered an advantage of quick reaction kinetics so that complete utilization of liberated iodine is ensured.



(2)

Variamine blue Violet coloured (oxidized dye)

Optimization of parameters for iodometric reaction

The optimization of different parameters related to the reaction was done. The concentration of the dye was varied in the range of 0.61×10^{-6} to 12.2×10^{-6} mol L^{-1}. Figure 2 shows the effect of dye concentration on its absorbance. It was observed that the maximum absorbance value was obtained for the dye concentration of 2.44×10^{-6} mol L^{-1}. However, the absorbance values were lower at dye concentrations below and above this value. This concentration of the dye was used for all further experiments. The amount of iodide was varied between 250 and 1,000 μg. It was found that 250 μg of I^- was enough to convert IO_3^- to I_2 quantitatively (Bhagat et al. 2008). The pH of the reaction mixture was varied between 2.5 and 11. It was found that the maximum absorbance was recorded at pH 5 as the oxidized form of

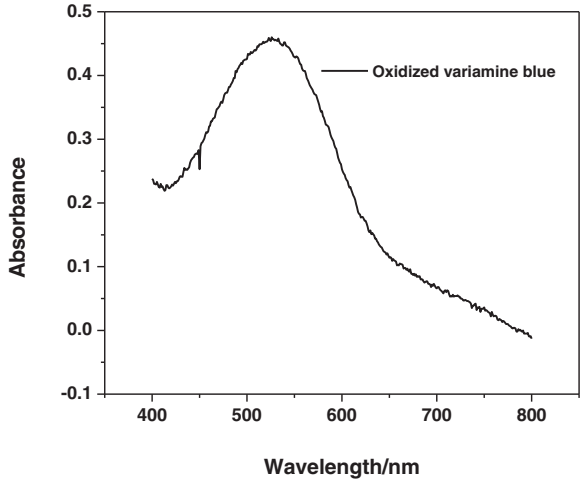


Figure 1 Visible spectrum of the oxidized variamine blue dye. $[IO_3^-] = 30$ μg, KI = 250 μg, $H_2SO_4 = 1$ mL [2 M], dye = 2.44 μM, CH_3COONa [2 M] = 2 mL, equilibration time = 300 s.

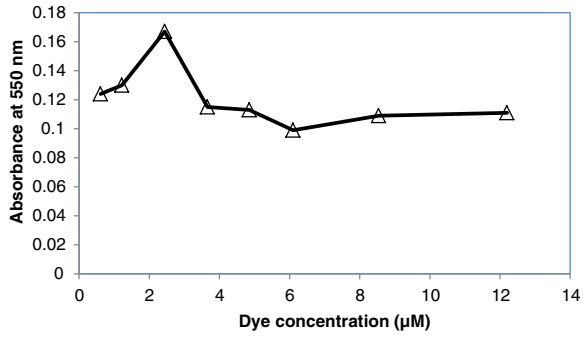


Figure 2 Effect of the concentration of variamine blue dye on absorbance at 550 nm. [IO_3^-] = 10 μg, KI = 250 μg, H_2SO_4 = 1 mL [2 M], CH_3COONa [2 M] = 2 mL, equilibration time = 300 s.

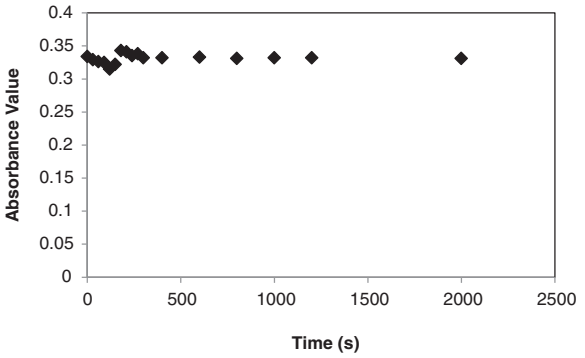


Figure 4 Absorbance of variamine blue dye as a function of the time of reaction. [IO_3^-] = 10 μg, KI = 250 μg, H_2SO_4 = 1 mL [2 M], dye = 2.44 μM, CH_3COONa [2 M] = 2 mL.

variamine blue is stable at this pH (Figure 3). The effect of acid concentration on the uptake of iodate was studied by varying the amount of H_2SO_4 (1 M). It was found that 1 mL of H_2SO_4 gave maximum absorbance. To study the effect of time on the absorbance of VB dye, all other conditions were kept fixed and the absorbance was recorded at intervals of 30 s for 30 min. It was found that the time required for completion of the reaction was 300 s, after which the absorbance values remained constant (Figure 4). The optimized parameters in the method are given in Table 1.

Calibration curve and detection limits for iodate determination

The quantitative determination of iodate in aqueous solutions was done by constructing a calibration plot. The reaction was carried out using an iodate amount in the range of 2 to 30 μg in a final volume of 10 mL. Then addition of excess iodide was done followed by addition of acid, VB, and sodium acetate in that sequence. The absorbance values of the solutions were plotted as a function of the iodate amount in the solutions and used as a calibration plot (Figure 5) for further quantifications. The plot was found to be linear till 30 μg of iodate. The regression value obtained for the calibration plot is 0.987, and the equation of the calibration plot calculated using 15 standards in the range of 2 to 30 μg in a final volume of 10 mL is $y = 0.013x$. A good linear relationship between absorbance values and amount of iodate suggests the use of the present method for quantitative determination of iodate in aqueous samples. The detection limit of the method is 0.25 μg, calculated using the relation DL = 3 s/S, where s is the standard deviation of the reagent blank and S is the slope of the calibration curve.

Effect of interfering anions on determination of iodate

The effect of interfering anions on determination of iodate in aqueous samples like Cl^-, SO_4^{2-}, NO_3^-, Br^-, PO_4^{3-}, HCO_3^-, $C_2O_4^{2-}$, and BrO_3^- was studied. The amount of iodate in aqueous samples was kept as 5.72×10^{-8} M,

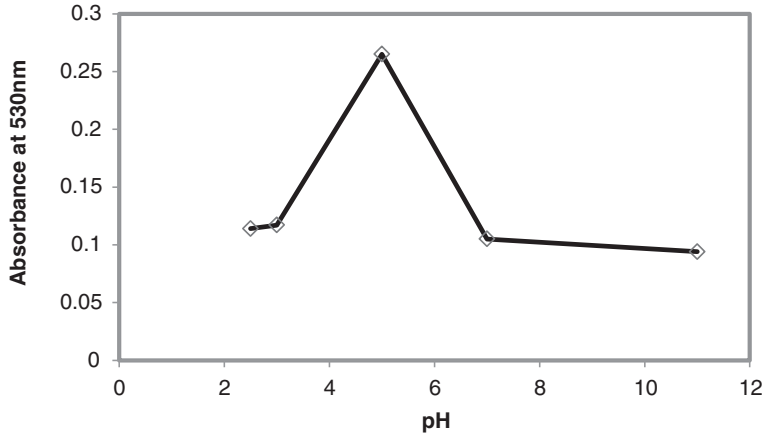


Figure 3 Effect of the pH of reaction mixture on the absorbance value. [IO_3^-] = 10 μg, KI = 250 μg, H_2SO_4 = 1 mL [2 M], dye = 2.44 μM, CH_3COONa [2 M] = 2 mL, equilibration time = 300 s.

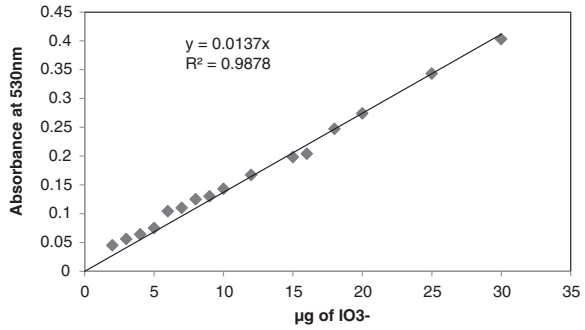


Figure 5 Calibration curve of iodate. $[IO_3^-]$ = 2 to 30 µg, KI = 250 µg, H_2SO_4 = 1 mL [2 M], dye = 2.44 µM, CH_3COONa [2 M] = 2 mL, equilibration time = 300 s.

and the amount of interfering anions in the equilibrating solution was varied. The uptake of IO_3^- in the presence of excess of anions likely to be encountered in the food samples and other aqueous samples was calculated by measuring the absorbance of VB in the solution as a function of the ratio $[X^-]/[IO_3^-]$, where $[X^-]$ is the concentration of the interfering anion. The tolerance limits of various anions are given in Table 2.

Determination of iodate in iodized salt samples

Fortification of table salt is done with KIO_3 in order to meet the requirements of iodine in human beings. Iodate is added in the range of 15 to 50 ppm to table salt. Various brands of iodized salt samples were subjected to the method described above for determination of iodate content. Before analyzing the iodized salt samples, the protocol was used for iodate determination in A.R. grade NaCl (lab reagent), and it was found that there was no effect of NaCl on the absorbance of VB. Consequently, the analysis method was applied to various iodized salt brands. The iodate concentrations obtained in these samples are given in Table 3. It is found that the iodate content was found to be in the range of 10 to 22 ppm. A set of five measurements were carried out for each sample, and the mean values are reported along with standard deviations. The standard deviation is in the range of 0.40 to 3.8. Brand number 3 and 5 showed less values of iodate as compared to the quoted value when analyzed by this method. The iodine content as quoted by the manufacturer is also given in Table 3. The amount of iodine obtained by conventional iodometric titration is also given in the table.

According to WHO, the daily dietary intake of iodine is 150 µg for adults. Considering the spicy food habits in India, the average intake of salt through food may be in the range of 2 to 3 g per day. Using this approximation, the contribution of iodine from table salt can be calculated to be around 30 to 40 µg per day. The bioavailability of iodine may be considered to be 100% due to its solubility in digestive fluids. The contribution of iodine from table salt is estimated to be 20% to 40% of the total iodine requirement. This contribution may not be enough in regions where the soil is deficient in iodine content. Consequently, iodine deficiency disorders will be prevalent in these regions.

Table 1 Optimized parameters used for analysis

Serial number	Optimized parameters	Value
1	IO_3^-	2 to 30 µg
2	KI	250 µg
3	H_2SO_4	1 mL [2 M]
4	pH	5.0
5	Dye	2.44 µM
6	Sodium acetate	2 mL of 2 M
7	Time	300 s

Table 2 Effect of some interfering anions on iodate determination

Serial number	Interfering anion $[X^-]$	Tolerated ratio $[X^-]/[IO_3^-]$
1	Cl^-	500
2	NO_3^-	100
3	SO_4^{2-}	50
4	Br^-	50
5	PO_4^{3-}	50
6	HCO_3^-	5
7	$C_2O_4^{2-}$	25
8	BrO_3^-	5

Table 3 Iodate values obtained in local brands of table salt

Serial number	Brand name	Iodate (ppm) ± SD (n = 3)	Iodate (ppm) ± SD (n = 3)
		by variamine blue method	by iodometry
1	Brand 1	15.31 ± 2.645	14.3 ± 0.2
2	Brand 2	14.67 ± 2.336	13.6 ± 0.1
3	Brand 3	11.83 ± 1.98	10.8 ± 0.2
4	Brand 4	15.76 ± 3.80	16.3 ± 0.1
5	Brand 5	10.78 ± 0.46	9.8 ± 0.1
6	Brand 6	15.22 ± 1.90	15.5 ± 0.2
7	Brand 7	16.01 ± 1.46	14.3 ± 0.1
8	Brand 8	21.09 ± 2.50	23.2 ± 0.1
9	Brand 9	16.02 ± 0.48	15.6 ± 0.2
10	Brand 10	16.20 ± 0.56	15.9 ± 0.1
11	Brand 11	18.20 ± 0.66	19.3 ± 0.2
12	Brand 12	17.60 ± 2.34	18.5 ± 0.2

Conclusions

A simple and rapid method has been developed for determination of iodate in aqueous samples. The method is applicable to iodate determination in the concentration range of 2 to 30 μg in a final equilibration volume of 10 mL. Optimized parameters for the method are IO_3^- (2 to 30 μg), KI (250 μg), 2 M H_2SO_4 (1 mL), pH (5.0), time of equilibration (20 min), 2.44 μM dye (20 μg, 1 mL), and 2 mL sodium acetate (2 M). The concentration of IO_3^- obtained in the salt samples was in the range of 10 to 22 ppm. The results obtained by the present method are in good agreement with those obtained by conventional iodometry, thus validating the method.

Competing interests

Authors declare that there are no competing interests.

Authors' contributions

PSK: Original idea, design of work, SDD: Execution of experiments, SDK: Data interpretation and manuscript writing. All authors read and approved the final manuscript.

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Received: 20 June 2013 Accepted: 18 October 2013
Published: 15 Nov 2013

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10.1186/2093-3371-4-21
Cite this article as: Kulkarni *et al.*: **A rapid assessment method for determination of iodate in table salt samples.** *Journal of Analytical Science and Technology* 2013, 4:21