A Sensitive Method For Iodate Determination As A Function Of Chloride By Spectrophotometry

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ABSTRACT

A simple spectrophotometric method has been developed for the determination of IO_3^- as a function of Cl^- in 0.1% KI - 0.16 NH_2SO_4 medium. The calibration graphs for IO_3^- estimation in 0.1% KI - 0.16 NH_2SO_4 medium in various %Cl^- are determined by following the bands at 288 and 351 nm. The influence of Cl^- on the determination of IO_3^- is studied and an empirical equation involving the %Cl^- for IO_3^- estimation is proposed. At %Cl^- = 0, the lower detection limits for IO_3^- are 0.01 µM at both wavelengths while the upper determination limits are 40 µM and 60 µM at 288 nm and 351 nm, respectively. In chloride medium, both the lower and upper limit increases with the increase in Cl^- concentration. At 6%Cl^-, the lower limit 1 µM at both wavelengths while the upper detection limit increased to 80 and 100µM, respectively, at 288 and 351 nm. The relative standard deviation found in five repetitive experiments are 0.74 and 1.45% at 288 nm band and 1.01 and 1.87% at 351 nm in Cl^- free, and 3.03 and 0.91% at 288 and 351 nm, respectively in 6 % Cl^- medium. The effect of K^+, Ca^{2+} and Mg^{2+} commonly present in most edible salts, on the absorption intensities are reported.   © 2006 Trade Science Inc. - INDIA

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INTRODUCTION

Iodine is a trace nutrient essential for healthy biological growth of humans and animals[1,2]. Its deficiency for long time, leads to biological disorders like gout, mental retardation, deaf mutism, short stature, cretinism and risk of death during the childhood[1-6]. The recommended daily intake of iodine as 110 µg/day for young infants (0-6 months), 130 µg/day for older infants (7-12 months), 90 µg/day for children (1-8 years), 120 µg/day for children (9-13 years), 150 µg/day for adolescents and adults; 220 µg/day for pregnant ladies (18-50 years)[7]. Iodine intake from food supply through natural resources is generally inadequate in most parts of the world and must be supplemented. To do so, edible salt is considered as the most common vector among other tested possibilities[8]. Tropical countries like India and other parts of Asia preferentially use KIO_3 as iodizing agent while the non-tropical countries like USA use KI for iodization of salt. Both of these forms of iodine however, are absorbed as iodide ions and are completely bio-available[9]. On the contrary, excess intake of iodine/iodized compounds may lead to thyrotoxicosis[1]. Therefore, monitoring of iodine level is essential for iodine supplementation procedures.

Several analytical methods have been reported for the determination of iodate and iodide including titrimetry[10], electrochemistry[11-14], chemiluminescence[15] and ICP-MS[16]. Kumar et al.[17] have suggested an anion exchange chromatographic method with conductometric detector for the estimation of iodate in iodized common salts. This method requires the use of a fresh on guard silver cartridge for the pretreatment of each sample to avoid the interference of chloride ion present in the sample matrix.

Spectrophotometric methods reported so far on determination of iodate and iodide, are based on the formation of the iodine–starch complex or catalytic reactions[18,19]. Choengchan et al.[20] have reported a simple flow injection method for the determination of iodate in iodized salts. The method involves the conversion of iodate to triiodide which subsequently forms a blue (I_3^- starch) complex in the presence of starch enabling to detect 2 mg/kg salt colorimetrically at 590 nm. However, the thiosulfate treatment is essential after completion of each sample to prevent the accumulation of the blue complex residue on the walls of tubing and the flow cell. Xie et al.[21] have reported reverse flow injection method for the determination of iodate and iodide. The iodate is reacted with excess iodide in acidic medium to form tri-iodide and monitored spectrophotometrically at 351 nm. However, the effect of chloride ion concentration on the absorption band 351 nm has not been studied.

Recently, Jakmunee and Grudpan[22] have reported a flow injection amperometric method for iodate determination at 35 injections h⁻¹ sampling frequency. A Flow injection spectrophotometric method[23] using an ion associate of iodate with 3,5-Br_2-PADAP and thiocyanate with the detection limit of 63 ng ml⁻¹ and a sampling frequency of 80 h⁻¹ has also been reported.

Most of the above methods used for determination of iodate may be sensitive, but some of them are time consuming and needs various reagents for the pre/post chemical treatment or expensive apparatus. Further, the effect of chloride ion concentration in particular the determination of iodate in iodized salts has not been established.

In an attempt to prepare potassium iodate from elemental iodine and KOH solution through non-catalytic chromium (VI) route for edible purpose using electro-membrane flow cell under single pass conditions[24], we needed a method for the direct determination of iodate in the presence and in the absence of chloride ion.

It is of course well known that iodate reacts with iodide in acid medium producing three molecules of iodine or triiodide in the presence of excess iodide, which enables its direct determination by photometric in lower or titrimetric method at higher concentration levels. However, in photometric methods, the affect of variable concentrations of chloride on the observed absorbance of triiodide in the visible region has never been reported and consequently can cause a significant error in its determination. In fact the visible spectral changes that whether fading of triodide color in solution with the increase in chloride ion concentration is due to an actual change in molar absoptivity of triodide ion in a highly saline

Zmedium or a different amount of triiodide formed has never been elucidated earlier. We discuss these results in this paper with the quantitative data on the effect of chloride concentration on the apparent triiodide absorptivity by following the absorption bands at 290 and 351 nm. The sensitiveness of these bands with respect to low and upper limits of detection has been determined and the coefficient of chloride ion dependence on the determination of iodate in table salts has been reported.

EXPERIMENTAL

Reagents

Highly pure potassium iodate (KIO_3) from Qualigens Fine Chemicals Limited, India, potassium iodide (KI) from Ranbaxy Fine Chemicals Limited, India were obtained and employed as received in the present investigations. All other chemicals such as NaCl, (Qualigens), KCl (Rankem), $CaCl_2$ (fused, Rankem) $MgCl_2.6H_2O$ (S.D. Fine Chem.Rankem), H_2SO_4, etc. were of the highest purity grade. Standard solutions of (100 mM) KIO_3 prepared weekly in double distilled water and diluted to the desired concentration between 10 mM and 1 µM as and when required. 25% (w/v) NaCl solution was prepared by dissolving 62.5 g of dry NaCl in deionized water in a 250 ml standard flask. Stock, 10% and 1% (w/v) solutions of KI, (1 M) $MgCl_2$, (0.1 M) $KCl/CaCl_2$ were prepared and used in the present studies. A solution of 18 or 2 N H_2SO_4 was prepared by diluting appropriately the concentrated H_2SO_4 and used in the present studies.

All glassware were cleaned with detergent solution, rinsed with tap water, soaked in 2% (v/v) HNO_3, followed by rinsing with water and drying in the oven at 120°C. Doubly distilled water was used to prepare all experimental solutions.

Commercially available iodized salts of some branded Indian companies were procured from retail shops in well-packed condition. A stock 10% (w/v) solution of iodized salt was prepared from oven-dried sample and used for the chloride and iodate determination.

Procedures

1. Absorption spectra of triiodide or iodate in ex-

cess acidic iodide-chloride and -chloride free media

Absorption spectra of IO_3^- were recorded in the range 1 µM to 0.1 mM from KIO_3 stock solution while maintaining the %KI to 0.1 (w/v); %Cl$^-$ to 0, 0.61, 1.82, 3.03 or 6.06 (w/v) with NaCl; and [H$^+$] to 0.04, 0.16 or 1.44 N with H_2SO_4 in the experimental solution. To an aliquot (0.25-5 ml of 0.1 mM or 1 to 2.5 ml of 1 mM) of KIO_3 stock in a standard flask containing 2.5 ml of 1%(w/v) KI; 0, 1, 3, 5 or 10 ml of 25% (w/v) NaCl; 0.5 or 2 ml of 2 N or 2 ml of 18 N H_2SO_4 was added, diluted to 25 ml with distilled water and allowed 5-10 min for equilibration. The absorption spectra of these experimental solutions were recorded between 200 nm and 800 nm.

2. Calibration plots of iodate ion estimation in chloride free medium.

Working standards for iodate ion estimation in Cl$^-$ free medium were prepared in the range between 0.01 µM and 0.1 mM from KIO_3 stock solutions while maintaining the acid concentration to 0.04, 0.16 or 1.44 N with H_2SO_4 in the experimental solution. To an aliquot (0.25 to 5 ml of 1 µM or 0.1 mM or 1 to 2.5 ml of 10 µM or 1 mM) of KIO_3 stock in a standard flask containing 2.5 ml of 1% (w/v) KI, 0.5 or 2 ml of 2 N or 2 ml of 18 N H_2SO_4 was added, diluted to 25 ml with distilled water and allowed 5-10 min for equilibration. The absorption spectra of these experimental solutions were recorded between 200 nm and 800 nm.

3. Calibration plots of iodate ion estimation in chloride medium.

Working standards for iodate ion estimation in Cl$^-$ medium were prepared in the range from 0.1 µM and 100 µM from KIO_3 stock solutions while maintaining the %Cl$^-$ to 0.61, 1.82, 3.03 or 6.06 (w/v) and [H$^+$] to 0.16 N with H_2SO_4 in the experimental solution. To an aliquot (0.25 to 5 ml of 100 µM or 1 to 2.5 ml of 1 mM) of KIO_3 stock in a standard flask containing 2.5 ml of 1% (w/v) KI, 1, 3, 5 or 10 ml 25% (w/v) NaCl and 2 ml of 2 N H_2SO_4 was added, diluted to 25 ml with distilled water and allowed 5-10 min for equilibration. The absorption spectra of these experimental solutions were re-

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corded between 200 nm and 800 nm. The influence of Cl^- on the iodate ion estimation was followed by keeping the $[IO_{3v}^-]$ constant at 0.04 mM in 0.1% (w/v) KI−0.16 N H_2SO_4 while varying its concentration between 0.0% and 6.1%.

4. Estimation of chloride ion

The chloride ion composition in 10% (w/v) iodized edible samples was determined to a precession of ± 0.05% by the well-known volumetric (Mohr's) method as described earlier[25]. The samples were diluted appropriately and used in the chloride ion estimation.

5. Estimation of iodate in commercial iodized salts

The iodate ion estimation in commercial iodized salts was carried out in 0.16 N H_2SO_4 medium maintaining the %Cl^- between 6 and 8.5 (w/v) by adding NaCl externally. To 5-15 ml of the 10% (w/v) iodized salt solution, 2.5 ml of 1% (w/v) KI, 2.0 g of NaCl (6.06%, w/v, Cl^-) and 2 ml of 2 N H_2SO_4 were added. The resulting solution was diluted to 25 ml with distilled water and allowed to stand for 5-10 min for equilibration. The absorbance at 288 and 351 nm of the equilibrated solution was noted and the IO_3^- concentration in it was determined. The above experiment in each case was repeated at least five times and the standard deviation was calculated.

6. Determination of iodate in electrolyzed solutions

The iodate composition in electrochemically prepared 3% (w/v) expected KIO_3 solution from 1.78% elemental iodine in 0.99% (w/v) KOH using anion-exchange membrane flow cell under single pass conditions[24] was estimated by the present method. To a 0.5-1.0 ml of 100 fold diluted analyte solution, 2.5 ml of 1% (w/v) KI and 2 ml of 2N H_2SO_4 were added. The resulting solution was diluted to 25 ml with distilled water and allowed to stand for 5-10 min for equilibration. The absorbance at 288 and 351 nm of the equilibrated solution was noted and the IO_3^- concentration in it was determined assuming chloride-free medium.

7. Interference of other cations on iodate estimation

The cations K^+, Ca^{2+} and Mg^{2+}, which commonly present in considerable amounts in iodized sea-salt or iodized mined salt were studied for potential interference. In these studies K^+, Ca^{2+} and Mg^{2+} concentrations were maintained at 0.02. 0.02 and 0.10 M, respectively, and the spectra were recorded as stated in the above experiments. To an aliquot (1 ml of 1 mM) of KIO_3 stock in a standard flask containing 2.5 ml of 1% (w/v)KI, 10 ml 25% (w/v)NaCl, 2 ml of 2 N H_2SO_4 and 2.5 of 1 M $MgCl_2$ (5 ml of 0.1 M KCl/$CaCl_2$) was added, diluted to 25 ml with distilled water and allowed 5-10 min for equilibration. The absorbance at 288 and 351 nm of the equilibrated solution was measured.
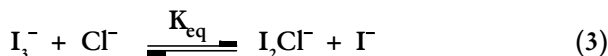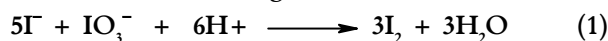
Apparatus

Electronic absorption spectra were recorded employing a quartz cell of 1 cm path length on Varian-Cary 500 Scan UV-Vis NIR spectrophotometer.

RESULTS AND DISCUSSION

It is of course well known that iodate reacts with iodide in acid medium producing three molecules of iodine (Eq 1) or triiodide (Eq 2) in the presence of excess iodide. Both, iodine and triodide exhibit a characteristic color in solution on account of two absorption bands in the ultraviolet region at 288 and 351 nm, low in the former case and intense in the later case[20,21,26,27], which have been formed the basis for their photometric determination[20,21]. The color of these species in solution predictably reduces in the presence of added chloride ion and incrementally fades as the latter's concentration increases and can cause a pivotal error in iodine determination. In fact these visible changes that whether this affect is due to an actual change in molar absoptivity of triodide ion in a highly saline medium or a different amount of triiodide formed on account of its possible establishment of an equilibrium with I_2Cl^- species [Eq 3][26,28-30], in solution has never been revealed earlier. In order to generate a quantitative data on the effect of chloride ion concentration over the apparent absorptivity of bands at 290 and 351 nm, the spectral behavior of triiodide by using (0.1%) KI - (0.16 N) H_2SO_4 mixture as a reaction medium

having Cl^- set to 0% or between 6 and 8.5% (w/v) has been reinvestigated so as to facilitate the determination of iodate through triiodide in iodized salts.

$$5I^- + IO_3^- + 6H+ \longrightarrow 3I_2 + 3H_2O \qquad (1)$$

$$I_2 + I^- \longrightarrow I_3^- \qquad (2)$$

$$I_3^- + Cl^- \xrightleftharpoons{K_{eq}} I_2Cl^- + I^- \qquad (3)$$

Absorption spectra of triiodide in chloride free medium

Figure 1A depicts the absorption spectra of I_3^- ion resulted in accordance with the above reactions (Eqs 1 and 2) between KIO_3, I^- and H^+. As reported in the literature[26], the spectrum has showed two intense absorption bands at 288 and 351 nm, characteristic of I_3^-. The spectrophotometric studies of solutions with a constant percentage of I^- as KI and with changeable concentrations of KIO_3 (0.01 µM to 150 µM) showed that at $[H^+]$ 0.16 N the solution absorbance obeyed Beer's law for $[IO_3^-]$ = 0.01 to 60 µM at 351 and for $[IO_3^-]$ = 0.01 to 40 µM at 288 nm (Figure 1B). The molar absorptivities of I_3^- were found to be 1.931 x 10^5 and 2.922 x 10^5 M^{-1} cm^{-1}, respectively at these wavelengths. These values co-incide with literature data (2.500 x 10^5 M^{-1} cm^{-1} for 288 nm and 3.694 x 10^5 M^{-1} cm^{-1} for 351 nM) from Kazantseva et al.[26]

The spectrophotometric studies of I_3^- solutions with a constant percentage of I^- as KI and with changeable concentrations of KIO_3 (0.01 µM to 150 µM) showed that at $[H^+]$ = 0.16 N and 0.04 N as H_2SO_4, the solution absorbance for I_3^- changed negligible at both 351 and 288 nm. However, the studies when repeated in 1.44N H_2SO_4, the solution absorbance for I_3^- increased at both the wavelengths 351 and 288 nm by about 1.07 and 4.5 times depending on the KIO_3 concentration. These changes may be accounted for large deviations in the viscosities of the medium.

Absorption spectra of tri iodide in chloride medium

Absorption spectra of I_3^- ion produced in figure1 A were studied in the presence of various percentages (0.61, 1.82, 3.03, 6.06) of Cl^- as NaCl. The data obtained in 6.06 % Cl^- in (0.01 to 150 µM) KIO_3, 0.1% KI and 0.16 N H_2SO_4 solution is presented in figure 2A. The spectra were similar to those observed
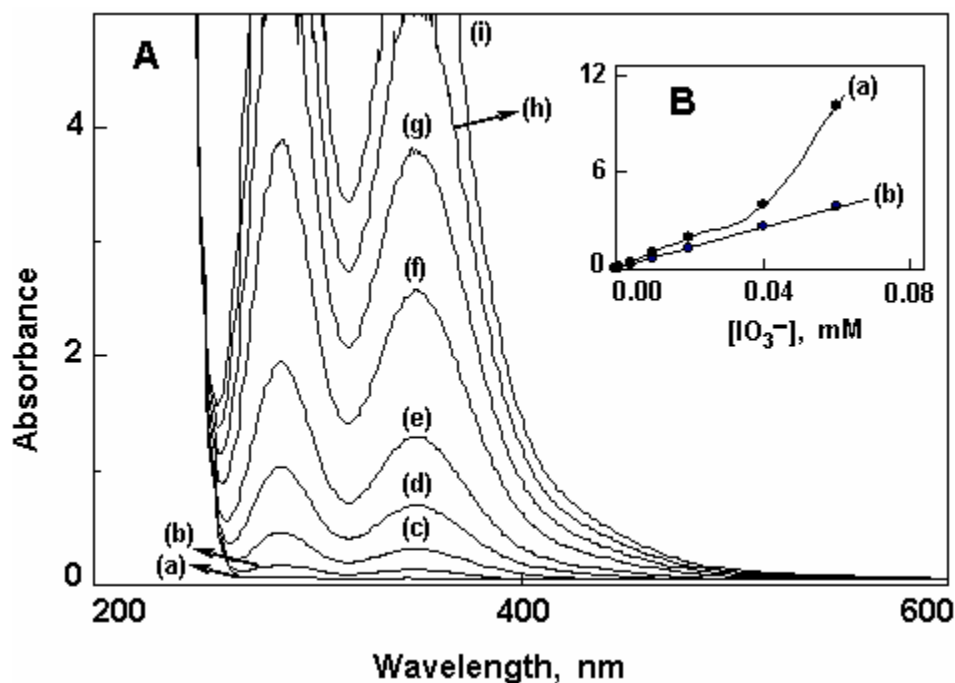

Figure 1: A) Absorption spectra of I_3^- in chloride free medium. KI, 0.1%; H_2SO_4, 0.16 N; $[KIO_3]$: (a) 0 mM; (b) 1 µM; (c) 4 µM; (d) 10 µM; (e) 20 µM; (f) 40 µM; (g) 60 µM; (h) 80 µM; (i) 100 µM. at 25°C. B) Variation in absorbance at (a) 288 nM, (b) 351 nM with $[IO_3^-]$.

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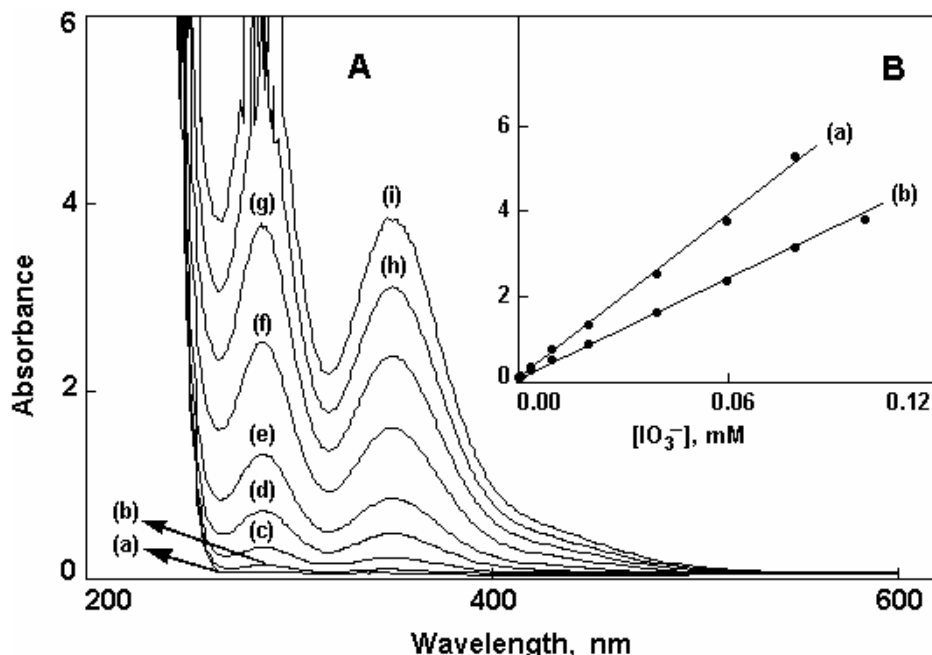
Figure 2: A) Absorption spectra of I_3^- in 6.06 %Cl^- (NaCl) KI, 0.1%; H_2SO_4, 0.16 N; [KIO_3]: (a) 0 μM; (b) 1 μM; (c) 4 μM; (d) 10 μM; (e) 20 μM; (f) 40 μM; (g) 60 μM; (h) 80 μM; (i) 100 μM. at 25°C. (B) Variation in absorbance at (a) 288 nM, (b) 351 nM with [IO_3^-].

in the absence of Cl^- (Figure 1A) except a considerable reduction in the absorbance of both the characteristic intense bands (288 and 351 nm) of I_3^-. The solution absorbance obeyed Beer's law for extended concentration of I_3^- upto 300 μM at 351 and 240 μM at 288 nm (Figure 2B). However, the lower limit of detection of I_3^- was reduced in either case to 3 μM in Cl medium. The reduction in the absorbance of I_3^- especially in chloride medium indicates the decrease in the concentration of it. This may be attributed to the formation of low-absorptive inter-halogen compounds. The most probable mixed halogenated compounds in the present experimental conditions are expected to be I_2Cl^- and ICl_2^-[26,29]. The former species I_2Cl^- results by the exchange of I^- in an equilibrium (K_{eq}) with Cl^- present in solution as shown in Eq 3, while the later species, ICl_2^- contains I^+ and does not exist in presence of excess I^- as it readily reacts further with the former species to give ultimately I_2Cl^-. From the absorption data at 288 and 351 nm of 40 μM KIO_3, 0.1% KI and 0.16 N H_2SO_4 in 0.61-6.10% Cl^-, the value of K_{eq} was evaluated as 0.376424 M^{-1} and 0.414311 M^{-1}, respectively which are in close agreement with the ($1/K_{eq}$) values reported by Cason et al. (0.60 M)[31] and by Wang et al.

(0.013 M in μ = 1.0 and 0.5)[32].

The species I_2Cl^- has low absorptivity at 288 and 351 nm[26], which could be the reason for the fading of I_3^- solution or decrease in the absorbance at 288 and 351 nm in figure 2 with the increase in %Cl^-. Therefore, the ignorance of the variation in chloride ion composition in the determination of iodate in different commercialized iodized salts is not proper. Similarly, while in the determination iodide in the natural brines through the formation of I_3^- ions, the chloride concentrations whose concentration is 3–4 magnitudes of order greater than the iodide concentrations is not forgettable[26].

The effect of H^+ concentration of the absorption bands at 288 and 351 nm of I_3^- was verified by changing its concentration to 0.04 and 1.44 N while varying KIO_3 between 1 to 120 μM keeping KI at 0.1% and %Cl^- at 6.06. Unlike in the absence of Cl^-, the plots of absorbance versus [IO_3^-] of 351 and 288 nm in 0.04 and 1.44 N H_2SO_4 are linear and have slope identical to that observed in 0.16 N H_2SO_4.

Evaluation of standard equations for iodate ion estimation

The decrease in the absorption intensity of the I_3^- bands (λ) at 288 and 351 nm in chloride medium proves that the formation of low absorptive species I_2Cl^- while the regular decrease in the absorbance of 288 and 351 nm bands with the enhancement in %Cl$^-$ could be explained for the influence of chloride ion on the equilibrium (Eq 3) involving I_3^-, Cl$^-$ and I_2Cl^-. Thus, the observed absorbance at λ (288 or 351 nm) is then accounted for

$$\text{Abs}\lambda = m_1 [I_3^-] - m_2¢ [I_2Cl^-] \qquad (4)$$
$$\text{Abs}\lambda = m_1 [I_3^-] + m_2 \%Cl_T^- [I_3^-] \qquad (5)$$

where $m_2 = 0.282\ m_2¢\ K_{eq}$, %Cl$_T^-$ = Total percentage of Cl$^-$ ion in the experimental solution. In the present experimental conditions, $[I_3^-] = [IO_3^-]$, the Eq 5 reduces to Eq 6.

$$\text{Abs}\lambda = m_1 [IO_3^-] - m_2 \%Cl_T^- [IO_3^-] \qquad (6)$$

At %Cl$_T^-$ = 0 i.e. in the absence of chloride, Eq 6 reduces to Eq 7

$$\text{Abs}\lambda = m_1 [IO_3^-] \qquad (7)$$

Eq 7 explains the absorption spectra of IO_3^- in chloride free medium under the present experimental conditions as described in figure 1. Whereas, the difference in Eqs 6 and 7 resulting to Eq 8 explains the difference of absorption (Figures 1 and 2) of spectra IO_3^-.

$$\Delta\text{Abs}\lambda = -m_2 [\%Cl_T^-] [IO_3^-] \qquad (8)$$

The coefficients m_1 and m_2, in Eq 6 were determined experimentally by constructing calibration graphs independently in a mixture of 0.1% KI and 0.16 N H_2SO_4 in chloride and chloride free medium as discussed in the following sections.

Determination of the coefficient m_1 in chloride free medium

Absorption spectra of 0.01 - 100 µM IO_3^- in 0.1% KI - 0.16 N H_2SO_4 medium were studied. The plot of $[IO_3^-]$ vs absorbance at 288 and 351 nm (Figure 3) showed a linear increase between 0.01-60 µM obeying the linear equations $\text{Abs}_{288} = 95.132 [IO_3^-]$ ($R^2 = 0.9999$) and $\text{Abs}_{351} = 62.458 [IO_3^-]$ ($R^2 = 0.9999$) passing through the origin, respectively. The lower detection limit for IO_3^- under the present set of experimental conditions was noted as 0.01 µM with respect to both the 288 and 351 nm bands while the higher detection limit was 40 µM with respect to 288 nm and 60 µM with respect 351 nm, implying that the determination of IO_3^- in chloride free medium is better to follow the 351 nm band concentration as high as 60 µM.

The precision of the method was established by five replicate determinations of standard IO_3^- solution. Using 20 µM and 0.02 µM of IO_3^- in 0.1% KI - 0.16 N H_2SO_4 medium, the relative standard deviation was found to be 0.74 and 1.45% with respect to 288 nm band and 1.01 and 1.87% with respect to 351 nm band, respectively.
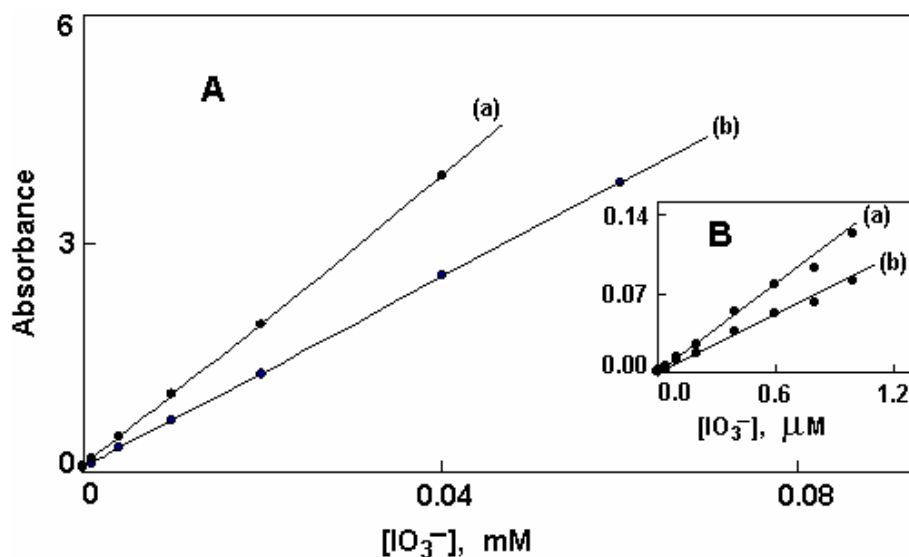

Figure 3: Calibration plots of $[IO_3^-]$ vs Absorbance at (a) 288 nm, (b) 351 nm. in a mixture of 0.1% KI and 0.16N H_2SO_4 with 0% Cl$^-$. $[IO_3^-]$: (A) 0.0 – 6 µM; (B) 0.0 – 1.0 µM at 25°C.

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Calibration plots of iodate estimation in chloride medium

The absorption spectra of I_3^- was recorded by varying KIO_3 between 1 to 120 μM, while keeping KI at 0.1% and H_2SO_4 at 0.16 N in different %Cl⁻ (0, 0.61, 1.82, 3.03 and 6.06) medium. The plots of absorbance at 288 and 351 nm against $[IO_3^-]$ are depicted in figure 4. The plots, in all %Cl⁻, were linear beyond 60 but below 120 μM at λ = 351 nm and beyond 40 and below 100 μM at λ = 288 nm with distinct slopes but passed through the origin. However, the slope of these plots gradually decreased from 95.132 and 62.458 to about 75.203 (20.95%) and 37.783 (39.51%) for 288 and 351 nm bands, respectively as the %Cl⁻ increases from 0 to 6.06, which has further confirmed both the reaction between I_3^- and externally added Cl⁻ (Eq 3) to give I_2Cl^- and the validity of Eq 6. The coefficients, m_2 of Cl⁻ ion were evaluated independently by varying

Cl⁻ composition while keeping all other parameters constant as discussed in the following section.

The lower and upper detection limits for IO_3^- determination in chloride medium were dependent on the Cl⁻ composition. The lower limit decreases withy increase in % of Cl⁻. Concomitantly, the upper limit increases with the increase in %Cl⁻. In 6.06 %Cl⁻ the lower limit decreased to about 1 μM from 0.01 μM while the upper detection limit increased to 80 μM from 40 μM with respect to 288 nm and 100 mM from 60 mM with respect 351 nm bands, respectively.

The precision of the method was established by five replicate determinations of standard IO_3^- solution in 6.06% Cl- medium. Using 20 μM of IO_3^- in 0.1% KI⁻ 0.16 N $H_2SO_4^-$ 10% NaCl medium, the relative standard deviation was calculated to be 3.03 and 0.91% with respect to 288 and 351 nm bands, respectively.
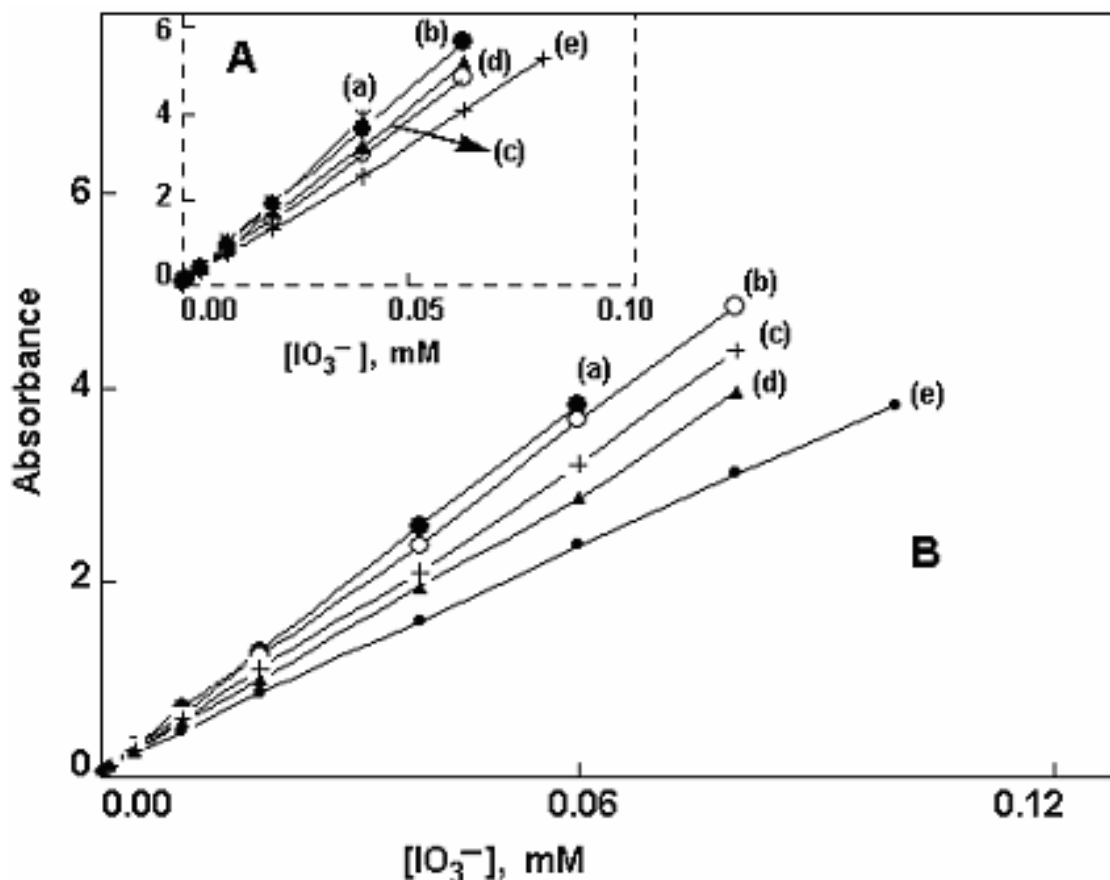

Figure 4: Calibration plots of [IO₃⁻] vs Absorbance at (A) 288 nm, (B) 351 nm in a mixture of 0.1% KI and 0.16 N H₂SO₄ with %Cl⁻ (a) 0.00, (b) 0.61, (c) 1.82, (d) 3.03, (e) 6.06 at 25°C

Evaluation of the coefficient m_2 of the chloride ion on iodate estimation

In order to determine the values of m_2 appeared in Eq 6, the absorption spectra of I_3^- were recorded with different %Cl^- between 0.6 and 6.1 while keeping [KIO_3] at 40 μM in 0.1% KI and 0.16 N H_2SO_4 mixture, and the absorbance (Abs_{288}, Abs_{351}) was plotted against %Cl_T^- (Figure 5). From the slopes of these plots figure 5(a,b), the values of m_2 were obtained as -0.193 and -0.135. Then, Eq 6 describing the IO_3^- ion determination by following the bands 288 and 351 nm under present experimental conditions (%Cl^{-3}0) get simplified to Eqs 9 and 10, respectively.

$$Abs_{288} = 95.132 [IO_3^-] - 0.193 [\%Cl_T^-][IO_3^-] \qquad (9)$$
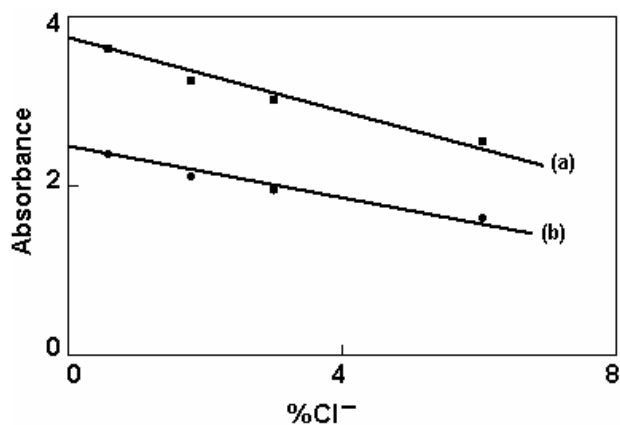$$Abs_{351} = 62.458 [IO_3^-] - 0.135 [\%Cl_T^-][IO_3^-] \qquad (10)$$

Figure 5: Plots of %Cl^- vs Absorbance at (a) 288 nm, (b) 351 nm. [IO_3^-] = 0.04 mM; KI=0.1% (6.0241 mM); [H_2SO_4] = 0.16 N, at 25°C. The data fits to the linear equation y = −0.1934 x + 3.6545, R^2= 0.9764 in the case of 288 nm and y = −0.1354x + 2.3962, R^2 = 0.9705 nm in the case of 351 nm

Interference of other cations ions in iodate estimation

The iodized salts are normally produced from seawater or under ground brines. The most five ions that are commonly present as impurities in edible salts of seawater/underground brine are F^-, Br^-, K^+, Ca^{2+} and Mg^{2+}. The concentrations of F^- and Br^- are in the order of $10^{-2} – 10^{-4}$ and are too small as compared to Cl^- and hence their influence on the iodate determination in iodized salt is considered to be negligible. On the other hand, the concentrations of K^+ ($\sim 10^{-2}$ M), Ca^{2+} ($\sim 10^{-2}$ M) and Mg^{2+} ($\sim 10^{-1}$ M) in ed-

ible salts are in the considerable range, hence were studied for their possible affect on the analysis. A solution of standard I_3^- solution was prepared while keeping [KIO_3] at 40 μM in 0.1% KI and 0.16 N H_2SO_4 mixture containing 6.06 %Cl^- and K^+/Ca^{2+}/Mg^{2+} species as chloride at the concentration level normally found in edible sea salts[33]. The observed data (TABLE 2) indicate that the absorbance at 288 and 351 nm increased by 0.31 and 0.50% in 0.02M K^+ but decreased by 4.06 and 4.38% in 0.02 M Ca^{2+} and 7.35 and 7.83% in 0.1 M Mg^{2+}, respectively. These alterations are meager and negligible as compared to those found with the change in %Cl^-. Choengchan et al.[20] have found to alter the absorbance by these ions to less than ± 5% at 288 or 351 nm. Thus, it was concluded that these cations ions present as impurities in the edible salt matrix do not interfere with the present method even if iodized salt is used as such without any dilution for iodate determination.

Determination of iodate in commercial iodized salts and electrolyzed solution

Six iodized edible salts of some well-known brand were collected from local market and the iodate content was determined by the present method. A 10% solution of each of these salts were prepared and used. The %Cl^- present in these 10% salt solutions was measured. The %Cl^- was maintained between 6 and 8.5 by adding non-iodized NaCl externally to the experimental solutions to minimize the errors due possible variations in the chloride ion. The absorbance at 288 and 351 nm and the %Cl_T^- were substituted in Eq 11, and the composition of IO_3^- present in the salt samples was then computed. The %Cl^- in all 10% solutions and the KIO_3 composition in all edible salts thus obtained as the average of three experiments of three different concentrations are tabulated in TABLE 1. The KIO_3 composition in all salt samples is below the recommended level[1]. In the case of branded salts, N, A and C, the KIO_3 level was near to 50 ppm while in other brands, it was 40 ppm. The low KIO_3 content in S-branded salt may be due to its chemical decomposition caused by the impurities present in the salt. The possible percentage of deviation in KIO_3 content (TABLE 1) esti-

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TABLE 1: Iodate compositions in commercial iodized salts and electrolyzed solution

Source code	Manufacture date	$\%Cl^-$ in 10% stock	λ	$[KIO_3]$ (ppm) considering Cl^-		
				With	Without	% Deviation
T	10/2005	6.06	288	35.79	35.19	−1.68
			351	35.81	35.17	−1.78
N	12/2005	6.06	288	47.14	46.35	−1.68
			351	46.85	46.02	−1.77
A	11/2005	6.06	288	46.24	45.46	−1.69
			351	46.60	45.76	−1.80
S	10/2005	5.85	288	27.06	26.62	−1.62
			351	28.34	27.85	−1.73
C	9/2005	6.06	288	46.17	45.38	−1.71
			351	46.31	45.47	−1.85
K_1	10/2005	6.06	288	37.06	36.43	−1.73
			351	37.66	36.98	−1.84
Electrolyzed solution	6/2005	---	288	---	2.975%	−0.83%
			351		2.984%	−0.53%

TABLE 2: %Alteration in the absorbance at 288 and 351 nm band of 40 µM IO_3^- in 0.1% KI, 0.16 N H_2SO_4 and 6.06 %Cl_T^- mixture in the presence of cations K^+, Ca^{2+}, Mg^{2+}.

Cation	λ, nm	%Alteration
K^+, 0.02 M	288	+0.31
	351	+0.50
Ca^{2+}, 0.02 M	288	−4.06
	351	−4.39
Mg^{2+}, 0.10 M	288	−7.35
	351	−7.83

mated by ignoring the Cl^- content in Eq 11 was near about 2 less than its actual value. The influence of K^+, Ca^{2+} and Mg^{2+} on iodate determination in iodized salt has been ignored due to their negligible concentration present in the experimental solution.

$$[KIO_3] = \frac{Abs_\lambda}{m_1 - m_2(\%Cl_T^-)} \tag{11}$$

The KIO_3 composition in electrolyzed solution was calculated by substituting the absorbance data at 288 and 351 nm in Eq 11 assuming $\%Cl^-$ as zero. The data inscribed in TABLE 1, revealed that $\%KIO_3$ formed under the single pass conditions is nearly (99.17 and 99.47% with respect to 288 and 351 nm bands, respectively) complete.

CONCLUSION

A simple and reliable spectrophotometric method is developed for the determination of IO_3^- in excess I^- in the presence and the absence of Cl^-. The calibration graphs for IO_3^- estimation in 0.1% KI - 0.16 N H_2SO_4 medium in the presence of 0 - 6.07% Cl^- are determined by following two characteristic absorption bands of I_3^- at 288 and 351 nm. The influence of Cl^- on the determination of IO_3^- is studied and an empirical equation (Eq 11) for KIO_3 estimation is proposed. The effect of other cations, K^+, Ca^{2+} and Mg^{2+} that are commonly present as impurities in most of the edible salts, on alteration of the intensities of absorption bands are investigated. The precision of the method was established by five replicate determinations of standard IO_3^- solutions. The relative standard deviation are determined using 20 µM and 0.02 µM of IO_3^- in 0.1% KI - 0.16 N H_2SO_4 and 20 µM of IO_3^- in 0.1% KI - 0.16 N H_2SO_4 - 6.06 %Cl^- media with respect to 288 and 351 nm bands. The effect of other cations, K^+, Ca^{2+} and Mg^{2+} that are present as common impurities in most of the edible salts, on alteration of the intensities of absorption bands are investigated. Further, the KIO_3 composition in different commercial iodized salts with and without considering Cl^- effect are also determined and discussed. The KIO_3 composition in electrochemically prepared 3%KIO_3 solution using a membrane cell is also determined by the present method.

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