

A Facile Spectrophotometric Method for the Determination of Iodate in Table Salt using New Chromogenic Reagents

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ABSTRACT

A simple spectrophotometric method has been developed for the determination of iodate in table salt samples using thionin or azure B. The method is based on the reaction of iodate with potassium iodide in an acid medium to liberate iodine. The liberated iodine bleaches the violet colour of thionin or azure B, which are measured at 600 and 644 nm, respectively. This decrease in absorbance is directly proportional to the initial iodate concentration and obeys Beer's law in the range of 1–12 $\mu\text{g mL}^{-1}$ of iodate with thionin and 0.2–16 $\mu\text{g mL}^{-1}$ of iodate with azure B. The molar absorptivity and Sandell's sensitivity of using thionin and azure B were found to be $2.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $7.9 \times 10^{-2} \mu\text{g cm}^{-2}$ and $2.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.85 \times 10^{-2} \mu\text{g cm}^{-2}$, respectively. The proposed method has been successfully used for the determination of iodate in table salt samples.

KEYWORDS

Iodate determination, spectrophotometry, thionin, azure B.

1. 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 animals 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 delays in neurological development. On the other hand, an excess of iodine or iodide can cause goitre 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 40–60 ppm.²

Several methods have been reported for the determination of iodate, such as gas chromatography–mass-spectrometry,³ ion-chromatography,⁴ chemiluminescence,⁵ flow injection-ampereometry,⁶ potentiometric titrations,⁷ differential pulsed-polarography,⁸ spectrofluorimetry,⁹ flow injection-spectrophotometry,^{10,11} coulometry,¹² photometric analysis^{13–14} and gravimetry.¹⁵ Some reported spectrophotometric methods for the determination of iodate are based on its reaction with excess iodate to form triiodide.^{16–19} In other spectrophotometric methods iodate is determined after prior oxidation to periodate.^{20,21} Many spectrophotometric methods for the determination of iodate have been reported, with some chromogenic reagents, such as 2-oximino-dimedone dithiosemicarbazone,²² 3,4-dihydroxybenzaldehyde-guanyl-hydrazone,²³ 1,3-diphenyl-3-hydroxyamino-1-propanone oxime,²⁴ dithizone,²⁵ blue indamine dye,²⁶ isonicotinic acid hydrazide and 2,3,5 triphenyl tetrazolium chloride,²⁷ N,N'-di(β -hydroxypropyl)-o-phenylene diamine,²⁸ triphenyl tetrazolium chloride.²⁹ Of these reagents, some have been reported to be carcinogenic while a few others are less selective and time-consuming. The need for a sensitive, simple and reliable method for the determination of iodate is therefore clearly recognized.

2. Experimental

A Secomam 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. All chemicals were of analytical reagent or chemically pure grade and double-distilled water was used throughout the study. A standard stock solution (1000 $\mu\text{g mL}^{-1}$) of iodate (Merck) was prepared by dissolving 1.224 g of potassium iodate in 1000 mL of water and standardized using standard sodium thiosulphate.¹⁶ A 0.1% solution of thionin was prepared by dissolving 0.1 g thionin in water containing hydrochloric acid (2 mol L^{-1} , 1 mL) and made up to 100 mL with distilled water. A 0.1% solution of azure B was prepared by dissolving 0.1 g of azure B in 25 mL methanol and made up to 100 mL with distilled water.

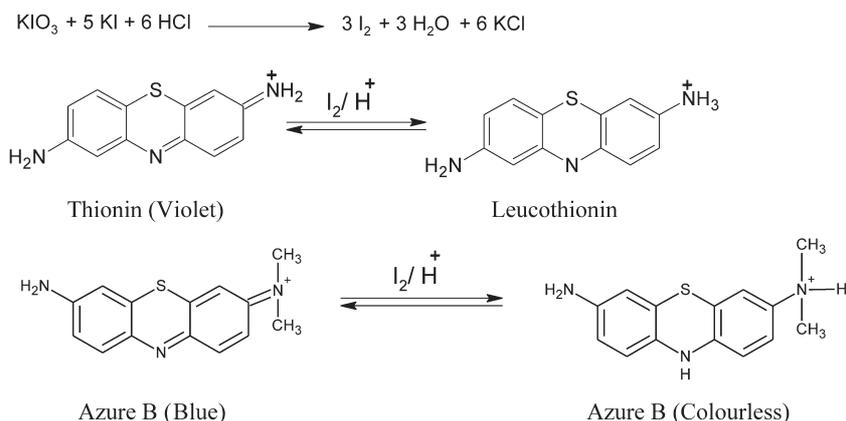
2.1. General Procedure for the Determination of Iodate

Sample solutions containing 0.2–20 $\mu\text{g mL}^{-1}$ of iodate were transferred into a series of 10 mL calibrated flasks. Potassium iodide (1%, 2 mL), then hydrochloric acid (2 mol L^{-1} , 1 mL), were added and the mixture was gently shaken until it turned yellow, indicating the liberation of iodine. A volume of 0.5 mL thionin (0.1%) or 0.5 mL azure B and followed by 2 mL of 1 mol L^{-1} sodium acetate were added and the mixture shaken for 2 min. The contents were diluted to 10 mL with distilled water and mixed well. The absorbance of the resulting solution was measured at 600 or 644 nm against a reagent blank which was prepared by replacing the analyte (iodate) solution with distilled water. The absorbance corresponding to the bleached colour, which in turn corresponds to the analyte (iodate) concentration, was obtained by subtracting the absorbance of the blank solution from that of the test solution. The amount of the iodate present in the volume was calculated using the calibration graph.

2.2. Determination of Iodate in Table Salt Samples

About 2.9215 g of table salt was dissolved in water and diluted up to the mark in a 25 mL volumetric flask. A 0.5 mL portion of this solution was transferred into a 10 mL volumetric flask. Then

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Scheme 1

the procedure described above for the standard solution was followed. The absorbance was measured and the iodate concentration was calculated using the calibration graph. The proposed method was also compared with a reference method.³¹

3. Results and Discussion

This method is based on the reaction of iodate with potassium iodide in acid medium to liberate iodine. The liberated iodine bleaches the violet colour of thionin or azure B. The decrease in absorbance at 600 or 644 nm is directly proportional to the iodate concentration. The absorption spectra of the coloured species of thionin and azure B are presented in Fig. 1, and the reaction is shown in Scheme 1.

3.1. Effect of Iodide Concentration and Acidity

The effect of iodide concentration and acidity on the colour 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 0.05 mol L^{-1} HCl in a final volume of 10 mL. It was found that 1 mL of 2% KI and 1 mL of 0.05 mol L^{-1} HCl were sufficient for the liberation of iodine from iodide by iodate and 0.5 mL of 0.1 % thionin or 0.5 mL of 0.1% azure B were used for subsequent decolorization. The variation of absorbance of known concentrations of the iodate with pH of the medium was studied using a series of buffer solutions differing by $\text{pH} = 0.5$. The maximum absorbance value was found at $\text{pH} = 4 \pm 0.5$. Hence, the pH was maintained at $\text{pH} = 4 \pm 0.5$ throughout the study by using acetate buffer.

3.2. Analytical Data

The adherence to Beer's law was studied by measuring the absorbance values of solutions varying the iodate concentration. A straight line graph was obtained by plotting absorbance against concentration of iodate. Beer's law was obeyed in the range of $1\text{--}12 \mu\text{g mL}^{-1}$ of iodate with thionin and $0.2\text{--}16 \mu\text{g mL}^{-1}$ of iodate with azure B. The molar absorptivity and Sandell's sensitivity of using thionin and azure B were found to be $2.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $7.9 \times 10^{-2} \mu\text{g cm}^{-2}$ and $2.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.85 \times 10^{-2} \mu\text{g cm}^{-2}$, respectively (Table 1). The detection limit ($D_L = 3.3 \sigma/S$) and quantitation limit ($Q_L = 10 \sigma/S$) [where σ is the

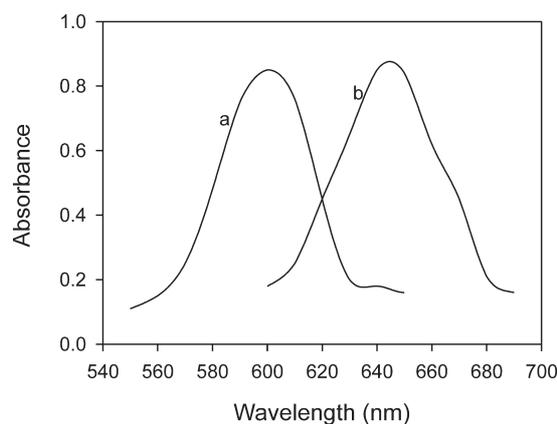


Figure 1 Absorption spectra of the coloured species of thionin (a) and azure B (b).

standard deviation of the reagent blank ($n = 5$) and S is the slope of the calibration curve] for the iodate determination with thionin and azure B were found to be $0.036 \mu\text{g mL}^{-1}$, $0.109 \mu\text{g mL}^{-1}$ and $0.07 \mu\text{g mL}^{-1}$, $0.21 \mu\text{g mL}^{-1}$, respectively.

3.3. Effect of Diverse Ions

The effect of various ions at microgram levels on the determination of iodate was examined. The tolerance limits of interfering species were established at those concentrations that do not cause more than $\pm 2.0\%$ error in absorbance values of iodate at $5 \mu\text{g mL}^{-1}$. The tolerance limits of foreign ions are listed in Table 2. The results indicate that Cu(II), Fe(III), Cr(VI) and Ce(IV) interfere severely. The interference of chromium can be removed by extraction with methylisobutylketone³², copper and iron can be masked with 2-mercaptoethanol and sodium fluoride, respectively.

3.4. Application

The method developed was applied to the quantitative determination of traces of iodate in table salt samples. The results are presented in the Table 3 and compare favourably with those from a reference method.³¹ Statistical analysis of the results by the use of t - and F -tests showed there was no significant difference between the accuracy and precision of the proposed and

Table 1 Comparison between the proposed and reference methods.

	Thionin method	Azure B method	Leuco crystal violet (reference method)
Molar absorptivity	$2.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	$2.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	$5.6 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$
Beer's law range	$1\text{--}12 \mu\text{g mL}^{-1}$	$0.2\text{--}16 \mu\text{g mL}^{-1}$	$0.04\text{--}36 \mu\text{g mL}^{-1}$

Table 2 Effects of diverse ions in the determination of (5.0 µg mL⁻¹) of iodate.

Foreign ions µg mL ⁻¹	Tolerance limit µg mL ⁻¹	Foreign ions	Tolerance limit
Ba ²⁺	500	MoO ₄ ²⁻	500
Co ²⁺	1000	In ³⁺	1000
Ni ²⁺	1000	Al ³⁺	1000
Zn ²⁺	1000	Ce ⁴⁺ *	5
Cr ³⁺	500	F ⁻	1000
Ca ²⁺	1000	WO ₄ ²⁻	1000
Fe ³⁺ *	10	PO ₄ ³⁻	1000
Cu ²⁺ *	15	SO ₄ ²⁻	1000
Gd ³⁺	500	IO ₄ ⁻ *	<1
Cd ²⁺	1000	Tartrate	1000
Bi ³⁺	500	Oxalate	1000
Mn ²⁺	500	Chloride	1000
V ⁵⁺ *	10	Nitrate	750
Sr ²⁺	750	Acetate	1000

* Masked with masking agents.

Table 3 Determination of iodate in table salt samples.

Sample	Thionin method				Azure B method				Reference method	
	IO ₃ ⁻ found ^a	RSD ^b (%)	<i>t</i> -test ^c	<i>F</i> -test ^d	IO ₃ ⁻ found ^a	RSD ^b (%)	<i>t</i> -test ^c	<i>F</i> -test ^d	IO ₃ ⁻ found ^a	RSD ^b (%)
TS-1	26.15 ± 0.02	0.08	1.86	2.25	26.17 ± 0.05	0.19	1.92	2.78	26.12 ± 0.03	0.11
TS-2	28.25 ± 0.05	0.18	1.04	1.96	28.27 ± 0.04	0.14	0.55	3.06	28.29 ± 0.07	0.25
TS-3	29.32 ± 0.03	0.10	1.34	1.78	29.30 ± 0.06	0.20	1.55	2.25	29.35 ± 0.04	0.14
TS-4	28.35 ± 0.03	0.11	1.92	2.78	28.37 ± 0.04	0.14	1.05	1.56	28.40 ± 0.05	0.18
TS-5	26.58 ± 0.05	0.19	0.78	1.96	26.56 ± 0.04	0.15	1.39	3.06	26.61 ± 0.07	0.26

^a Mean ± standard deviation (*n* = 5); concentration is expressed in mg kg⁻¹.^b Relative standard deviation (RSD).^c Tabulated *t*-value for 8 degrees of freedom at *P* = 0.95 is 2.306.^d Tabulated *F*-value for 4,4 degrees of freedom at *P* = 0.95 is 6.39.

the reference method.³¹ The precision of the proposed method was evaluated by replicate analysis of samples containing iodate at different concentrations.

4. Conclusion

For the first time, thionin and azure B have been used as chromogenic reagents for the spectrophotometric determination of iodate. The proposed method, which is simple and rapid, offers the advantages of sensitivity over a wide range of concentrations without the need for extraction or heating. The method does not involve any stringent reaction conditions and compares favourably with other methods. The proposed method has been successfully applied to the determination of iodate in table salt samples.

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