CHAPTER 2

SPECTROPHOTOMETRIC DETERMINATION OF IODATE IN IODIZED TABLE SALT AND SEA WATER SAMPLES

2.1 INTRODUCTION

2.2 ANALYTICAL CHEMISTRY

2.3 APPARATUS

2.4 REAGENTS AND SOLUTIONS

2.5 PROCEDURES

2.6 RESULTS AND DISCUSSION

2.7 APPLICATIONS

2.8 CONCLUSIONS

2.9 REFERENCES
2.1 INTRODUCTION

Iodine appears to be the trace element essential to plants and animal. Iodine occurs naturally not only as iodide but also as iodate in the form of minerals such as lautarite \( \text{Ca(IO}_3\text{)}_2 \) and dietzeite \( 7\text{Ca(IO}_3\text{)}_28\text{CaCrO}_4 \). 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]. Truesdale et al. reported that the iodate is also present in seawater in the range 0-60 \( \mu \text{gL}^{-1} \) [3]. Iodine essentially, in the iodine cycle iodo-methane and other iodo-alkanes are produced in near surface water of the sea and pass into the atmosphere where the iodine forms a number of iodine compounds. These are taken into cloud water where, after several reactions, the iodine appears in rainwater at ground level as iodate and iodide-iodine. The iodate and iodide-iodine are then involved in other cycles within soil, lake and seawater, which involve uptake and regeneration from plant tissue.

Several isotopes of iodine, an element with multiple oxidation states, are of radiological health importance in relation to nuclear weaponry and the nuclear fuel cycle. \(^{131}\text{I} \) has been a major concern in fall out from atmospheric nuclear testing, releases from fuel reprocessing and the Chernobyl accident. However, due to the short half life of \(^{131}\text{I} \) (8 days), its environmental fate is determined more by decay time than geochemical processes. In contrast, another fission product \(^{129}\text{I} \) has a half life of 1.6-107 years. Long-term (105–109 years) models of radionuclide release to the biosphere from high-level waste repositories show \(^{129}\text{I} \) to contribute a significant fraction to the population dose [4].

Iodate is more stable than iodide and most health authorities preferentially recommend iodate as an additive to salt for correcting iodine deficiency. Even though this results in a low exposure of at most 1700 \( \mu \text{gL}^{-1} \), doubts have recently been raised whether the safety of iodate has been adequately documented. In humans and rats, oral bioavailability of iodine from iodate is virtually equivalent to that from
iodide [5]. When given intravenously to rats, or when added to whole blood or tissue homogenates in vitro or to foodstuff, iodate is quantitatively reduced to iodide by nonenzymatic reactions and thus becomes available to the body as iodide. Therefore except for the gastrointestinal mucosa, exposure of tissues to iodate might be minimal. At much higher doses given intravenously (i.e., above 10 mg kg\(^{-1}\)), iodate is highly toxic to the retina. Ocular toxicity in human has occurred only after exposure to doses of 600 to 1200 mg per individual. Oral exposures of several animal species to high doses, exceeding the human intake from fortified salt by orders of magnitude, pointed to corrosive effects in the gastrointestinal tract, hemolysis, nephrotoxicity, and hepatic injury. The studies do not meet current standards of toxicity testing, mostly because they lacked toxicokinetic data and did not separate iodate specific effects from the effects of an overdose of any form of iodine. With regard to tissue injury, however, the data indicate a negligible risk of the small oral long-term doses achieved with iodate-fortified salt. Genotoxicity and carcinogenicity data for iodate are scarce or non-existing. The proven genotoxic and carcinogenic effects of bromate raise the possibility of analogous activities of iodate. However, iodate has a lower oxidative potential than bromate, and it did not induce the formation of oxidized bases in DNA under conditions in which bromate did, and it may therefore present a lower genotoxic and carcinogenic hazard. This assumption needs experimental confirmation by proper genotoxicity and carcinogenicity data. These in turn will have to be related to toxicokinetic studies, which take into account the potential reduction of iodate to iodide in food, in the intestinal lumen or mucosa, or eventually during the liver passage.

The element iodine is dissolved in sea water at concentrations of about 0.45 mM with some as iodide in near surface waters, but largely as iodate in deeper ones. It has been assigned a quasi-nutrient status because of the similarity in the distribution of nitrate, phosphate and iodate. In disproportionation iodine [6] in a given oxidation state produces compounds with both higher and lower oxidation states. For example, hypoiodous acid forms iodate and iodide. This reaction has been studied because of its possible importance in formation of iodide and iodate in rainwater and at the sea-surface. The reaction is also of incidental interest in decreasing the volatility of radio iodine present in fission reactors at the time of
catastrophic failure. Thus, when alkaline waters are sprayed into the reactor any iodine present converts to iodate and iodide, which are both non-volatile. Of course, without such measures the radio-iodine will escape as a cloud from the ruptured reactor and is able to contribute to the formation of thyroid cancer.

Iodate is the thermodynamically stable species of iodine in seawater [7,8]. However, iodide has been shown to be the dominant iodine species in many marine surface waters [9,10]. Some postulated mechanisms for the observed abundance of iodide in surface seawaters and other systems include inorganic reducing agents such as bisulfide [11], sulfite [12] or ferrous iron [13]. Other studies suggest that the reduction of iodate to iodide may be microbial enzymatically mediated in soils and water. Tsunogai and Sase [14] and Hackett [15] using sterilized seawater media spiked with iodate and amended with bacteria possessing the enzyme nitrate reductase, observed increases in iodide accompanied by decreases in iodate in the amended samples. It was further noted by Hackett, that the iodate reduction only occurred at low (<0.25 mM) oxygen levels.

2.2 ANALYTICAL CHEMISTRY

Several methods have been reported for the determination of iodate, such as GC-MS [16], ion-chromatography [17], chemiluminescence [18], flow injection-amperometry [19], potentiometric titrations [20], differential pulse-polarography [21], spectro-fluorimetry [22], flow injection-spectrophotometry [23, 24], coulometry [25], photometric analysis [26, 27] and gravimetry [28].

Fuchs et al. reported the spectrophotometric determination of iodate and iodide with p-aminophenol [29]. Salinas et al. reported 2-oximinodimedone dithiosemicarbazone as a reagent for the spectrophotometric determination of iodate and bromate [30]. The reagent produced colored solution with iodate and bromate ions acid medium. Beer’s law was obeyed in the concentration range 0.24–5.00 μg/mL⁻¹ of iodate and 0.16–3.60 μg/mL⁻¹ of bromate. The maximum absorption was at 400 nm. Reagents such as 3,4-dihydroxybenzal-dehydeguanylylhydrazone(3,4-DBGH) [31], 1,3-diphenyl-3-hydroxyamino-1-pro-panoneoxime [32], dithizone [33],
isonicotinic acid hydrazide and 2,3,5-triphenyl tetrazolium chloride [34] and N, N’-di(β-hydroxypropyl)-o-phenylene diamine [35] were also used for the spectrophotometric determination of iodate.

In some of the other spectrophotometric methods iodate was determined after prior oxidation to periodate [36, 37]. The ion-associate of periodate with a suitable ion pairing agent was then extracted into an organic solvent and determined by spectrophotometric methods. Most of the proposed methods are either not sensitive enough, or require complicated and expensive instruments, or are time consuming.

Kamburova reported iodonitrotetrazolium chloride [38] as a new reagent for the spectrophotometric determination of iodate and periodate. The calibration plot was linear within the range of 0.02-0.5 μg mL⁻¹ of IO₃⁻ or IO₄⁻.

Rosa Lina et al. [39] reported a new method for the determination of iodate in table salt. Potassium iodate in table salt was spectrophotometrically determined at two well-defined UV absorption maxima (352 and 288 nm), after being converted to I₃⁻ by reaction with iodide in the presence of phosphoric acid. The molar absorptivity of the methods were found to be 7.320×10⁴ and 1.103×10⁵ Lmol⁻¹cm⁻¹ at 352 and 288 nm respectively at 22°C. Typical results of 37.39 (±0.15) and 63.67 (±0.16) mg KIO₃ per Kg of salt were obtained with samples of 0.15-0.21 g, comparable with results from a standard.

Wei-Xing et al. reported rhodamine-6G as a reagent for the spectrophotometric determination of iodate in table salt [40]. It was based on color reaction of rhodamine-6G with iodate and potassium iodide in HCl medium. The maximum absorption of the reaction product was exhibited at 560 nm and Beer’s law was obeyed within the concentration range of 0-2.0 mg L⁻¹ of KIO₃ with the regression coefficient r=0.9998.

Weixing described a simple and sensitive spectrophotometric method for the determination of micro amounts of iodate in table salt [41]. The method was based on chromogenic reaction of crystal violet on I₃⁻ produced from iodate reacting on KI in HCl medium. Kang et al. used 3, 3’, 5, 5’-tetramethylbenzidine(TMB) [42] as a new
reagent for the spectrophotometric of iodate in table salt. In the acid medium, TMB was oxidized by iodate. The yellow imine formed showed strong absorption at 450 nm with an apparent molar absorptivity $2.13 \times 10^5$ L mol$^{-1}$ cm$^{-1}$. Beer's law was obeyed in the range 0-0.7 mgL$^{-1}$ for iodate.

Ensafi and Dehaghi described a simple and accurate procedure for simultaneous spectrophotometric determinations of iodate and periodate in aqueous media [43]. In this method periodate and iodate react with iodide to produce iodine, which was determined by spectrophotometric detection at 349 nm. The stream was treated with iodide and sulfuric acid and then passed through the flow cell of the spectrophotometer. The increase in absorbance at 349 nm was due to periodate and iodate. The influences of the acid concentration, reagent concentration and manifold variables were studied. The effect of diverse ions on the determination of periodate and iodate by the proposed method was also investigated. Within the detection limit ($3\sigma/s$) was $3.5 \times 10^{-6}$ M for periodate and $1.0 \times 10^{-6}$ M for iodate, respectively. Iodate and periodate in artificial fresh-water samples were determined by this method.

Afkhami and Zarei reported a spectrophotometric determination of periodate and iodate by differential kinetic method [44]. The method was based on their reaction with iodide in the presence of methylene blue. The reactions can be monitored spectrophotometrically by measuring the decrease in absorbance at 665 nm. Two sets of conditions were established. In the first set of conditions only periodate reacted with iodide but in the other set both the ions reacted with iodide during the first 180 s after the initiation of the reaction. The data were evaluated by proportional equations. The method was allowed the determination of periodate and iodate at concentrations between 0.1 and 1.0 and 0.1 and 1.3 μg mL$^{-1}$, respectively. The method was applied to the determination of periodate and iodate in tap water and spring water with satisfactory results. Afkhami et al. also described spectrophotometric determinations of periodate, iodate and bromate based on the reaction with iodide ion at different pH values [45].

Afkhami and Mosaed described a simple, precise, sensitive and accurate method for rapid determination of trace quantities of iodate [46]. The method was based on the accelerating effect of iodate on the reaction of bromate and chloride acid
in the presence of hydrazine in acidic medium. The decolorization of methyl orange with the reaction products was used to monitor the reaction spectrophotometrically at 525 nm. Iodate was determined in the concentration ranges of 0.03-1.2 µg/mL. The relative standard deviation for ten replicate determinations of 0.3 µg/mL of iodate was 1.65%. The reported method was applied to the determination of iodate in table salts with satisfactory results.

Afghani and Zarei reported a simultaneous kinetic spectrophotometric determination iodate–bromate by the H-point standard addition method (HPSAM) [47]. The method was based on the difference between the rates of their reactions with iodide in acidic medium. The results showed that simultaneous determinations could be performed with the ratio 15:1–1:15 for iodate–bromate. The proposed method was successfully applied to the simultaneous determination of iodate–bromate in water and synthetic samples.

Barzegar et al. used molybdisilicic acid blue as a reagent for the kinetic spectrophotometric determination of trace amounts of iodate in table salt and water [48]. Xu et al. describes a method for the determination of iodate was developed by reversed-phase high-performance liquid chromatography [49] with UV detection. Iodate was converted to iodine, which was separated from the matrix using a reversed-phase Ultrasphere C18 column (250×4.6 mm, 5 µm) with methanol (1M) H3PO4 (1:4) as mobile phase at 1.00 mL/min and UV detection at 224 nm. The calibration graph was linear from 0.05 µg/mL to 5.00 µg/mL for iodine with a correlation coefficient of 0.9994 (n=7). The detection limit was 0.01 µg/mL. The method was successfully applied to the determination of iodate in iodized salt. The recovery was from 96% to 101% and the relative standard deviation was in the range of 1.5% to 2.9%.

Dian-Wen et al. described a method for the spectrophotometric determination of iodine based on the decoloration of arsenazo-III by iodate in H2SO4 medium [50]. The maximum absorption was at 530 nm. Beer's law was obeyed from 0-4 mg/L for iodine. The apparent molar absorptivity was 2.07×105 Lmol⁻¹cm⁻¹. This method was used for the determination of iodine in celery salt with satisfactory results.
Ghasemi *et al.* used pyrogallol red reagent for the simultaneous kinetic spectrophotometric determination of iodate and periodate in sulfuric acid medium [51]. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of pyrogallol red at 470 nm. The calibration curve was linear over the concentration ranges of 0.1–12 and 0.1–14 \( \mu \text{g mL}^{-1} \) for iodate and periodate, respectively. The experimental calibration matrix for partial least squares (PLS) and orthogonal signal correction (OSC–PLS) method was designed with 35 mixtures.

Abbas *et al.* reported a simple kinetic spectrophotometric method for the simultaneous determination of binary mixtures of iodate and bromate in water samples [52]. The method was based on the mean centering of ratio kinetic profiles, allows rapid and accurate determination of bromate and iodate. The analytical characteristics of the method such as detection limit, accuracy, precision, relative standard deviation and relative standard error for the simultaneous determination of binary mixtures of iodate and bromate were calculated. The results show that the method was capable of simultaneous determination of 0.05-1.50 \( \mu \text{g mL}^{-1} \) each of iodate and bromate. The results allowed simultaneous determination with the ratio 30:1-1:30 for iodate-bromate. The proposed method was successfully applied to the simultaneous determination of iodate and bromate in several water samples.

Ghasemi *et al.* reported a simultaneous spectrophotometric determination of iodate and iodide by partial least squares regression (PLS) using original and derivate data named as absorbance and rate data [53]. The method was based on the catalytic effect of the cited anions on the reaction rate between Ce(IV) and As(III) in 2 M sulfuric acid medium. The Savitzky-Golay convolution method is used for calculating and smoothing the rate data. Results show that PLS is an excellent calibration method to resolve the mixtures of two anions by first-order or pseudo first-order kinetic procedures without any previous knowledge about rate constant values. The 26 calibration solutions were made of iodide and iodate in the range of 10-48 and 55-235 \( \text{ng mL}^{-1} \). The application of the method was confirmed by the analysis of these anions in real matrix samples.

Chen *et al.* described a non-suppressed ion chromatography (IC) with inductively coupled plasma mass spectrometry (ICP-MS) for simultaneous
determination of trace iodate and iodide in seawater [54]. An anion-exchange column was used for the separation of iodate and iodide with an eluent containing 20 mM NH₄NO₃ at pH 5.6, which reduced the build-up of salts on the sampler and skimmer cones. The influences of competing ion (NO₃⁻) in the eluent on the retention time and detection sensitivity were investigated to give reasonable resolution and detection limits. Linear plots were obtained in a concentration range of 5.0-500 µg L⁻¹ and the detection limit was 1.5 µg L⁻¹ for iodate and 2.0 µg L⁻¹ for iodide. The proposed method was used to determine iodate and iodide in seawaters without sample pretreatment with exception of dilution.

Cherian and Narayana described a simple spectrophotometric method for the determination of iodate in table salt samples using thionin and azure B [55]. The method was 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 µg mL⁻¹ of iodate with thionin and 0.2–16 µg mL⁻¹ of iodate with azure B. The molar absorptivity and Sandell’s sensitivity of the methods using thionin and azure B were found to be 2.7×10⁴ Lmol⁻¹cm⁻¹, 7.9×10⁻² µg cm⁻² and 2.06×10⁴ Lmol⁻¹cm⁻¹, 0.85×10⁻² µg cm⁻² respectively. The proposed method was successfully used for the determination of iodate in table salt samples. Most of the proposed methods are either not sensitive enough or required complicated and expensive instruments, or are time consuming, or provide high detection limits. Thus the need for a simple and sensitive spectrophotometric method for the determination of iodate is therefore clearly recognized.

The present chapter describes simple and sensitive spectrophotometric method for the determination of iodate using methylene blue, rhodamine B and leuco xylene cyanol FF(LXCFF) as new reagents. The proposed method has been successfully applied for the determination of iodate in table salt samples and sea water samples.
2.3 APPARATUS

A Secomam Anthelic NUA 022 UV-Visible spectrophotometer with 1 cm quartz cell was used. A WTW pH 330 pH meter was used.

2.4 REAGENTS AND SOLUTIONS

All chemicals were of analytical reagent grade or chemically pure grade and distilled water was used throughout the study. Iodate stock solution (1000 μg/mL) was prepared by dissolving 1.2220 g of potassium iodate in 1000 mL of water and standardized using standard sodium thiosulphate solution [28]. The following reagents were prepared by dissolving appropriate amounts of reagents in distilled water: methylene blue (0.01 %), rhodamine B (0.01 %), leuco xylene cyanol FF(LXCF) (0.1%) (prepared by dissolving 100 mg of xylene cyanol FF in 25 mL of water containing 30 mg of zinc dust and 2 mL of 1M acetic acid, stirred well and kept aside for 20 minutes. The resulting solution was then filtered and diluted to 100 mL with water), potassium iodide (2 %), acetate buffer (1 M), sulfuric acid (0.05 M) and hydrochloric acid (2 M).

2.5 PROCEDURES

2.5.1 Using Methylene Blue as a Reagent

Aliquots of sample solution containing 0.5–14 μg/mL of iodate were transferred into a series of 25 mL calibrated flasks and potassium iodide (2 %, 1 mL) then 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) and 2 mL of acetate buffer solution were added and the reaction mixture was shaken for 2 minutes. The contents were diluted to 25 mL with distilled water and mixed well. The absorbance of the resulting solutions were measured at 665.6 nm against distilled water. 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 (Figure IIB1).

2.5.2 Using Rhodamine B as a Reagent

Aliquots of sample solution containing 0.5–7.0 μg/mL of iodate were transferred into a series of 25 mL calibrated flasks and potassium iodide (2 %, 1 mL) then 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. Rhodamine B (0.01 %, 0.5 mL) and 2 mL of acetate buffer solution were added and the reaction mixture was shaken for 2 minutes. The contents were diluted to 25 mL with distilled water and mixed well. The absorbance of the resulting solutions were measured at 553 nm against distilled water. 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 (Figure IIB2).

2.5.3 Using Leuco Xylene Cyanol FF as a Reagent

Aliquots of sample solution containing 0.4-14 μg/mL of iodate were transferred in to a series of 10 mL calibrated flasks. Volumes of 0.5 mL each of the 0.05 M H₂SO₄ and 0.1 % LXCFF were added, and the mixture was kept in a water bath (≈90°C) for 15 minutes, after being cooled to room temperature (27±2°C), the contents were diluted to the mark with acetate buffer of pH 4, and mixed well. The absorbance of the xylene cyanol FF dye formed was then measured at 620 nm against the reagent blank prepared in the same manner, without iodate. The amount of the iodate present in the volume taken was computed from the calibration graph (Figure IIB3).

2.5.4 Determination of Iodate in Table Salt Samples

A Table salt sample (2.9215g) 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 the procedure described above for the standard
solution was followed. The absorbance was measured and the iodate concentration was calculated using the calibration graph and proposed method was also compared with reference method [56]. The results are listed in Table 2B1, 2B2 and 2B3.

2.6 RESULTS AND DISCUSSION

2.6.1 Absorption Spectra

2.6.1.1 Using methylene blue as a reagent

This method is based on the reaction of iodate with potassium iodide in acid medium to liberate iodine. This liberated iodine bleaches the blue color of methylene blue. The decrease in absorbance at 665.6 nm is directly proportional to the iodate concentration. The absorption spectrum of the colored species of methylene blue is presented in Figure IIA1 and reaction system is presented in Scheme II.

2.6.1.2 Using rhodamine B as a reagent

Similarly this method is also based on the reaction of iodate with potassium iodide in acid medium to liberate iodine. This liberated iodine bleaches the color of the rhodamine B. The decrease in absorbance at 553 nm is directly proportional to the iodate concentration. The absorption spectrum of the colored species of rhodamine B is presented in Figure IIA2 and reaction system is presented in Scheme II.

2.6.1.3 Using leuco xylene cyanol FF as a reagent

In this method iodate quantitatively oxidized leuco xylene cyanol FF into its blue color xylene cyanol FF dye in a sulfuric acid medium (pH 1.4 – 3.9) in a boiling water bath (~90°C for 15 min), the resulting colored dye shows a maximum absorbance at 620nm in an acetate buffer medium. The reagent blank has negligible absorbance at this wavelength. The absorption spectrum of the colored species of LXCFF against reagent blank is presented in Figure IIA3 and reaction system is presented in Scheme II.
2.6.2 Using Methylene Blue and Rhodamine B as a Reagents

2.6.2.1 Effect of iodide concentration and acidity

The oxidation of iodide to iodine is effective in the pH range 1.0 to 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 KI in an acid medium is quantitative. The appearance of yellow color indicates the liberation of iodine. Although any excess of iodine in the solution will not interfere. It is found that 1 mL of each 2 % KI and 2M HCl are sufficient for the liberation of iodine from iodide by iodate and 0.5 mL of 0.01 % methylene blue and 0.5 mL of 0.01% rhodamine B are used for the decolorization reaction. The bleached reaction system is found to be stable for more than a week for both methylene blue and rhodamine B reagents.

The variation of absorbance of known concentration of the iodate with pH of the medium is studied. A series of buffer solutions differing by pH=0.5 is prepared, and using these buffers the system is studied. The maximum absorbance value is found at pH= 4±0.2 Hence, the pH is maintained at pH= 4±0.2 throughout the study by using acetate buffer (pH= 4). Effect of pH on color stability is presented in Figure IIA4 and IIA5.

2.6.3 Using Leuco Xylene Cyanol FF as a Reagent

2.6.3.1 Effect of the acidity and temperature

The oxidation of LXCFF by iodate is studied. Of the various acids (sulfuric, hydrochloric and phosphoric) studied, sulfuric acid is found to be the best acid for the system. Constant absorbance readings were obtained in the range (0.1-1.5 mL) of 0.05 M sulfuric acid (pH 1.4-3.9) at a temperature 90°C for 15 minutes. An increase of the pH above 3.9 markedly affected the stability and sensitivity of the dye. Color development did not take place below pH 1.4. Hence a volume of 0.5 mL of 0.05M sulfuric acid (or maintained pH=2) in a total volume of 10 mL is used in all subsequent work.

2.6.3.2 Effect of reagent concentration and buffer media

The optimum concentration of LXCFF leading to maximum color stability is

44
found to be 0.5 mL of 0.1% reagent per 10 mL of the reaction mixture. The absorbance values are measured in the pH range of 3.5-4.6. This could be achieved by adding 3 mL of acetate buffer of pH 4. Appreciable results are obtained when the entire reaction mixture is diluted with the same acetate buffer solution of pH 4. A change in the pH of the final reaction mixture is affected by the intensity of the colored dye. The formed colored dye is stable for more than 24 hours.

2.6.4 Analytical Data

2.6.4.1 Using methylene blue as a reagent

In this method adherence to Beer’s law is studied by measuring the absorbance values of solutions varying iodate concentration. A straight line graph is obtained by plotting absorbance against concentration of iodate. Beer’s law is obeyed in the concentration range of 0.5-14 μg mL⁻¹ of iodate (Figure IIB1). The molar absorptivity and Sandell’s sensitivity of the system is found to be $1.24 \times 10^4$ L mol⁻¹ cm⁻¹ and $1.41 \times 10^2$ μg cm⁻² respectively. The detection limit ($D_L = 3.3\sigma/S$) and quantitation limit ($Q_L = 10\sigma/S$) [where $\sigma$ is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration- curve] of iodate determination is found to be 0.048 μg mL⁻¹ and 0.145 μg mL⁻¹ respectively.

2.6.4.2 Using rhodamine B as a reagent

In rhodamine B method also adherence to Beer’s law is studied by measuring the absorbance values of solutions varying iodate concentration. A straight line graph is obtained by plotting absorbance against concentration of iodate. Beer’s law is obeyed in the range of 0.5–7.0 μg mL⁻¹ of iodate (Figure IIB2). The molar absorptivity and Sandell’s sensitivity of the system is found to be $1.406 \times 10^5$ L mol⁻¹ cm⁻¹ and $1.23 \times 10^3$ μg cm⁻² respectively. The detection limit ($D_L = 3.3\sigma/S$) and quantitation limit ($Q_L = 10\sigma/S$) [where $\sigma$ is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration- curve] of iodate determination is found to be 0.132 μg mL⁻¹ and 0.400 μg mL⁻¹ respectively.
2.6.4.3 Using leuco xylene cyanol FF as a reagent

In this method also adherence to Beer’s law is studied by measuring the absorbance values of solutions varying iodate concentration. A straight line graph is obtained by plotting absorbance against concentration of iodate. Beer’s law is obeyed in the range of 0.4 to 14 μgmL$^{-1}$ of iodate (Figure II B3). The molar absorptivity and Sandell’s sensitivity of the colored system is found to be $1.71 \times 10^4$ Lmol$^{-1}$cm$^{-1}$ and $1.02 \times 10^2$ μgm$^{-2}$ respectively. The detection limit ($D_L = 3.3\sigma/S$) and quantitation limit ($Q_L = 10\sigma/S$) [where $\sigma$ is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration curve] of iodate determination is found to be 0.026 μgmL$^{-1}$ and 0.0806 μgmL$^{-1}$ respectively.

2.6.5 Effect of Divers Ions

The effect of a various ions at microgram levels on the determination of iodate is examined. The tolerance limits of the interfering species are established as those concentrations, which cause not more than ± 2.0 % changes in the absorbance value during the determination of a fixed amounts of iodate. The tolerance limits of various foreign ions are given in Table 2A1 and 2A2. In this reaction system, various oxidants such as Fe$^{3+}$, Ce$^{4+}$, V$^{5+}$ and Cr$^{6+}$ are found to interfere. The interference of chromium was removed by extracting with methyl isobutyl ketone. However, the tolerance limit of iron, cerium and vanadium can be increased by the addition of appropriate (2% NaF) amount of sodium fluoride.

2.7 APPLICATIONS

The method developed is applied to the quantitative determination of traces of iodate in table salt and sea water samples. The results are listed in the Table 2B1, 2B2, 2B3 and 2C1, 2C2, 2C3, compare favorably with those from a reference method [56]. Statistical analysis of the results by the use of t–test and F–tests show that, there is no significant difference between the accuracy and precision of the proposed and reference method. The precision of the proposed method is evaluated by replicate analysis of samples containing iodate at five different concentrations.
2.8 CONCLUSIONS

1. The reagents provide a simple and sensitive method for the spectrophotometric determination of iodate.

2. The reagents have the advantage of high sensitivity and low absorbance of reagent blank (LXCFF).

3. Common ions do not interfere seriously.

4. The developed method does not involve any stringent reaction conditions and offers the advantages of high stability of the reaction system for both methylene blue, rhodamine B (more than a week) and leuco xylene cyanol FF (more than 24 hours).

5. The statistical analysis of the results by t and F- tests show that, there is no significant difference in accuracy and precision between the proposed method and reference method.

6. The proposed method has been successfully applied to the determination of traces of iodate in table salt and sea water samples. A comparison of the method reported is made with earlier methods and is given in Table 2C4.

FIGURE IIA1
ABSORPTION SPECTRUM OF COLORED SPECIES OF METHYLENE BLUE

FIGURE IIA2
ABSORPTION SPECTRUM OF COLORED SPECIES OF RHODAMINE B

FIGURE IIA3
ABSORPTION SPECTRA OF COLORED SPECIES OF LEUCO XYLENE CYANOL FF (IO₃⁻, 2 μg/mL) Vs REAGENT BLANK (a) AND REAGENT BLANK Vs DISTILLED WATER (b)

FIGURE IIA4
EFFECT OF pH ON COLOR INTENSITY USING METHYLENE BLUE AS A REAGENT

FIGURE IIA5
EFFECT OF pH ON COLOR INTENSITY USING RHODAMINE B AS A REAGENT

FIGURE IIB1
ADHERANCE TO BEER’S LAW FOR THE DETERMINATION OF IODATE USING METHYLENE BLUE AS A REAGENT

FIGURE IIB2
ADHERANCE TO BEER’S LAW FOR THE DETERMINATION OF IODATE USING RHODAMINE B AS A REAGENT

FIGURE IIB3
ADHERANCE TO BEER’S LAW FOR THE DETERMINATION OF IODATE USING LEUCO XYLENE CYANOL FF AS A REAGENT

SCHEME II
**SCHEME OF REACTIONS**

\[
\text{KIO}_3 + 5 \text{KI} + 6 \text{HCl} \rightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O} + 6 \text{KCl}
\]

---

Methylene blue (colored)  
Methylene blue (colorless)

---

Rhodamine B (colored)  
Rhodamine B (colorless)

---

Xylene cyanol FF  
(Xeucoform)  
Xylene cyanol FF  
(Blue color)

---

**TABLE 2A1**
EFFECT OF DIVERSE IONS ON THE DETERMINATION OF IODATE (1.0 μgmL⁻¹) USING METHYLENE BLUE AND RHODAMINE B AS REAGENTS

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance limit in μgmL⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺, Br⁻, Cl⁻</td>
<td>2000</td>
</tr>
<tr>
<td>Mn²⁺, Mg²⁺, Zn²⁺</td>
<td>1500</td>
</tr>
<tr>
<td>Gd³⁺, PO₄³⁻, Yb³⁺, Sm³⁺, Eu³⁺</td>
<td>1000</td>
</tr>
<tr>
<td>Cr³⁺, NO₂⁻, La³⁺, Al³⁺, SCN⁻</td>
<td>500</td>
</tr>
<tr>
<td>*Cr₂O₇²⁻, *Fe³⁺, *Ce⁴⁺, *VO₃⁻, oxalate, citrate, tartarate</td>
<td>≤ 1</td>
</tr>
<tr>
<td>MoO₄²⁻, AsO₄³⁻, Co²⁺, WO₄²⁻</td>
<td>≤ 100</td>
</tr>
</tbody>
</table>

* Masked with masking agents.

TABLE 2A2
EFFECT OF DIVERSE IONS ON THE DETERMINATION OF IODATE (1.0 μgmL⁻¹) USING LEUCO XYLENE CYANOL FF AS A REAGENT

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerance limit in μgmL⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺, Br⁻, Cl⁻</td>
<td>2500</td>
</tr>
<tr>
<td>Mn²⁺, Mg²⁺, Zn²⁺</td>
<td>2000</td>
</tr>
<tr>
<td>Sm³⁺, Eu³⁺, Gd³⁺, PO₄³⁻, Yb³⁺</td>
<td>1500</td>
</tr>
<tr>
<td>Cr³⁺, NO₂⁻, La³⁺, Al³⁺, SCN⁻</td>
<td>1000</td>
</tr>
<tr>
<td>*Cr₂O₇²⁻, *Fe³⁺, *Ce⁴⁺, *VO₃⁻, oxalate, citrate, tartarate</td>
<td>≤ 1</td>
</tr>
<tr>
<td>AsO₄³⁻, Co²⁺, MoO₄²⁻, WO₄²⁻</td>
<td>≤ 500</td>
</tr>
</tbody>
</table>

* Masked with masking agents.

TABLE 2B1
DETERMINATION OF IODATE IN TABLE SALT SAMPLES USING METHYLENE BLUE AS A REAGENT

<table>
<thead>
<tr>
<th>Table Salt Samples</th>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iodate found&lt;sup&gt;a&lt;/sup&gt;, mgKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Std. deviation</td>
</tr>
<tr>
<td>1</td>
<td>25.67</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>29.09</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>34.23</td>
<td>0.01</td>
</tr>
</tbody>
</table>

a. Iodate concentration expressed in mgKg<sup>-1</sup> (n=5)
b. Tabulated t-value for 8 degree of freedom at P (0.95) is 2.306
c. Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39.

TABLE 2B2
DETERMINATION OF IODATE IN TABLE SALT SAMPLES USING RHODAMINE B AS A REAGENT

<table>
<thead>
<tr>
<th>Table Salt Samples</th>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iodate found&lt;sup&gt;a&lt;/sup&gt;, mgKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Std. deviation</td>
</tr>
<tr>
<td>1</td>
<td>25.67</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>30.80</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>34.20</td>
<td>0.02</td>
</tr>
</tbody>
</table>

a. Iodate concentration expressed in mgKg<sup>-1</sup> (n=5)
b. Tabulated t-value for 8 degree of freedom at P (0.95) is 2.306
c. Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39.

TABLE 2B3
DETERMINATION OF IODATE IN TABLE SALT SAMPLES USING LEUCO XYLENE CYANOL FF AS A REAGENT

<table>
<thead>
<tr>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table Salt Samples</td>
<td>Iodate found (\text{mgKg}^{-1}) (n=5)</td>
</tr>
<tr>
<td>Iodate found (\mu\text{gmL}^{-1})</td>
<td>Std deviation</td>
</tr>
<tr>
<td>1</td>
<td>23.48</td>
</tr>
<tr>
<td>2</td>
<td>27.64</td>
</tr>
<tr>
<td>3</td>
<td>33.76</td>
</tr>
</tbody>
</table>

a. Iodate concentration expressed in \(\text{mgKg}^{-1}\) (n=5)
b. Tabulated \(t\)-value for 8 degree of freedom at \(P (0.95)\) is 2.306
c. Tabulated \(F\)-value for (4, 4) degree of freedom at \(P (0.95)\) is 6.39.

TABLE 2C1
DETERMINATION OF IODATE IN SEA WATER SAMPLES USING METHYLENE BLUE AS A REAGENT

<table>
<thead>
<tr>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water Samples</td>
<td>Iodate added (\mu\text{gmL}^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>2.00</td>
</tr>
<tr>
<td>2</td>
<td>4.00</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
</tr>
<tr>
<td>4</td>
<td>12.00</td>
</tr>
</tbody>
</table>

a. Iodate concentration expressed in \(\mu\text{gmL}^{-1}\) (n=5)
b. Tabulated \(t\)-value for four degree of freedom at \(P (0.95)\) is 2.306
c. Tabulated \(F\)-value for (4,4) degree of freedom at \(P (0.95)\) is 6.39.

TABLE 2C2
DETERMINATION OF IODATE IN SEA WATER SAMPLES USING RHODAMINE B AS A REAGENT

<table>
<thead>
<tr>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water samples</td>
<td>Iodate added ( \mu g mL^{-1} )</td>
</tr>
<tr>
<td>1</td>
<td>2.00</td>
</tr>
<tr>
<td>2</td>
<td>4.00</td>
</tr>
<tr>
<td>3</td>
<td>6.00</td>
</tr>
</tbody>
</table>

\(^a\) Iodate concentration expressed in \( \mu g mL^{-1} \) (n=5)
\(^b\) Tabulated t-value for four degree of freedom at P (0.95) is 2.306
\(^c\) Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

TABLE 2C3
DETERMINATION OF IODATE IN SEA WATER SAMPLES USING LEUCO XYLENE CYANOL FF AS A REAGENT

<table>
<thead>
<tr>
<th>Proposed method</th>
<th>Reference method [56]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea water samples</td>
<td>Iodate added ( \mu g mL^{-1} )</td>
</tr>
<tr>
<td>1</td>
<td>4.00</td>
</tr>
<tr>
<td>2</td>
<td>8.00</td>
</tr>
<tr>
<td>3</td>
<td>12.00</td>
</tr>
</tbody>
</table>

\(^a\) Iodate concentration expressed in \( \mu g mL^{-1} \) (n=5)
\(^b\) Tabulated t-value for four degree of freedom at P (0.95) is 2.306
\(^c\) Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

TABLE 2C4
COMPARISON OF THE METHOD REPORTED WITH EARLIER METHODS

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Method</th>
<th>Beer’s law (µg/mL⁻¹)</th>
<th>ε in (Lmol⁻¹cm⁻¹)</th>
<th>λ_max (nm)</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid</td>
<td>Spectrophotometry</td>
<td>0.0</td>
<td>ε = 7.320×10⁴</td>
<td>352</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0</td>
<td>ε = 1.103×10⁵</td>
<td>288</td>
<td>39</td>
</tr>
<tr>
<td>3, 3’, 5, 5’-Tetramethylbenzidine</td>
<td>Spectrophotometry</td>
<td>0.0-0.7 mgL⁻¹</td>
<td>ε = 2.13×10⁵</td>
<td>450</td>
<td>42</td>
</tr>
<tr>
<td>Thionin</td>
<td>Spectrophotometry</td>
<td>1.0-12</td>
<td>ε = 2.7×10⁴</td>
<td>600</td>
<td>55</td>
</tr>
<tr>
<td>Azure B</td>
<td>Spectrophotometry</td>
<td>0.2–16</td>
<td>ss = 7.9×10⁻² ε = 2.06×10⁴</td>
<td>644</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ss = 0.85×10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Proposed Method</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Spectrophotometry</td>
<td>0.5–14</td>
<td>ε = 1.24×10⁴</td>
<td>665.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ss = 1.41×10⁻² ε = 1.406×10⁵</td>
<td>553</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ss = 1.23×10⁻³ ε = 1.71×10⁴</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ss = 1.02×10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>Spectrophotometry</td>
<td>0.5–7.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leuco xylene cyanol FF</td>
<td>Spectrophotometry</td>
<td>0.4 to 14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ε = Molar absorptivity, ss = Sandell’s sensitivity
2.9 REFERENCES


