Scientific Paper

A Highly Sensitive Spectrophotometric Method for the Determination of Iodate Using Leuco Xylene Cyanol FF

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Abstract

A highly sensitive and selective spectophotometric method has been developed for the determination of iodate (IO_3^-) in table salt and sea water. The proposed method is based on the oxidation of leuco xylene cyanol FF (LXCFF) to its blue form of xylene cyanol FF by iodate in sulfuric acid medium, the absorbance of the dye is measured in an acetate buffer medium (pH 4.0) at 620 nm. Beer's law is obeyed in the range 0.4-14 $\mu g\ mL^{-1}$ of iodate. The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit of the method were found to be $1.71 \times 10^4\ L mol^{-1} cm^{-1}$, $1.02 \times 10^{-2}\ \mu g\ cm^{-2}$, 0.026 $\mu g\ mL^{-1}$ and 0.0806 $\mu g\ mL^{-1}$ respectively. The optimum reaction conditions and other analytical conditions were evaluated. The effect of interfering ions on the determination is described. The proposed method has been successfully applied to the determination of the iodate in the table salt and sea water.

Key words: Iodate determination, spectrophotometry, leuco xylene cyanol FF.

Introduction

Iodine appears to be a trace element essential to animal and plants. Iodine occurs naturally not only as iodide but also as iodate in the form of minerals such as lautarite [$Ca(IO_3)_2$] and dietzeite $7[Ca(IO_3)_2]8CaCrO_4$. 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] Iodate is also present in sea water in the range 0-60 $\mu g\ L^{-1}$.[3]

Several methods have been reported on the determination of iodate, such as gas chromatography–mass spectrometry,[4] ion-chromatography,[5] chemiluminescence,[6] flow injection-amperometry,[7] potentiometric titrations,[8] differential pulse-polarographic method,[9] spectroflurometry,[10] flow injection-spectrophotometry,[11-12] coulometry[13] and photometric analysis[14-16] and gravimetric[17] method. Some reported spectrophotometric methods for the determination of iodate are based on its reaction with excess iodide to liberate iodine which forms tri iodide.[18-21] In other spectrophotometric methods iodate was determined after prior oxidation to periodate[22,23] Many spectrophotometric methods for the determination of iodate have been reported with chromogenic reagents, such as 2-oximinodimedonedithiosemicarbazone,[24] 3,4-dihydroxybenzalde-hydeguanylhydrazone (3,4–DBGH),[25] 1,3–diphenyl–3-hydroxyamino–1- propanoneoxime,[26] dithizone[27] blue indamine dye,[28] isonicotinicacidhydrazide and 2,3,5–triphenyl tetrazoliumchloride[15] and N,N'–di(β - hydroxypropyl)–o-phenylene diamine.[29] Of these reagents, some have been reported to be carcinogenic[25,15] while few others are less selective such as Alizarin Navy Blue[18] (ions like Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} were found to interfere) and tetramethylammonium iodide[22] method (Mn^{2+}, Cr^{3+}, Mn^{7+} and Ru^{3+} were found to interfere severely even at low concentrations). The need for a sensitive, simple and reliable method for the determination of iodate is therefore clearly recognized.

In the present investigation, a highly, sensitive and selective method has been reported for the determination of iodate with a new reagent leuco xylene cyanol FF, the developed method has been successfully employed for the determination of iodate in table salt samples and sea water.

Results and discussion

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. Absorption spectrum of the colored species of LXCFF against reagent blank is presented in Figure 1 and the scheme of the reaction system is presented in Scheme 1. The reagent blank had negligible absorbance at this wavelength.

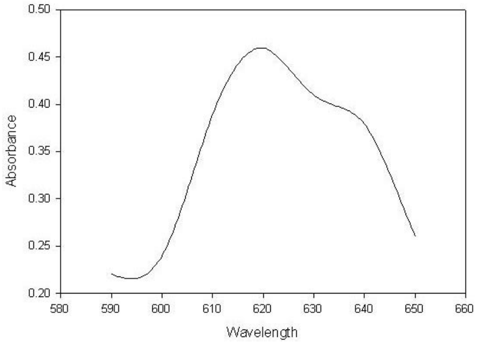
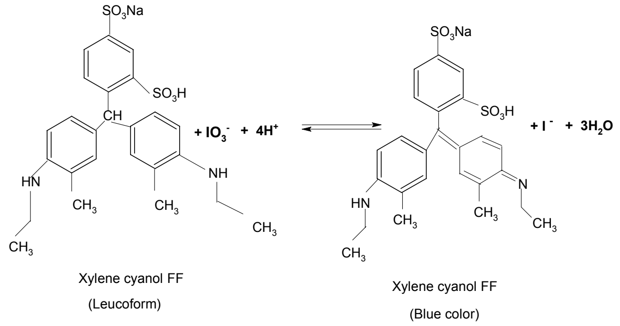


Figure 1. Absorption spectrum of coloured species of leuco xylene cyanol FF



Sheme 1

Effects of the acidity and temperature

The oxidation of LXCFF by iodate was 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 0.1-1.5 mL range of 0.05 M sulfuric acid (or pH 1.4-3.9) at 90°C for 15 min. 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 0.05 M sulfuric acid (or maintained pH 2) in a total volume of 10 mL was used in all subsequent work.

Effect of reagent concentration and buffer media

The optimum concentration of LXCFF leading to maximum color stability is found to be 0.5 mL of 0.1% reagent per 10 mL of the reaction mixture. The absorbance values were 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 were obtained when the entire reaction mixture was diluted with the same acetate buffer solution of pH 4. A change in the pH of the final reaction mixture affected the intensity of the colored dye. The formed colored dye is stable for more than 24 hours.

Analytical data

A linear calibration graph is obtained for 0.4 to 14 μg of iodate in a final volume of 10 mL. The molar absorptivity and Sandell's sensitivity for colored system is found to be 1.71×10^4 Lmol^{-1}cm^{-1}, 1.02×10^{-2} μgcm^{-2} respectively. The detection limit ($D_L = 3.3\ \sigma /s$) and quantitation limit ($Q_L = 10\ \sigma /S$) [where, "σ" is the standard deviation of the reagent blank (n=5) and "S" is the slope of the calibration curve] of the iodate determination were found to be 0.026 μg mL^{-1} and 0.0806 μg mL^{-1} respectively.

The reproducibility of the method was established by an analysis of standard solutions of 4, 8 and 12 μg mL^{-1} of iodate in a final volume of 10 mL. Five replicate determinations of each concentration gave relative standard deviations of ≤ 0.2%.

Effect of diverse ions

The effect of various diverse ions on the determination of iodate by the proposed procedure is examined. The tolerance limits of interfering species are established at the concentration required to cause not more than a ±2% error in the recovery of iodate at 1 μg mL^{-1}. The tolerance limits of diverse ions are listed in Table 1. The oxidising agents such as Fe(III), Ce(IV), V(V) and Cr(VI), interfere severely with the determination of iodate. The interference of chromium is removed by extracting with methyl isobutyl ketone.[30] However, the tolerance limit of iron, cerium and vanadium can be increased by the addition of appropriate amount of sodium fluoride (1mL of 2% NaF).[31]

Table 1: Effects of diverse ions in the determination of (1.0 μg mL^{-1}) of iodate

Foreign ion	Tolerance limit in μg mL^{-1}
Hg^{2+}, Ca^{2+}, Br^-, Cl^-	2500
NO_3^-, Mn^{2+}, Mg^{2+}, Zn^{2+}	2000
Sm^{3+}, Eu^{3+}, Gd^{3+}, PO_4^{3-}, Yb^{3+}	1500
Cr^{3+}, NO_2^-, La^{3+}, Al^{3+}, SCN^-	1000
$^*Cr_2O_7^{2-}$, $^*Fe^{3+}$, $^*Ce^{4+}$, $^*VO_3^-$, oxalate, citrate, tartarate	≤ 1
AsO_4^{3-}, Co^{2+}, MoO_4^{2-}, WO_4^{2-}	≤ 500

* Masked with masking agents.

Table 2: Determination of iodate in iodized table salts

Proposed method				Reference method [32]				
Table salt samples	Iodate found[a] mg kg^{-1}	Std deviation	Rel. Std deviation (%)	Iodate found mg kg^{-1}	Std. deviation	Rel. Std Deviation (%)	[b]t-test	[c]F-test
1	23.48	0.67	2.86	23.49	0.65	2.76	0.02	1.06
2	27.64	0.35	1.26	27.67	0.36	1.30	0.14	1.06
3	33.76	0.62	1.83	33.77	0.64	1.88	0.02	1.06

a. Iodate concentration expressed in mg kg^{-1}
b. Tabulated t-value for 8 degree of freedom at P (0.95) is 2.78
c. Tabulated F-value for (4,4) degree of freedom at P (0.95) is 6.39.

Table 3: Determination of iodate in sea water

Proposed method					Reference method [32]				
Sea water samples	Iodate added µg mL^{-1}	Iodate found[a] µg mL^{-1}	Std deviation	Rel. Std Deviation (%)	Iodate found µg mL^{-1}	Std. deviation	Rel. Std Deviation (%)	[b]t-test	[c]F-test
1	4.00	4.00	0.007	0.17	4.01	0.009	0.21	2.02	1.51
2	8.00	8.01	0.009	0.11	8.02	0.007	0.09	2.02	1.51
3	12.00	11.99	0.009	0.07	12.01	0.01	0.08	0.55	1.35

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

Application

The method developed is applied to the quantitative determination of traces of iodate in table salt and sea water. The results, listed in the Table 2 and Table 3, compare favorably with those from a reference method.[32] Statistical analysis of the results by F–and t–tests showed that there is no significant difference between the accuracy and precision of the proposed and reference methods. The precision of the proposed method is evaluated by replicate anaylsis of 5 samples containing iodate at different concentrations.

Conclusions

For the first time, leuco xylene cyanol FF has been used as a chromogenic reagent for the spectrophotometric determination of iodate. The proposed method, which is simple and rapid, offers the advantages of sensitivity and wide range of determinations without the need for extraction or heating. The method does not involve any stringent reaction conditions and the reaction system is found to be stable for more than 24 hours. The proposed method has been successfully applied to the determination of iodate in table salt samples and seawater.

Experimental

Apparatus

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

Reagents

All the chemicals used were of analytical reagent or chemically pure grade and double distilled water was used throughout the study. Standard iodate solution (1000 µg mL^{-1}) was prepared by dissolving 1.224 g of potassium iodate in 1000mL of water and standardized using standard sodium thiosulphate.[17] Leuco xylene cyanol FF (LXCFF, 0.1%) was 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 min. The resulting solution was then filtered and diluted to 100 mL with water. A 0.05 M sulfuric acid, acetate buffer (pH 4.0) was prepared by dissolving 13.6 g of sodium acetate trihydrate in 80 mL of water. The solution pH was adjusted to 4.0 with acetic acid, and the mixture was diluted to 100 mL with water.

General Procedure

An aliquot of a sample solution containing 0.4-14 μg mL^{-1} of iodate was transferred into a series of 10 mL calibrated flasks. Then volumes of 0.5 mL each of the 0.05 M H_2SO_4 and 0.1% LXCFF were added, and the mixture was kept in a water bath (≈90°C) for 15 min. 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.

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Povzetek

Razvili smo visoko občutljivo in selektivno spektrofotometrično metodo za določevanje jodata v kuhinjski soli in morski vodi. Predlagana metoda je osnovana na oksidaciji reagenta leuco xylene cyanol FF z jodatom v kislem mediju (H_2SO_4). Produkt xylen cyanol FF daje modro obarvano raztopino z molarnim ekstinkcijskim koeficientom 1,71 × 10^4 Lmol^{-1}cm^{-1}, absorbanco pa izmerimo v acetatnem pufru (pH 4,0) pri 620 nm. Linearno območje metode za jodat je 0,4 do 14 μg mL^{-1} in zagotavlja Sandellovo občutljivost 1,02 × 10^{-2} μg cm^{-2}, spodnjo mejo zaznavnosti 0,026 μg mL^{-1} in spodnjo mejo določljivosti 0,806 μg mL^{-1}. Ocenili smo optimalne reakcijske in analitske pogoje ter vplive motečih ionov. Metodo smo uspešno uporabili za določevanje jodata v kuhinjski soli in morski vodi.