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Spectrophotometric Methods For The Determination Of Iodate In Iodized Edible Salt And Periodate In Water Samples

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ABSTRACT

N-1-Napthylethylenediamine dihydrochloride (NEDA) is proposed as new sensitive spectrophotometric reagent for the determination of iodate and periodate in the presence of 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) as electrophilic coupling reagent. The reaction was carried out in mild acid medium. The blue color formed indicated maximum absorbance at 590 nm for iodate and 580 nm for periodate. The methods obeyed Beer's law. The color developed was stable up to 24h at room temperature. The molar absorptivity and Sandell's sensitivity were 3.2×10^5, 1.7×10^5 L mol^{-1} cm^{-1}, 5.26×10^{-3} and 1.62×10^{-3} μg cm^{-2} respectively. Interference was not observed with 10 cations and 8 anions. The methods showed good reproducibility and can be satisfactorily applied for the determination of iodate in iodized edible salt and periodate in water samples.

KEYWORDS

FIA;
Electrochemical detection;
Hydroquinone;
Composite electrode;
Polyurethane.

INTRODUCTION

Iodine is an essential component of 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]. Iodide ions sometimes found in brackish water and, to a lesser extent in fresh water and may form iodate during ozonization.

Iodine deficiency disorders can be prevented by iodine supplementation. Although various methods for iodine supplementation are available, the most popular methods include iodination of culinary salt and bread. Potassium iodate is preferred over sodium iodate as the latter is susceptible for environmental moisture and temperature. The concentration used in different countries ranges from 10 to 80 μg ml^{-1} of elemental iodine[2].

Iodate and periodate are thermodynamically potent and kinetically facile oxidants hence, are very useful in organic chemistry. Because of the potential negative and positive health effects of iodate

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and periodate, maintaining the correct level of iodate and periodate in drinking water and in foods meant for human consumption is extremely important. A survey of the literature revealed that most of the methods available for the determination of iodate and periodate are less sensitive, require complicated and expensive instruments and or time consuming. Thus, the need for sensitive, simple, reliable and rapid methods for the determination of iodate and periodate is therefore clearly recognized.

Several methods have been reported for the determination of iodate and periodate, which include chromatographic[3,4,5,6,7], electrochemical[8,9,10,11], and optical methods[12,13,14,15,16,17,18]. Among the optical methods visible spectrophotometry is the most appropriate analytical approach for the determination of iodate and periodate, as it provides sensitive and reliable data of the analytes and offers practical and economical advantages over other methods. Besides, visible spectrophotometric detection is much more viable as a useful technique to develop on-line or at-line systems.

The visible spectrophotometric methods available for the determination of iodate and periodate can be classified into two groups based on the type of reaction. One group of spectrophotometric methods is based on the reaction with excess iodide to form triiodide[19, 20, 21], while, another group of spectrophotometric methods for the determination of iodate involves a prior step to oxidize iodate to periodate[22].

For the first time NEDA is proposed as sensitive spectrophotometric reagents in presence of 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) as coupling reagent for the determination of iodate and periodate. Hence, the chemical reactions involved have been systematically studied and procedures for spectrophotometric determination of iodate in iodized edible salt and periodate in environmental water samples have been standardized. The results showed that these reagents offer several advantages over most of the chromogenic reagents currently being used and the procedures indicate positive features over existing methods.

MATERIALS AND METHODS

Apparatus

UV-VIS spectrophotometer UVIDEC-610 TYPE with 1.0-cm matched cell (Jasco, Tokyo, Japan) was employed for measuring the absorbance.

Reagents

Standard solutions (1000μg ml^{-1}) of iodate and periodate were prepared by dissolving known quantities of potassium iodate and potassium periodate (BDH, India) in one liter of distilled water. Solutions of the required strength were prepared by diluting this stock solution with distilled water. Aqueous solutions of MBTH (0.05% w/v) was prepared by dissolving 50 mg of the compound in 100ml of distilled water; the solution was stored in amber bottle to protect from sunlight. Fresh solutions of NEDA (0.1% w/v) was prepared by dissolving 100 mg in 100 ml of distilled water. Solutions of diverse ions were prepared by dissolving the respective salts. All other chemicals used were of Analar grade.

General procedure

Iodate

To a series of 25 ml standard flask 1 ml of 0.1 % (w/v) NEDA, 2.0 ml of 0.05 % (w/v) MBTH, 1 ml of 1N (v/v) hydrochloric acid and different aliquots of iodate solutions were added. The contents were mixed thoroughly and the flasks were kept aside for 20 min at room temperature for the development of blue color. The solutions were made up to the mark using distilled water. The absorbance was measured at 590 nm against a corresponding reagent blank as a reference.

Periodate

To a series of 25 ml standard flask different aliquots of periodate solution were taken to which 1 ml of 1N (v/v) hydrochloric acid, 1 ml of 0.1% (w/v) NEDA and 2 ml of 0.05 % (w/v) MBTH were added. The contents were mixed thoroughly and the flasks were kept aside for 20 min at room temperature for the development of blue color. The solutions were made up to the mark using distilled water. The absorbance was measured at 580 nm against a corresponding reagent blank as a reference.

RESULTS AND DISCUSSION

MBTH was first introduced for the determination of aromatic amines and imino heteroatomic compounds and aliphatic aldehydes. Later, it was extended for the determination of a large number of organic compounds such as those containing methylene groups, carbonyl compounds, Schiff's bases, aromatic hydrocarbons, saccharides, steroids, olefins, phenols, furfural and heterocyclic bases[23]. N-1-Napthylethylenediamine dihydrochloride (NEDA) was earlier used to couple with hydroazino groups of 4-nitrophenylhydrozone to give azo dye[24]. However, the diazotization reaction has limitations of temperature, time of reaction and toxicity of the reagents. Hence, electrophilic coupling reactions were adapted to yield the color derivatives.

Reaction mechanism

The chemical reaction in the method described for the spectrophotometric determination of iodate or periodate in acidic medium involves the reduction of species by MBTH which subsequently couples with the NEDA to form a blue colored product having maximum absorption at 590 and 580 nm respectively. The color intensity remains constant up to 24 h. The factors affecting the color development, as also the reproducibility, sensitivity and adherence to Beer's law were investigated and presented in TABLE 1.

Spectral characteristics

TABLE 1: Optical characteristics for the determination of iodate and periodate with NEDA using MBTH

Parameters	Iodate	Periodate
Colour	Blue	Blue
λ_{max} (nm)	590	580
Stability (h)	24	24
Beer's law (μg ml^{-1})	0.9 – 3.9	0.3 -1.1
Recommended ion concentration (μg ml^{-1})	2.4	0.6
Molar absorptivity (L $mol^{-1}cm^{-1}$)	3.20×10^5	1.70×10^5
Sandell's sensitivity (μg cm^{-2})	5.26×10^{-3}	1.62×10^{-3}
Regression equation*		
Slope (a)	0.135	0.441
Intercept (b)	-0.024	-0.00
Correlation coefficient	0.990	0.997
Reaction time (min)	20	20

*y = ax + b where x is the concentration of residual chlorine in μg ml^{-1} (n = 5)

The absorption spectrum of the blue colored complex with iodate and periodate shows a wavelength of maximum absorption at 590 and 580nm respectively. The reagent blank shows negligible absorption at this wavelength.

Optimization of analytical variables

The reagents concentrations and quantity needed as also the reaction conditions were optimized to arrive at a standard procedure. Each parameter was optimized by setting other parameters constant.

Order of addition

The sequence of addition of iodate or periodate, MBTH, NEDA and acid was studied *via* the formation of the blue colored product. It was found that there was no appreciable change either in the absorbance or development of color of the product when the sequence of addition of these reactants was altered.

Effect of reagents and acid concentration

The effect of NEDA was studied in the range of 0.5-3.0 ml of (0.1% w/v) solution of each to achieve the maximum color intensity, volume of 0.5–2.0 ml of the solution gave good result. Hence, 1 ml of (0.01 % w/v) NEDA solution was selected for further studies.

Preliminary investigations showed that hydrochloric acid was better than sulphuric, phosphoric or acetic acid. Maximum intensity of the blue color was achieved in the range of 1.0-5.0 ml of 1N HCl. Therefore, 1 ml of 1N HCl used for getting the best results. Similarly, the same procedure was adopted to ascertain the volume of MBTH required for getting constant and maximum color intensity. It was found that 0.5–3.0 ml of the solution was needed to get good result. Hence, 2.0 ml of (0.05% w/v) MBTH solutions is sufficient to get reproducible results.

Effect of temperature and stability

The effect of temperature on chemical reaction was investigated. The absorbance decreased with increase in temperature. It was found that when at room temperature (~ 27°C) the color intensity was stable up to 24 h.

Analytical parameters

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TABLE 2: Effect of cation on the determination of iodate and periodate.

Salt of the cation added	Amount added mg	% recovery of ion* ± RSD**	
		Iodate	Periodate
Aluminium ammonium sulphate	100	99.1 ± 0.52	98.2 v 0.81
Ammonium molybdate	100	97.4 ± 1.01	99.4 ± 1.00
Barium sulphate	100	99.0 ± 0.87	98.4 ± 0.88
Cadmium sulphate	100	100.1 ±0.76	99.7 ± 0.81
Lead nitrate	100	96.8 ± 1.76	99.9 ± 0.78
Magnesium sulphate	100	99.4 ± 0.62	97.4 ± 0.82
Selenium sulphate	100	100.6 ± 0.78	99.2 ± 1.04
Sodium arsenate	100	98.8 ± 1.08	97.8 ± 0.76
Strontium nitrate	100	98.2 ± 0.94	101.6 ± 0.78
Tin chloride	100	102.4 ± 0.80	99.7 ± 0.60
Zinc sulphate	100	100.6 ± 1.06	100.2 ± 1.08

*100 mg ml^{-1} of iodate and periodate taken **relative standard deviation (n = 5)

TABLE 3: Effect of cation on the determination of iodate and periodate.

Salt of the anion added	Amount added mg	% recovery of ion* ± RSD**	
		Iodate	Periodate
Ammonium tartarate	100	99.8±1.04	99.0±1.70
Potassium chloride	100	98.4± 1.02	97.6±1.09
Potassium sulphate	100	99.2±0.60	99.4±1.12
Sodium sulphate	100	97.2± 1.06	99.2±0.96
Sodium fluoride	100	101.3±1.12	99.8±0.80
Sodium nitrate	100	100.6±0.92	101.4±0.62
Sodium phosphate	100	98.4±0.88	99.4±1.08
Sodium thiosulphate	100	101.0±0.64	99.0±0.72

* 100 mg ml^{-1} of iodate and periodate taken
** relative standard deviation (n = 5)

The colored product obeyed Beer's law. The optical characteristics such as optimum range for the determination of the ions as evaluated from a Rigbom plot, molar absorptivity, Sandell's sensitivity, slope, intercept, correlation coefficient are presented in TABLE 1, which conclusively proves that the reagents are sensitive.

Selectivity

Effect of cations and anions was studied by adding known amounts of different cations and anions to solutions containing 500 mg ml^{-1} iodate and periodate and color was developed as per the described procedure. An error of ± 3% was considered tolerable. Various cations and anions which did not interfere with our experimental method and their maximum tolerance limit are presented in TABLE 2 and 3.

APPLICATIONS

(i) Iodate in iodized edible salts

The applicability of the proposed method (MBTH-NEDA) was tested in three brands of iodate added edible salts, which were purchased from the local market. It is clear from TABLE 4 that the iodate concentrations determined in commercial samples of salts are in close agreement with the values claimed by the manufacturer.

TABLE 4: Concentration of iodate in iodized salts of different brands (NEDA-MBTH method)

Brand No	Concentration of iodate (μg ml^{-1})		Error %
	Expected value[a]	Proposed method	
1	33	32.6	-0.7
2	15	13.9	-0.2
3	30	29.0	0.5

[a]as indicated on the cover of the packet.

(ii) Periodate in water samples

In order to access the validity of the method for the determination of periodate, different water samples were collected and analyzed by employing conventional standard addition method (TABLE 5). In tap water the iodate percentage recovered was erratic. This is understandable as the tap water is

TABLE 5: Periodate in water samples (NEDA-MBTH method)

Sample	Periodate mg ml^{-1}		Recovery % ± RSD**
	Added	Recovered by the proposed method	
Tap water	250	251	99.20 ±0.92
	300	296	99.61 ± 1.04
	350	354	102.05 ± 0.78
Bore well water	250	252	98.02 ± 1.12
	300	295	98.04 ± 1.74
	350	347	99.42 ± 0.90
Lake water	250	246	99.22 ± 0.02
	300	296	97.33 ± 1.60
	350	349	99.42 ± 0.88
Ozonoated water*	250	250	100.43 ± 0.72
	300	302	100.61 ± 1.08
	350	352	101.73 ± 0.68

* samples were free from ozone at the time of determination
** relative standard deviation (n = 5)

chlorinated. While the bore-well water gave lesser values. The cause of low values in the lake water (~ -3.5%) may be attributed to various levels of organic and biological pollutants.

CONCLUSION

The developed method is simple, inexpensive, sensitive and precise and have the advantage of determinations without the need for extraction or heating taking not more than 20 min for the assay. NEDA is very useful spectrophotometric reagents for the determination of iodate and periodate, in edible salts and in water samples. This compound when used as spectrophotometric reagent, it is necessary to use 3-methyl-2-benzothiazoline hydrazono hydrochloride hydrate (MBTH) as electrophilic coupling reagent. The use of most common reagents and also the aqueous medium make the method cost-effective and versatile. Further, the method can be made popular if the procedure is made on-line or at line system and currently this aspect is under investigation.

In summary, we recommend NEDA for routine analysis in industries and laboratories.

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