

Research Article

Exploitation of Oxidative Coupling Reaction in Spectrophotometric Determination of Iodate in Iodized Salt

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A simple and sensitive spectrophotometric method has been described for the determination of iodate. The method was based on the oxidation of Procainamide in hydrochloric acid medium and coupling with phenoxazine (PNZ), which can be spectrophotometrically monitored at 520nm, and the absorbance is directly related to the concentration of iodate in the sample. The calibration curve is linear in the range of 0.08 – 1.13 $\mu\text{g ml}^{-1}$. The reaction conditions and other important analytical parameters were optimized to enhance the sensitivity of the method. Interference if any, by non-target ions was also investigated. The method was applied successfully for determining iodate in iodized salt with high percentage of recovery, good accuracy and precision.

Introduction

Iodate is not a natural component of water but maybe formed during ozonization (disinfection) of raw water which may contain iodide ions (brackish water and to a lesser extent, in freshwater) [1,2].

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 $[\text{Ca}(\text{IO}_3)_2]$ and dietzeite $7[\text{Ca}(\text{IO}_3)_2]8\text{CaCrO}_4$ [3].

Iodine is an essential trace element for human nutrition. The safe dietary intake of iodine as recommended by the World Health Organization (WHO) is $100\mu\text{g day}^{-1}$ for infants and $150\mu\text{g day}^{-1}$ for adults [4].

There are various analytical methods for determination of iodate in seawater and iodized salt samples [4,5]. Some of the recent methods include spectrophotometry [6,7], spectrofluorometry [8], chemiluminescence [9], colorimetry [10], ion chromatography [11,12], gas chromatography-mass spectrometry [13], transient isotachopheresis- capillary zone electrophoresis [14,15], and electroanalytical methods [16,17], have been reported for the determination of iodate and only a few of them accompanied with a sample preparation step [18].

Most of the techniques are complex and involve sophisticated instruments and complex procedures. It is also observed that application of these analytical methods for iodate determination in table salt is complicated due to the presence of huge excess of chloride [4].

Hence, the aim of the present study is to develop a rapid, reliable and precise, an accurate method for the determination of iodate in table salt, which is based on oxidation of Procainamide in hydrochloric acid medium followed by coupling with phenoxazine (PNZ) in presence of iodate to form red color chromogen, detectable in visible spectroscopic, 520nm (Figure 1).

Experimental**Apparatus**

All spectral and absorbance measurements were carried out on a Shimadzu UV- Visible-260 digital double-beam recording spectrophotometer (Tokyo-Japan), 007.

Reagents

All chemicals used were of analytical reagent grade. Procainamide hydrochloride (PNH), PNZ was from Aldrich and NaIO_3 from (Merck).

Stock solution of NaIO_3 ($2000\mu\text{g ml}^{-1}$): Was prepared by dissolving of 0.5g NaIO_3 in water and made up to 250ml with water.

Stock solution of PNZ (0.05% w/v): 25mg of PNZ was dissolved in distilled ethyl alcohol and made up to 100ml with distilled ethyl alcohol.

Stock solution of PNH (0.10% w/v): Was prepared by dissolving 100mg and diluting quantitatively to 100mL with water.

Hydrochloric acid solution (2M): Was prepared by diluting quantitatively 176.99mL of 35% HCl (Merck, German) to 1L with distilled water.

Preparation of NaCl sample solution (12% (w/v): From the sample that was oven dried at 120°C overnight and stored in desiccators until constant weight, the solution was prepared by dissolving an accurate weight of 30g of salt in water and making up

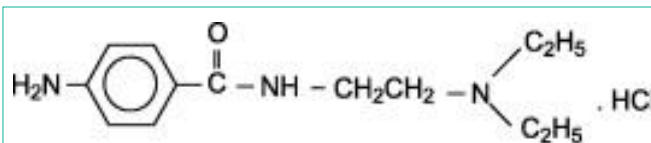
**Procainamide hydrochloride (1)**

Figure 1: Procainamide hydrochloride.

Table 1: Analytical parameters of spectrophotometric method.

Parameters	
Colour	Red
λ_{\max} (nm)	520
Stability (h)	1
Beer's law ($\mu\text{g mL}^{-1}$)	0.08-1.13
Recommended ion concentration ($\mu\text{g mL}^{-1}$)	0.5
Molar absorptivity ($\text{L mol}^{-1}\text{cm}^{-1}$) x 104	8.250
Detection Limit ($\mu\text{g mL}^{-1}$)	0.042
Regression equation*:	-
Slope (a)	0.0424
Intercept (b)	0.0328
Correlation coefficient	0.9972
R.S.D** % (n=5)	1.30

* $y=ax+b$ where x is the concentration of iodate in $\mu\text{g mL}^{-1}$.

**Relative Standard Deviation.

to 250ml (note: filtration may be necessary for some sample solutions that contain particulate matter).

Results and Discussion

Oxidative coupling reaction has attracted considerable attention for quantitative analysis of many environmental active compounds and pharmaceutical preparations. In the present investigation the reactive electrophilic intermediate formed *in situ* from PNH upon treatment with an oxidant, Iodate, was found to oxidative couple with PNZ forming red color.

Optimization of the experimental conditions

The effect of various parameters such as effect of reagents and acid concentration time, temperature and order of addition of reagents, on the absorption intensity of the dye formed was studied by varying one parameter at a time and controlling all others fixed.

Effect of reagents

The influence of PNZ reagent on the development of color was studied in the range of 0.10 – 5.00 mL of (0.05% w/v) solution of each. The maximum color intensity was observed in the range of 0.50 – 3.00 mL of the solution. Hence, 1mL of (0.05% w/v) PNZ solution in 25-mL standard flask was selected for further studies.

Similarly, the same procedure was adopted to ascertain the amount of PNH required for getting constant and maximum color intensity. Good results was obtained in the range of 0.50 – 3.00 mL of the solution. As result of, 1mL of (0.10% w/v) PNH solutions is sufficient to get reproducible results.

Effect of concentration and type of acid

Preliminary investigations showed that hydrochloric acid was better than sulphuric, phosphoric or acetic acid. Hence, the influence of acidity (HCl) on the maximum and stable color development was studied using different volumes (1-6 mL) of 2MHCl. The maximum color intensity was observed with 1mL of 2MHCl and therefore, used throughout the experiment.

Effect the time and temperature

The effect of temperature and time on the oxidative coupling

Table 2: Interference of selected excipients in the determination of iodate (standard potassium iodate (1ppm) in 6% NaCl).

Foreign species	
Mg^{2+}	100
K^+	98
Ca^{2+}	99
F^-	95

Table 3: Recovery study of iodate untreated salt.

Sample	Added	Found	Recovery%
1	0.6	0.571	95.2
	1.2	1.21	100.8
2	0.6	0.61	101.7
	1.2	1.186	98.8
3	0.6	0.575	95.8
	1.2	1.182	98.5
4	0.6	0.573	95.5

reaction were studied to optimize temperature and time of the reaction. It was found that the maximum color developed within 2min at room temperature and remained almost stable for about 2h. It was noticed that the increase in the temperature decreases the intensity of the red color. Hence, 2min reaction at room temperature was selected as optimum result.

Order of reagents addition

It was observed that the order of addition of reagents plays also important role as it influence the intensity and the stability of the color of the product a to great extent. The sequence (i) PNZ–HCl-iodate-PNH and (ii) iodate-HCl-PNZ- PNH, gave less intense and unstable color. While, (iii) PNZ-PNH- HC - iodate gave more intense and stable red color. This is expected as the reaction (i) and (ii) produced radical cation, while, in (iii) electrophilic reaction was evident.

Recommended procedure

A series of labeled 25mL calibrated flasks were arranged. To each flask, 1mL of PNZ, aliquots of the solution of NaIO_3 (0.25-4 ml of $10\mu\text{g/ml}$), 1mL of PNH reagent and 1mL of 2M HCl were added and the mixture shaken thoroughly and allowed to stand for 2min and the volume was made up with water. Absorbance at 520nm was measured in 1.0-cm quartz cell against reagent blank which was prepared without iodate. The optical characteristics for the determination of iodate with PNZ using PNH is detailed in the Table 1.

Interferences

The effect of the presence of some common excipients (Mg^{2+} , K^+ , Ca^{2+} and F^-) on the selectivity of suggested method has been studied at concentration level normally found in a sample of sea salt(providing the salt was prepared from complete evaporation). The results calculated, as shown in Table 2, based on the elemental abundance in seawater [19] indicate that there was no significant interference produced by these foreign substances on the suggested method.

Accuracy

The accuracy of the proposed method was determined by

Table 4: Determination of iodate in different iodized salt samples by PNZ/PNH method.

Sample	Proposed method		Reported method		t-value**	F-value***
	Iodate found $\mu\text{g/mL}$	RSD*	Iodate found $\mu\text{g/mL}$	RSD*		
1	25	0.59	26	0.51	1.68	2.3
2	26	0.5	27	0.62	2.1	3.1
3	29	0.54	28	0.37	1.88	4.1
4	25	0.34	26	0.61	1.47	3.9
5	27	0.4	28	0.56	2.41	3.41
6	32	0.65	30	0.57	1.23	4.1

standard addition method, which involved the addition of different concentrations of iodate to an iodate untreated salt sample and the concentration was determined using the proposed method. The percent recovery was found to be 95.2%-101.7% as shown in Table 3.

Application of the proposed method

The proposed method was applied to the determination of iodate in water samples. The same samples were analyzed, simultaneously by the proposed method and the reported method [20]. The results were compared statistically by applying Student's t-test for accuracy and the variance ratio F-test for precision with results from the reported method at a 95% confidence level. The calculated t-test and F-values (Table 4) did not exceed the tabulated values of 2.77 and 6.39, respectively, indicating no significant difference between the proposed method and the reported method in terms of accuracy and precision.

Conclusions

The proposed method was found to be simple and sensitive. The method does not require heat treatment and sophisticated instruments. The statistical parameters and recovery study data clearly indicate the reproducibility and accuracy of the method. The proposed method does not involve any critical reaction conditions or tedious sample preparation. The results of iodate determination by the reported method are in good agreement with the reported method.

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