

A rapid and simple fluorimetric determination of iodide in iodized table salts

V. A. Kabasakalis* and M. G. Mitrakas

*Lab. of Analytical Chemistry, Chemical Engineering Department, Faculty of Engineering,
Aristotle University of Thessaloniki, Thessaloniki 54006, Greece*

Abstract. A new, simple and rapid fluorimetric method is proposed for the determination of iodide in iodized table salts based on the fluorescence exhibited by the ionic complex formed between AgI_2^- and the brilliant green cation ($\lambda_{\text{exc}} = 256 \text{ nm}$, $\lambda_{\text{em}} = 521 \text{ nm}$) at pH 3.0 and Ag^+ concentration of 0.8 mg/L. The relationship between fluorescent response expressed as Fluorescence Intensity Units (FIU) and KI concentration of standards in 20 g NaCl/L was linear in the range of 0.15 to 1.2 mg KI/L. The sensitivity of the method was 300 FIU for 1 mg KI/L with a detection limit of 0.15 mg KI/L. The proposed method was applied in commercial iodized table salts and the results obtained were correlated closely to those obtained by the official method of the AOAC.

Key words. Iodide determination – table salt – fluorimetry.

Introduction

Iodine is an essential trace element in human nutrition with the normal dietary requirements reaching up to approximately 75 mg iodine per year. In most countries this supply is secured by State regulations which demand the addition of KI to table salt intended for human consumption. Therefore, table salt industries are very much concerned about monitoring KI content in their products with an analytical method which should be rapid, inexpensive and sensitive. Several methods have been published for the quantification of iodide in table salts. The acceptable method by the Official Methods of Analysis of the AOAC [1] is time consuming, taking more than 2 hours for obtaining the results and so do the catalytic [2] and photometric [3] titration methods. Flow injection analysis [4] which involves photometric detection based on the catalytic fading effect of either iodate or iodide on the indicator reaction of iron(III) thiocyanate and nitrite, improves the detection limit and minimizes considerably the time consumed, but it is limited up to 2 % NaCl solution. A very low detection limit is also achievable by Negative Thermal Ionization Mass Spectroscopy [5] and atmospheric pressure helium Microwave Induced Plasma Atomic Emission Spectroscopy which is an indirect method and uses continuous-flow cold-vapor generation of mercury [6]. Both methods, however, employ particularly expensive equipment. Iodide in table salt has also been analyzed by High Performance Liquid Chromatography [7] with a detection limit of 20 mg iodide/kg salt which is not acceptable by the table salt industries.

The objective of this study was to develop and propose a new simple, rapid and inexpensive fluorimetric method for the determination of iodide in iodized table salts and concentrated NaCl solutions. The method, based on the fluorescent radiation emitted from the ion-associated complex, formed between AgI_2^- and the brilliant green cation, should possess low detection limit and increased sensitivity, attributes which meet the requirements of the table salt industries.

Experimental

Reagents

- A. Stock, standard KI solution: 1000 mg/L analytical grade KI, in distilled water.
- B. Working standards: 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mg KI/L in 20 g/L of NaCl, made by proper dilution of the stock standard solution.
- C. A 40 mg Ag^+ /L solution, prepared by proper solution of a BDH standard solution of 1000 mg Ag^+ /L.
- D. Brilliant green solution, made by dissolving 0.75 g reagent (BDH no C.I 42040) in 1 L of distilled water.
- E. 0.1 N H_2SO_4 solution
- F. Alternative working standards: i) 0, 0.08, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mg KI/L in 10 and 50 g/L NaCl and ii) 0, 2.0, 5.0, 15, 20, 25, 30, 35 mg KI/L in different concentrations of NaCl, namely, 100, 150 and 200 g/L made by proper dilution of the stock standard solution. The above mentioned NaCl concentrations were achieved by dissolving the proper quantities of analytical grade NaCl in distilled water.

*Correspondence and reprints.

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Table I. Linear range of the calibration graphs and detection limit of KI in different NaCl concentration. The results are also expressed as mg KI/kg salt.

NaCl, g/L	Linear Range		Detection Limit	
	KI, mg/L	mg KI / kg salt	KI, mg/L	mg KI / kg salt
10	0.08 - 0.6	8 - 60	0.07	7
20	0.15 - 1.2	7.5 - 60	0.10	5
50	0.35 - 1.4	7 - 30	0.32	6.4
100	2 - 6.5	20 - 65	1.9	19
150	5 - 20	33 - 133	4.4	30
200	10 - 32	50 - 160	9.5	48

Recommended procedure

A 10 g table salt sample is dissolved in 500 mL of distilled water and the solution is filtered through a 0.45 μm filter. To 50 mL of the sample solution as well as of the working standards (B), 1 mL of reagent C is added with continuous stirring, the pH is adjusted to 3.0 by small additions (0.1-0.3 mL) of reagent E and then 1 mL of reagent D is added. Fluorescence intensity measurements at 521 nm (ϵ_{em}) after excitation at 256 nm (ϵ_{exc}), of samples and standards are taken within 5 to 10 min after reagent D addition. The calibration graph of Fluorescence Intensity Units (FIU) versus KI concentration in solution is constructed and KI concentration of the unknown sample is read from the graph.

Checking the analytical conditions

The influence of high NaCl concentrations on complex formation and its fluorescent response was also tested by obtaining calibration graphs using the alternative working standards (F) and the procedure described above.

Materials tested

The recommended procedure was applied to five table salt samples (no 1-5, Tab. II) which were provided by the Greek salt industry AEGEAN S.A. These samples were intended to be distributed in Serbia and their KI concentration was expected to range between 15-30 mg/kg salt. Another five samples (no 6-10, Tab. II) were obtained from the Greek market and their KI concentration, according to the Greek Legislation, should range between 40-60 mg/kg salt.

Official method

Iodide analysis of the unknown samples was also performed by the Official Method AOAC (1990) and served as a standard for comparisons.

Results and discussion

Determination of KI content was based on measurements of the fluorescent radiation emitted from the ion-association complex, formed between AgI_2^- and the brilliant green cation and relate it to KI concentration in solution. In a pre-

Table II. Iodide analysis of table salts by the recommended fluorimetric method. The results are compared to those obtained using the Official method (AOAC, 1990).

Sample no	Fluorimetric method (x)		Official method (y)
	mg KI / kg salt	CV	mg KI / kg salt
1	18.2	2.8	17.4
2	19.1	2.5	18.1
3	25.1	3.1	24.6
4	28.9	2.6	28.2
5	28.5	2.2	28.3
6	30.8	4.2	32.7
7	58.6	1.4	58.9
8	34.9	1.9	35.8
9	45.9	1.6	44.5
10	29.9	3.8	30.2

Correlation coefficient $r^2 = 0.9969$ Regression equation $y = 1.0138 x - 0.56$

vious work [8] the optimum conditions for complex formation have been established, namely pH = 3.0, concentration of brilliant green 15 mg/L and measurement time within 10 min after complex formation. In this work the concentration of Ag^+ that would give the optimum fluorescent response was investigated. The experimental results showed that the fluorescent response, expressed as Fluorimetric Intensity Units (FIU), of a standard containing 0.5 mg KI/L in 20 g NaCl/L was increased as the concentration of Ag^+ increased up to 2 mg/L (Fig. 1). As it is seen from figure 1, fluorescent response (sensitivity) of 0.5 mg KI/L in 20 g/L, is approximately 200 FIU and would certainly increase for 1 mg KI/L (see follow discussion) at values that are considered satisfactory, since they could detect differences in concentration of 1 mg KI/kg salt. A 0.8 mg/L concentration of Ag^+ was chosen for convenience reasons and reagent saving. Higher Ag^+ concentrations could be used, however, in cases where increased sensitivity and a lower detection limit, is needed.

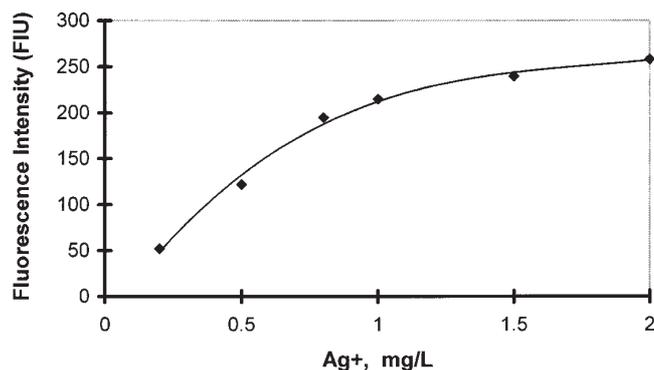


Figure 1. Effect of Ag⁺ concentration on the fluorescence intensity of 0.5 mg/L KI in 20 g/L NaCl solution.

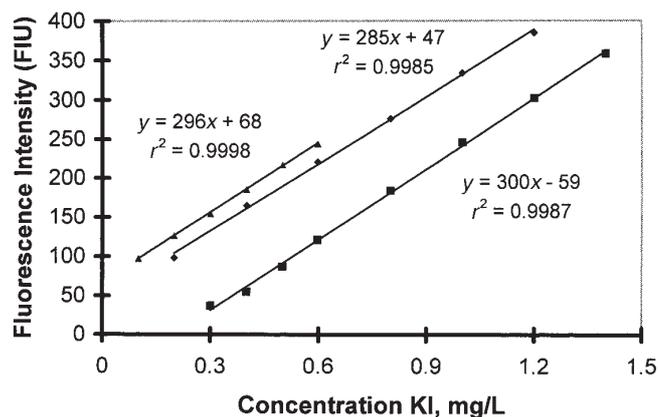


Figure 2. KI calibration graphs in various NaCl solutions: \blacktriangle 10 g/L, \blacklozenge 20 g/L, \blacksquare 50 g/L.

The calibration graphs relating fluorescent response (FIU) and KI concentration in 10, 20, 50, 100, 150 and 200 g/L NaCl solutions were obtained for studying the behavior of the complex formation and its subsequent fluorescence in the presence of varying concentrations of NaCl. The experimental results showed that the graph was linear between 0 to 1.4 mg KI/L and that NaCl concentrations from 10 g/L to 50 g/L did not affect the slope of the calibration graphs, which was almost constant at 290 ± 10 FIU (Fig. 2). However, as NaCl concentration was increased, the linear range of the calibration graph was displaced towards higher KI concentration (Fig. 2). The detection limit, defined as 3 of 7 replicates of blank solution [9] was also increased from 0.07 mg KI/L in 10 g/L NaCl solution to 0.32 mg/L KI in 50 g NaCl/L (Tab. I). At higher NaCl concentrations, apart from the displacement of the linear range towards higher KI concentration and the increase of the detection limit from 1.9 mg KI/L in 100 g NaCl/L to 9.5 mg KI/L in 200 g NaCl/L (Tab. I), a decrease of sensitivity (slope of the calibration graph) was noticeable as well. So, the slope decreased from 300.08 in 50 g NaCl/L to 91.5 in 100 g NaCl/L and 15.4 in 200 g NaCl/L (Fig. 3).

On the basis of the data of table I and figure 2, calibration standards in 20 g NaCl/L and dissolution of 20 g of the unknown sample in 1 L of water were chosen, for the determination of KI content of table salts. These analytical parameters cover the expected KI concentration in table salts, which ranges between 15 to 60 mg KI/kg salt in accordance to the State Legislation of the European countries. The proposed method was tested by analyzing samples no 1-5 (Tab. II) whose concentration varied between 15-30 mg KI/kg salt, and samples no 6-10 obtained from the Greek market.

Iodide content of all samples was also determined by the Official Method of Analysis of the AOAC (1990) as well. KI concentration values obtained by the proposed fluori-

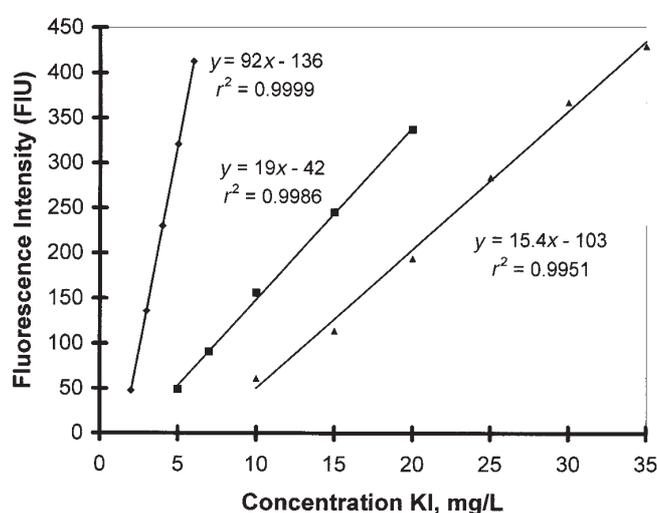


Figure 3. KI calibration graphs in NaCl solutions of high concentration: \blacklozenge 100 g/L, \blacksquare 150 g/L, \blacktriangle 200 g/L.

metric method were correlated closely to those obtained by the official method (Tab. II). The regression line had a slope and an intercept not statistically different from 1 and 0 respectively, at 1 % level of probability. The method was also proved precise since the coefficient of variation (CV), estimated from 7 replicates, was less than 5 % on the average (Tab. II). It is remarked that KI concentration of the AEGEAN industry samples, destined for Serbia, was within the limits imposed by Serbian Legislation. On the contrary, in 3 samples sold in the Greek market KI concentration was lower than the one written on the container.

In conclusion, the proposed fluorimetric method for iodide determination in iodized table salts gave reproducible results and similar to those obtained by the official method of analysis. An additional advantage of the fluorometric method stems from its simplicity and rapidity requiring less than 10 minutes time of analysis.

Acknowledgements

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