ISSN 2313-5891 (Online)
ISSN 2304-974X (Print)

Ukrainian Food Journal

Volume 4, Issue 2
2015

Kyiv **Київ**

2015

Iodine content determination in dried talli of laminaria by galvanostatic coulometry

Sergii Gubskyi[1], Sergii Nikitin[1], Victoriia Evlash[1], Oleksandra Nemirich[2]

1 – Kharkiv state university of food technology and trade, Kharkiv, Ukraine
2 – National university of food technologies, Kyiv, Ukraine

Keywords:

Iodine
Coulometry
Titrometry
Laminaria
Seaweed

Article history:

Received 13.03.2015
Received in revised form 15.04.2015
Accepted 20.05.2015

Corresponding author:

Sergii Gubskyi
E-mail:
s.gubsky@hduht.edu.ua

Abstract

Introduction. Dried seaweeds are well-known food source with rich iodine content that can be used for the prevention of iodine deficiency disorders (IDD) independently as well as functional ingredients in dietary foods. Considering the above, analysis of total iodine content in seaweeds is an important pursuit.

Materials and methods. The total content of iodine in samples of dried thalli laminaria, known as a commercial product Kombu, was determined by galvanostatic coulometry with potentiometric indication of the end point of the titration in aqueous solution obtained by mineralization samples.

Results and discussion. Contained in the samples iodinated compounds such as organic and inorganic nature, by a dry alkaline mineralization were transferred to the aqueous solution in the form of iodides. The procedure was carried out at the optimal temperature conditions within 420-480ºC which provides maximum yield.

Standard aqueous solutions of sodium iodide in the concentration range of 15-300 mg / 100 g of solution used for the analytical method validation of determining the concentration of iodide by galvanostatic coulometry with electrogenerated bromine. These key characteristics of validation procedure, such as the specificity, linearity, range of analytical procedure, accuracy and precision, led to the conclusion about the possibility of using galvanostatic coulometry for the determination of total iodide in the solutions. Was confirmed that the electrogenerated bromine reacts with iodide in the ratio 1:1.

The iodine content surveyed for four series of kombu was 394, 476, 587 and 743 mg/100 g dry algae, respectively.

Conclusions. Using the coulometric method for solving the problems of quantitative determination of iodine content in popular seaweed products as Kombu and others is suggested.

Introduction

Many different analytical techniques have been developed for iodine speciation in food, environmental and biological matrices but they are characterized as difficult procedures. It is associated with the complexity of the analysis: low levels of iodine in the study of multicomponent arrays, its volatility and polyvalent in redox reactions. Among these methods modern highly informative and sensitive methods are used. Interfacing various separation techniques, such as reversed-phase high-performance liquid chromatography, ion chromatography, size-exclusion chromatography and capillary electrophoresis with element selective ICP-MS (inductively coupled plasma- mass spectroscopy) has been employed in speciation studies of iodine to separate and characterize iodine species of different nature [6-10]. At the same time, we have not lost their relevance and affordable traditional titrimetric, spectrophotometric and electrochemical methods [11-16]. Among them, it should be isolated by coulometric titration as an absolute and rapid method, which gives a sufficiently high statistical certainty of outcome and sensitivity in the analysis of objects of vegetable origin [17].

One of the important sources of iodine in the human body is seafood, among which an important place belongs to the algae. Recent represented a large number of species, among which the most popular are the brown algae. The brown algae is the largest amount of iodine in the form of iodides and iodates, as well as the iodinated amino acids that can be regarded as an iodine-containing additive for the human diet [1-3]. On the recommendation of WHO, the recommended dietary allowance (RDA) of iodine is 150 μg/day for healthy humans [4]. This is an important issue for our country, which in terms of this indicator is epidemic [5].

Edible brown algae as a good dietary source of iodine have consumed in many countries. Furthermore, in Ukrainian Pharmacopoeia (Addition 4) dried thalli of laminaria are medicine. According to article "Laminaria thalli" of Pharmacopoeia, as the primary method for determining the iodine content using volumic titration. However, the visual indicator fixing the end-point of titration and the need for pre-standardization of the titrant, significantly increase the time of analysis, it should be known, it refers to the disadvantages of this method. Therefore, rapid procedure method of galvanostatic coulometry as an absolute method with low economic parameters of the tools design and the ability to automate of determining iodine process method gives clear advantages for the measurement.

Materials and methods

Materials. Objects of the present research was samples of seaweed as a food supplement – marine algae Kombu (thalli of Laminaria saccharina and Laminaria japonica). They were obtained from local drug stores. All seaweed samples were dried. In our work used samples from four parties with different series number on the package ("Lektravi" plant, Ukraine).

The above mentioned marine algae were analyzed for total iodine content after complete mineralization using by dry alkaline ashing technique to convert iodine into iodide [11,12,16,18]. Previously, the dried algae samples were ground in a household coffee grinder for 5 minutes. After weighing 1-2 g dry seaweed sample were putted into a porcelain crucible, 4 mL 0,5 N KOH solution was added with followed by soaking for 6-10 hours and drying at 105 ° C. The sample solution was heated on a hot plate into a slurry state. The sample slurry should be kept heated until it is completely dry. Then the crucible was placed into the ashing furnace to avoid loss of iodine. A complete and smooth

combustion is essential for a good recovery of iodine. In heating procedure the ashing temperature was 420–460 °C and lasted 7-8 hours. This values allowed to optimize the standard ashing technique. The maximum iodine contents is obtained in the temperature range 420-460 ° C, whereas, at 400 ° C there is no complete convert of organic compounds with too low a yield of 40% and at temperatures of 500 - 600 ° C ashing gives 50% final result .

After cooling down in a desiccator, 15 mL deionized water was added into the crucible. The sample crucible was placed on a hot plate to heat up and dissolve the ash. The ashing solution was then suction filtered. The ash was dissolved again in 15 mL hot water. Them the filtrated solutions were combined, and water was added volumetrically to 50 mL and that solution was weighted. The sample solution were analyzed for total iodine content.

Standard solutions of sodium iodide were prepared by dissolving precise portions in water with followed by masse diluted method.

In research was used dry reagent of chemically pure grade, bidistilatted water with pH=6,8 and electric conductance less 4 μSm/m.

Methods. The total iodide content in solutions was estimated by galvanostatic coulometry with electrogenerated bromine.

The electrogeneration of bromine as coulometric titrants–oxidants was performed using a T-201M1 titrator or PU-1 polarograf as potentiostat device in 0.2 M solutions of potassium bromide in a 0,1 M solution of sulfur acid (pH=1,1) with a platinum electrode (S = 200 mm2) at a constant current intensity of 2,0-5,0 mA. The cathode was a coiled platinum wire (l = 10 mm). A cathode chamber, wherein the auxiliary electrode was set, was separated from the anode chamber by a porous glass septum. A constant current intensity were carried by the combined V7-21s instrument with accuracy 0,2%.

Before each determination, platinum electrodes were stored in solution of potassium bromide and subjected to chemical cleaning (in nitrate acid 1:1) and electrochemical cleaning (in sulfur acid 0,2 M under 5 mA) [17].

A 80.0 mL portion of a supporting electrolyte was charged in a 100 mL electrochemical cell with the working, auxiliary, indicator and reference electrodes, and the generating circuits were switched on. The solution in the cell was stirred with a magnetic stirrer.

The aliquot portions (in g) were selected so that the titration time took no more than 300-400 seconds which provided express and the necessary accuracy of measurements.

The end-point of titration was established potentiometrically with indicator and reference electrodes: platinum redox electrode EPV-1 and Ag/AgCl system EVL-1M3.1 (Gomel ZIP, Belarus), respectively. The solution samples contains ions which are incompatible with the reference electrolyte, a double junction electrode were used.

Time that responsibility to the end-point of titration was controlled by two procedure: 1) the achievement of the initial value by the indicator redox potential ; 2) by an inflection in the titration curves with the regard for electrolysis time of a supporting electrolyte. Both procedures were yielded identical results. The theoretical quantity of substances released on the electrode (g) was established according to Faraday's law.

Redox potential, pH and temperature measurements of solutions were performed using a 692 pH/Ionmeter (Metrohm, Swiss) with accuracy 0,1 mV, 0,002 pH and 0,1° C, respectivelly. In this research using a combined glass electrode with temperature sensor Pt1000 (Combined LL pH glass electrode with Pt 1000 temperature sensor, № 6.0238.000 Metroohm, Swiss).

Potentiometric data of titration in form (voltage-time) were monitored and recorded in electronic file produced by a computer software PicoLog Recorder v.5.24 (PicoScope Ltd.,

UK). The statistical treatment of results was carried out for four measurements at a confidence level of 0,95. Results are presented as X ± ΔX, where X is the mean value and ΔX is the confidence interval. The corresponding values of the relative standard deviation (RSD) were also calculated. All calculations were performed using program Excel (Microsoft Office 2010) and IBM SPSS Statistic v.20.

Results and discussion

The validation procedure of the quantitative determination of total iodine content by galvanostatic coulometry was performed. In practice, it is usually possible to design the experimental work such that the appropriate validation characteristics can be considered simultaneously to provide a sound, overall knowledge of the capabilities of the analytical procedure, for instance: specificity, linearity, range, accuracy and precision. For this purpose was prepared the model solutions of sodium iodide aqueous solutions in the range of 15-300 mg, which corresponds to the level of concentration in the range from 70 to 130% of the possible concentration. This concentration was estimated on the basis of the following condition: 1) the amount of iodide in dried thalli of laminaria is the interval from 100 to 1000 mg / 100 g of dried algae, with an average value of about 150 mg [3,19-20]; 2) Ukrainian Pharmacopeia regulates the content of iodine in dried thalli of not less than 0.11%; 3) converting coefficient at procedure of the filtrated solution dilution.

The total iodide content in samples g (mg/100 g solution) was calculated from coulometric data by the equation (1):

$$g = \frac{100ItM}{nFm_p}, \quad (1)$$

where *I* is current, A; t is the time at which the end-point of titration is reached, s; M is the molar weight of the substance, g/mol; n is the number of electrons participating in the reaction; F is Faraday's constant, Coul/mol; is the weight of the aliquot portion, g; and m is the weight of dry sample, g.

To establish the stoichometry of the interaction iodide with electrogenerated bromine reactions, the coulometric titration of sodium iodide standard solutions was performed. When converting the equation (1) concerning the quantity of electricity Q required to generate bromine, we obtain the following equation (2):

$$Q = It = n\left(\frac{100F}{Mm_p}\right) = nf(g), \quad (2)$$

where *f(g)* is parameter equal to expression in brackets.

Figure 1 shows the dependence between the quantity of electricity Q and a function of f(g) for standart solutions of NaI for ten iodine concentration (25 measurements). The curve is linear. The correlation coefficient and slope of this curve are 0,9946 and 2,01, respectively. The slope value is numerically equal to the number of electrons n in the oxidation reaction of bromine. This confirms that electrogenerated bromine reacts with iodide in the ratio 1:1 [17]. So, the numbers of electrons participating in the reactions of iodide with titrants is two (n=2 in equation 1).

Figure 2 shows the dependence between the quantity of electricity Q and iodine concentration g for 6 standart solutions of NaI. The curve is linear over the iodine concentration range of 12-150 mg/100g of solution. The correlation coefficient of curve is 0.9996, as evidenced by the condition of linearity and the possibility of quantitative determination of iodide in the area of the proposed analytical methodology.

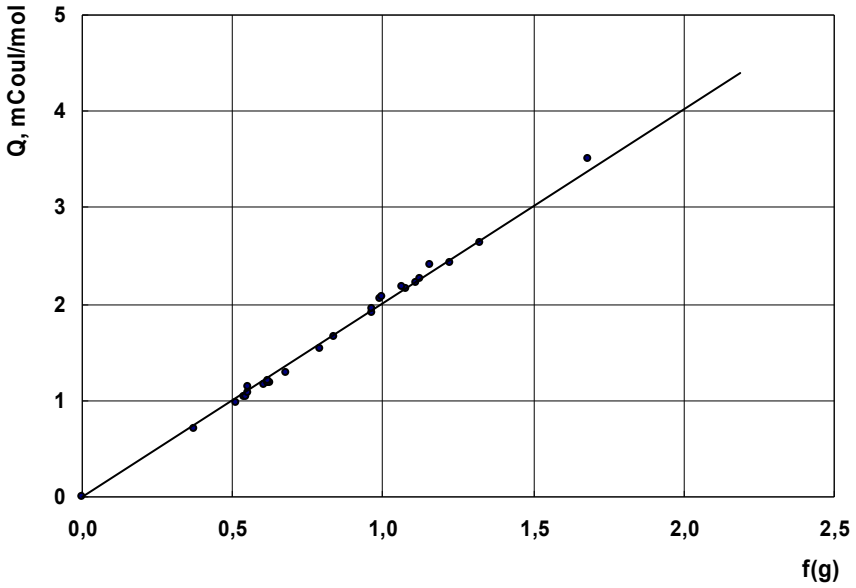

Fig. 1. The quantity of electricity Q as a function of f(g) for standard solution of sodium iodide

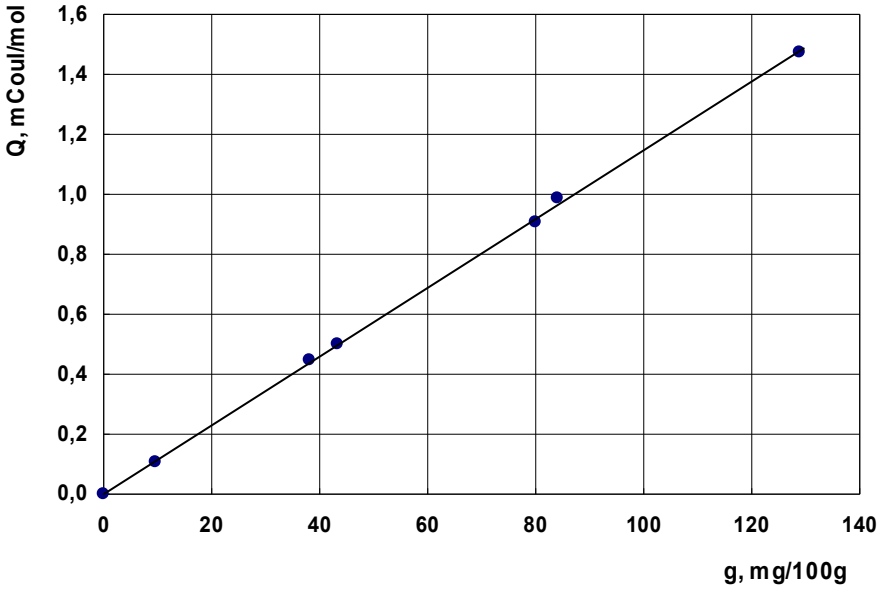

Fig. 2. The quantity of electricity Q as a function of concentration g for sodium iodide standard solution

Specificity was evaluated by the method of "added-found". The obtained values of the relative standard deviation is less than 0,05 (Table. 1).

Table 1

Coulometric determination of sodium iodide in standard solutions (n=5, P=95%)

Sample	Added g, mg/100 g of solution	Found g, mg/100 g of solution	RSD S_r
Sodium iodide	12,00	12,07	0,019
	59,60	58,34	0,014
	184,9	184,5	0,009
	318,3	322,1	0,053

The accuracy and precision were evaluated by varying the weighed portions at three levels of concentration using three portion on each level in comparison with iodinemetry method wich the recommended by Ukrainian Pharmacopoeia. Comparing dispersions series of measurements using F-test indicates statistically significant difference between the two methods and means the absence of significant systemic error. The calculated values of T-test is less than the tabular data. That facts corresponds to the validity of analytical procedure on characteristics of accuracy and precision.

The characteristics of validation procedure was showed that reliable experimental results are obtained. Adding in model solutions of chlorides and bromides at concentrations that may be present in the mineralized samples did not significantly alter these parameters do not affect the selectivity of the determination.

The total content of iodine in the ashing solutions was determinated for four manufacturer's serial numbers of dried algae at the level of the three samples in each series. The results of the measurements with the metrological characteristics are shown in Table. 2.

Table 2

Total iodine content for kombu (n = 4, P = 0.95)

Number of manufacturers series	Number of samples in series	Iodide amount g, mg/100 g solution	S_x	S_r	Mean value g±Δg, mg/100 g dry algae
10415	1	117,3	0,421	0,011	587 ± 21
	2	118,0	0,659	0,018	
	3	116,8	0,451	0,012	
50414	1	96,8	0,396	0,011	476 ± 9
	2	95,1	0,174	0,013	
	3	93,8	0,269	0,010	
30613	1	149,5	0,851	0,025	743 ± 19
	2	147,6	0,771	0,024	
	3	148,8	0,672	0,029	
30314	1	75,7	0,639	0,025	394 ± 8
	2	81,2	0,772	0,026	
	3	79,5	0,671	0,028	

As seen from Table. 2, the iodide content within the same lot is within measurement error, but there is a significant difference in the iodide content between manufacturer's series. The iodine content surveyed for four series of kombu was 394, 476, 587 and 743 mg/100 g dry algae, respectively. Apparently, the discrepancy confirms the fact that the iodine content in algae varies depending on the season and geographical location preform vegetable raw materials and is reflected in the final product. This result confirm the need to quantify determination the iodine content in the plant raw materials which can be used as a dietary supplement in fortified food.

It should be noted that these results are the total iodine content in the range of values determined by other experimental methods.

Conclusions

In this paper, the use of the most common ways of mineralization by dry alkaline digestion allowed to study the content of iodine in dried seaweed in an aqueous solution iodide. For detecting iodine content in seaweed the method of galvanostatic coulometry has been developed. Basic characteristics of validation for this analytical methods allows to conclude on the statistic reliability of the results. The iodine content surveyed was 394-743 mg per 100 g of dry sample for Kombu. These values were obtained for samples of various series of products. This fact proves the necessity of the quantitative control of the iodine content in food additives used for the development of iodine-containing functional foods and nutraceuticals.

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