ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN
2019 International Nuclear Atlantic Conference - INAC 2019
Santos, SP, Brazil, October 21-25, 2019

Agência Brasileira do ISBN
ISBN 978-85-99141-08-3

IODINE DETERMINATION IN EDIBLE ALGAE SPECIES USING ENAA METHODOLOGY

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ABSTRACT

Iodine is one of the essential trace elements of much interest in nutritional research being responsible for the production of the thyroid hormones, which has great importance for human metabolism. Edible algae species accumulate iodine from seawater and are considered a good dietary source of this nutrient. The Epithermal Neutron Activation Analysis (ENAA) was applied to determine the iodine concentration in edible algae species and derivatives. Twenty-one sample for 4 edible algae species *Porphyra umbilicalis* (common name: Nori), *Hijikia fusiforme* (Hijiki), *Undaria pinnatifida* (Wakame) and *Laminaria* spp. (Kombu) and 3 samples of the derivative sample, ágar, were analyzed. The results pointed out a great variability of I concentration in these species. The highest I concentration obtained was 9324±113 mg/kg in *Laminaria* spp. (Kombu). *Hijikia fulsiforme* (Hijiki) also presented high values (1803±86 mg/kg). The lowest I content was obtained in agar samples (3.18±0.29 mg/kg).

1. INTRODUCTION

Iodine is a trace element essential for the body because it is the main constituent of thyroid hormones. The thyroid gland is responsible for cell growth, brain development, and maintaining body temperature. About 99% of iodine available in the body is located in the thyroid gland [1,2].

Goitre is one of the most important disorders caused due to iodine deficiency, apart from hypothyroidism and cretinism. To overcome iodine deficiency in the diet of the population, mainly in underdeveloped countries, iodine supplementation in the diet has been performed, for example iodination on the cooking salt. On the other hand, iodine supplementation programs should be monitored to avoid the presence of diseases caused by its excess such as hyperthyroidism [3].

In food, iodine concentrations and total iodine dietary intake differ from one region to another, due to geochemical characteristics, soil, and cultural conditions that interfere with food choice [1].

Algae are excellent sources of minerals, and may present higher values in relation to vascular plants and terrestrial animals [4] since they absorb inorganic substances from the environment and store them [5,6].

Algae are also used as bioindicators of environmental contamination due to their morphological and physiological characteristics, as they have a high capacity to absorb and store certain potentially toxic elements [7,9] The group of brown algae, such as Hijikia fusiforme (Hijiki), Undaria pinnatifida (Wakame) and Laminaria spp. (Kombu) has greater capacity to store iodine in relation to the group of red algae (*Porphyra umbilicalis* (Nori)) [7]. The species red algae are the most commercially used for food and feed, for the extraction of Agar (manufacture of gums, laxatives, culture medium for bacteria) and for the extraction of carrageenan (use in dairy products , in the manufacture of jellies and jellies, as a thickener in soups, sauces and as a non-caloric substitute for starch and fat)[10].

In many countries, food industries employ a wide range of algae derivatives, which contains high levels of fiber, fatty acids, polyunsaturated polysaccharides, minerals, vitamins and antioxidants. The algae and its derivatives also have economic impact in several sectors, such as aquaculture, pharmaceutical industry, biomedicine, veterinary medicine, cosmetics industry and public health [8,9]. Studies about iodine concentration in algaes are increasing due to question related to public health, since there are several pathologies caused by the deficiency and excess consumption of this element.

The aim of this study was to determine the concentration of iodine in brown and red algae and its derivative agar, and check if the found levels are in agreement with the recommend limits for human health.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Twenty four samples from four species of commercially edible algae available to consumers were purchased from super markets around São Paulo city. All edible algae samples were imported from 4 different countries. The samples were ground and homogenized using a household mixer, fitted with titanium blade, until they acquire a powder consistency. Table 1 shows the different species of algae (with its commercial name), its origins and the number of each species acquired.

Table 1: Species of algae and derivatives, countries of origin and number of samples

Algae and Derivatives	Country	Number of samples
Porphyra umbilicalis (Nori)	China	1
Porphyra umbilicalis (Nori)	Korea	2
Porphyra umbilicalis (Nori)	Japan	2
Porphyra umbilicalis (Nori)	USA	1
Hijikia fusiforme (Hijiki)	Japan	2
Hijikia fusiforme (Hijiki)	China	2
Hijikia fusiforme (Hijiki)	Korea	1
Undaria pinnatifida (Wakame)	China	3
Undaria pinnatifida (Wakame)	Korea	2
Laminaria sp (Kombu)	Korea	1
Laminaria sp (Kombu)	Japan	2
Laminaria sp (Kombu)	China	2
Ágar	Brazil	3

2.2. Epithermal Neutron Activation Analysis (ENAA)

Iodine determination was carried out using Epithermal Neutron Activation Analysis (ENAA), due to its capability of reduce interferences from ^{24}Na, ^{38}Cl and other radionuclides, commonly present in high concentrations in algae samples. The principle of ENAA consists in irradiating sample and standard inside of a Cd capsule in order to reduce possible interferences due to activation of elements with high cross section for thermal neutrons present in the sample.

About 50 mg of the algae samples and reference materials were weighed in acid cleaned polyethylene bags and iodine standards were prepared by pipetting the KIO_3 solution (6,8 µg of I) on Whatman 40 paper and dried at room temperature.

The algae samples, reference materials and Iodine standards were placed inside of Cd capsules and then irradiated for 30 seconds under a neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 pneumatic system of IPEN - CNEN/SP. After decay time of about 600 seconds, the radioisotope ^{128}I was determined by measuring its gamma ray transition of 442.9 keV by gamma spectrometry.

Gamma ray measurements were performed using a GC2018 Canberra HPGe detector coupled to a Canberra DSA-1000 multichannel analyzer. The spectra were collected and processed using a Canberra Genie 2000 version 3.1 spectroscopy software.

3. RESULTS AND DISCUSSION

3.1 Quality control

To validate the ENAA method in respect of its precision and accuracy two standard reference materials (SRM) NIST: Whole milk (NIST RM 8435) and Whole egg powder (NIST RM 8415) were analyzed. The determined concentrations were compared with the value of their certificates by means of the E_n-*score*[1] method [13]. Figure 1 shows the *En-score* values for the element iodine in the SRM.

The table 2 shows relative errors less than 9% and relative standard deviations below 12%, indicating good precision and accuracy of the data.

Table 2 - Iodine concentration results obtained for Whole Milk Powder (RM 8435) and Whole Egg Powder (RM 8415) reference materials

CRM	Determined concentration(M ± DP)[a] mg/kg	SD Rel%	ER%	Certificate concentration (mg/kg)
WHOLE MILK POWDER	2.50 ± 0.16	6.4	8.7	2.3 ± 0.4
WHOLE EGG POWDER	2.08 ± 0.24	11.5	5.6	1.97 ± 0.50

[1] **The E_n-*score* test represents a normalized Gaussian centered at 0, and values between -2 and 2 for this test indicate that within a 95% confidence interval the value is satisfactory. [a] arithmetic mean and the standard deviation of 3 determinations.**

Figure 1: E_n-*score* values for Iodine determined in the RM

The E_n-*score* values obtained for iodine in the reference materials showed in Figure 1 are less than 1, so they are accurate with the values of the certificates.

3.2 Results of edible seaweeds

Table 3 presents the average results for I in algae samples, obtained in duplicates. All the results presented are related to the dry weight (dw) of the samples.
The results showed that there is a great variability between species in relation to the iodine concentration. The values of relative standard deviation (RSD) ranged from 0.9 to 17%. The higher RSD observed in all samples of *Undaria sp* (Wakame) is probably related to the high Na concentrations (from up 7 to 8.8%) and that the R_{Cd} (cadmium ratio) for sodium is 58 a significant amount of this element must be activated. According to the literature the brown algae present higher I level than the others due its greater affinity for this element. In this study the same was observed as shown in the Figure 2.

In Nagataki study in 2008 [14], the algae of the species *Laminaria spp* (Kombu) presented contents of 0.3% of I in dry weight (dw) and *Undaria sp* (Wakame) presented levels of 0.02-0.03% (dw), for the red algae *Porphyra* (Nori) the result was <0.01% (dw). Fukushika and Chatt, 2012 [15], also obtained high concentrations of I in brown algae of the species *Undaria pinnatifida* (Wakame), and *Hijikia fulsiforme* (Hijiki). Hijiki presented the I content of 514 ± 6 mg/kg, and Wakame 156 ± 3 mg/kg. In relation to other species of algae these are in fact those with higher I content.

In this study the highest determined concentrations for the brown algaes were: 9324 ± 113 mg/kg for *Laminaria* spp (Kombu), 1803 ± 86 mg/kg for *Hijikia fulsiforme* (Hijiki) and 430 ± 74 mg/kg for the *Undaria pinnatifida* (Wakame) can be observed in the Figure 2. For the red algae *Porphyra umbilicalis* the maximum concentration was 103 ± 1 mg/kg (Figure 3). The concentrations for Agar, a derivative of red algae, presented low levels of I, ranging from 3.18 ± 0.29 mg / kg up to 7.6 ± 0.5 mg / kg as can be shown on Figure 4.

It is important to notice that the daily intake of iodine according to DRI for adults is up 100 to 150 µg/day, and the maximum tolerable limit (UL) is 1100 µg/day [3]. The determined results of iodine concentration in brown algae varied from 116 to 9324 mg/kg which means that the ingestion of 1 g of brown algae (in case of Kombu) can exceed 62 times the DRI and 8 times the UL (for the higher I concentration).

Table 3 - Results of I concentration in seaweed samples by ENAA in dry basis

Specie	Origen	I mg/kg Median ± SD[a]	RSD(%)
Porphyra umbilicalis (Nori)	China	44.1 ± 8.9	20.1
	Korea	33.4 ± 4.0	12.1
	Korea	33.4 ± 2.4	7.2
	Japan	114.09 ± 0.02	0.01
	USA	54.5 ± 9.7	17.7
Hijikia fusiforme (Hijiki)	China	1975 ± 94	4.8
	China	1494 ± 252	16.9
	Korea	1365 ± 13	0.9
	Japan	734 ± 12	1.6
	Japan	836.8 ± 8.9	1.1
Laminaria sp (Kombu)	China	2826 ± 301	10.8
	China	259 ± 29	11.1
	Korea	9962 ± 121	1.2
	Japan	6810 ± 435	6.4
	Japan	4761 ± 195	4.1
Undaria pinnatifida (Wakame)	China	126 ± 12	9.7
	China	468 ± 80	17.2
	China	267 ± 45	16.8
	Korea	398 ± 66	16,6
	Korea	566 ± 109	19.3
Agar I	Brazil	8.29 ± 0.08	0.9
Agar II	Brazil	10.6 ± 2.3	21
Agar III	Brazil	4.03 ± 0.73	11.1

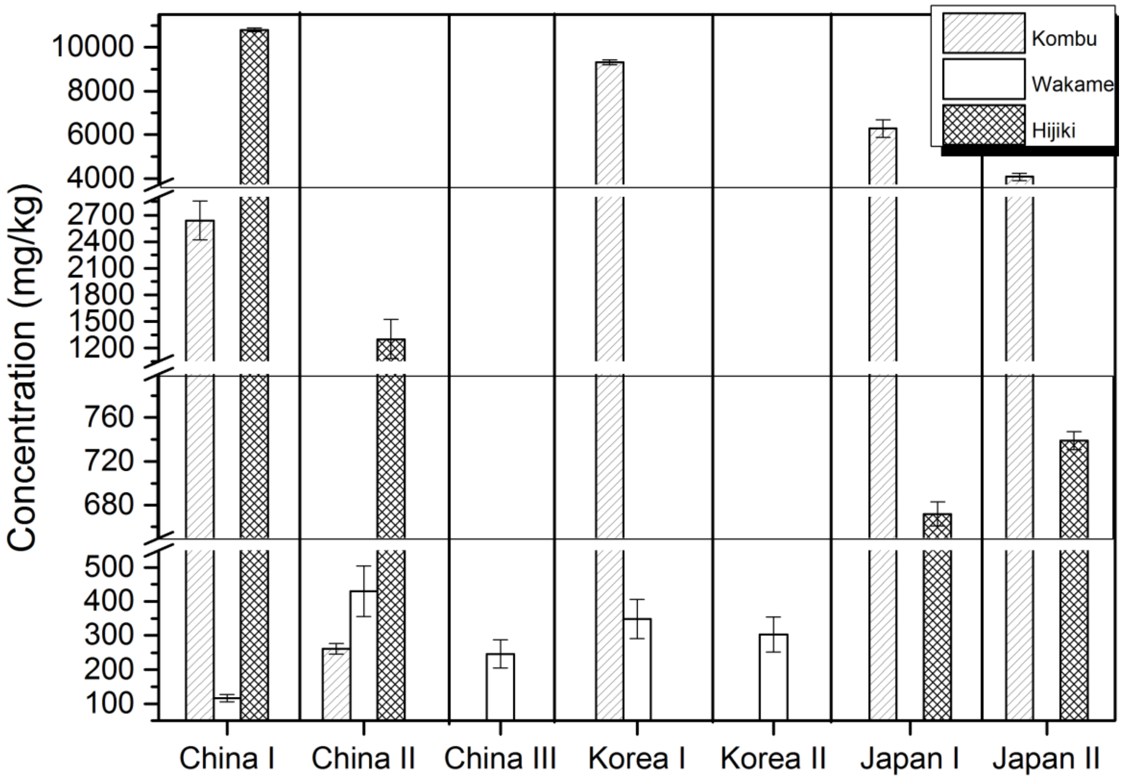

Figure 2: Values of the Iodine concentration in brown algaes.

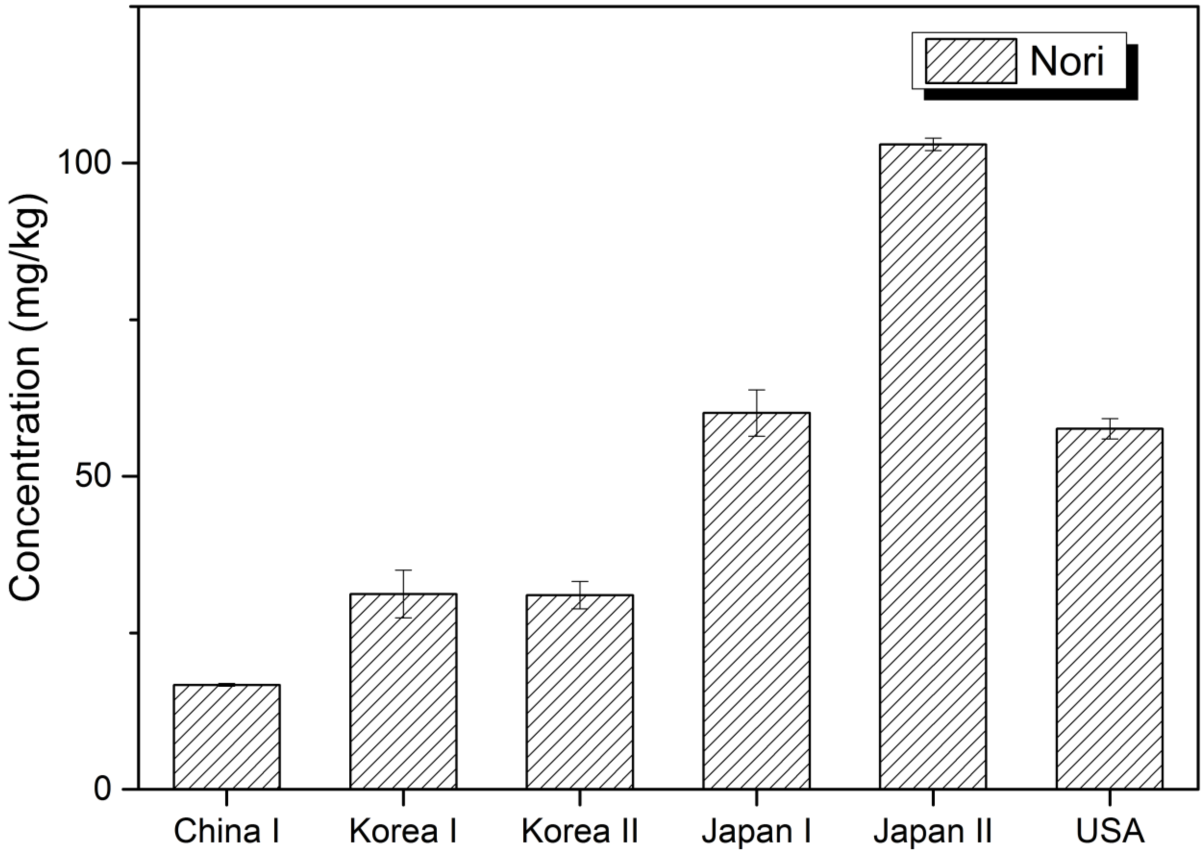

Figure 3: Values of the Iodine concentration in *Porphyra umbilicalis* (Nori)

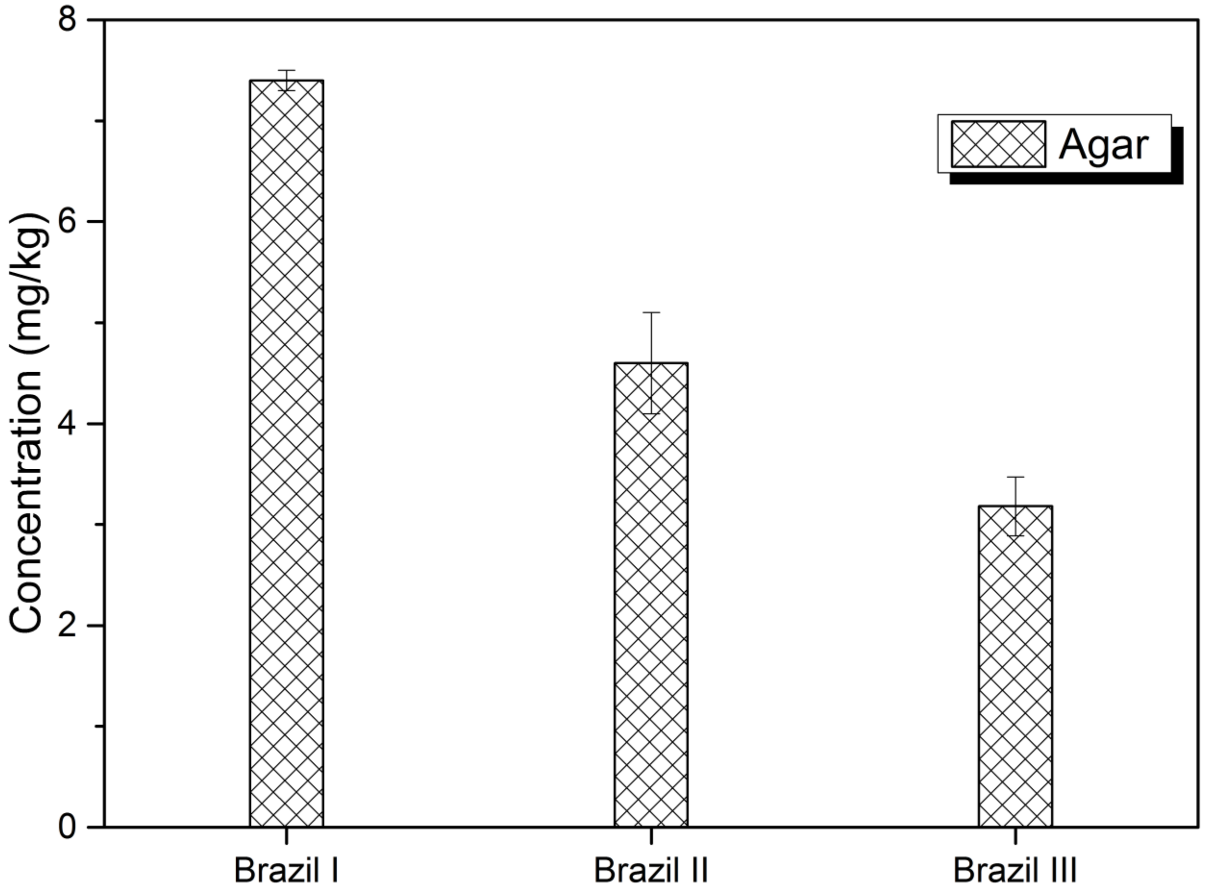

Figure 4: Values of the Iodine concentration in Agar

4. CONCLUSION

The ENAA technique proved adequate for the determination of iodine in seaweed samples. The results showed that edible marine algae can be a great source of iodine, especially brown algae, and can be used in food to meet some nutritional needs, but consumption must be controlled to avoid possible health problems. In relation to the agar a derivative of the red algae, it was possible to conclude that it does not present risks for the feeding, in relation to the element I.

ACKNOWLEDGMENTS

The authors would like to thank the Institute of Energy and Nuclear Research (IPEN-CNEN/SP) and the CNPq for the fellowship.

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