

Food Chemistry 79 (2002) 23–26

www.elsevier.com/locate/foodchem

Food Chemistry

Mineral content of edible marine seaweeds

P. Rupérez*

Departamento de Metabolismo y Nutrición, Instituto del Frío, Consejo Superior de Investigaciones Científicas (CSIC), Ciudad Universitaria s/n, 28040-Madrid, Spain

Received 7 August 2001; received in revised form 18 February 2002; accepted 18 February 2002

Abstract

Mineral content was determined in several brown (Fucus vesiculosus, Laminaria digitata, Undaria pinnatifida) and red (Chondrus crispus, Porphyra tenera) edible marine sea vegetables. Seaweeds contained high proportions of ash (21.1–39.3%) and sulphate (1.3– 5.9%). In brown algae, ash content (30.1–39.3%) was higher than in red algae (20.6–21.1%). Atomic absorption spectrophotometry of the ashes indicated that marine seaweeds contained higher amounts of both macrominerals $(8.083-17,875 \text{ mg}/100 \text{g};\text{Na}, \text{K}, \text{Ca}, \text{Ca})$ Mg) and trace elements $(5.1-15.2 \text{ mg}/100 \text{ g};\text{Fe}, \text{Zn}, \text{Mn}, \text{Cu})$, than those reported for edible land plants. Edible brown and red seaweeds could be used as a food supplement to help meet the recommended daily intake of some essential minerals and trace elements. \odot 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Mineral content; Edible seaweeds; Marine macroalgae; Sea vegetables; Atomic absorption spectrophotometry

1. Introduction

Seaweeds have been consumed in Asia since ancient times (Chapman & Chapman, 1980; Nisizawa, Noda, Kikuchi, & Watanabe, 1987). More recently marine algae have been utilized in Japan as raw materials in the manufacture of many seaweed food products, such as jam, cheese, wine, tea, soup and noodles (Nisizawa et al., 1987) and, in the Western countries, mainly as a source of polysaccharides (agar, alginates, carrageenans) for food and pharmaceutical uses (Indegaard & Ostgaard, 1991; Mabeau & Fleurence, 1993).

In Europe there is an increasing interest in marine seaweeds as a food; nevertheless, at present there are no European Union specific regulations concerning their utilization for human consumption. Seaweeds contain high amounts of carbohydrates, protein and minerals (Fleurence, 1999; Indegaard & Minsaas, 1991; Lahaye & Kaeffer, 1997; Mabeau & Fleurence, 1993; Rupérez & Saura-Calixto, 2001). Because of their low fat contents and their proteins and carbohydrates, which cannot be

* Tel.: $+34-91-5445607$ x223; fax: $+34-91-5493627$.

E-mail address: pruperez@if.csic.es (P. Rupérez).

entirely digested by human intestinal enzymes, they contribute few calories to the diet (Jurković, Kolb, $\&$ Colić, 1995; Kishi et al., 1982; Lahaye & Kaeffer, 1997).

Mineral content is generally high (8–40%) and the essential minerals and trace elements needed for human nutrition are present in seaweeds (Mabeau & Fleurence, 1993; Ortega-Calvo, Mazuelos, Hermosin, & Sáiz-Jiménez, 1993). This wide range in mineral content, not found in edible land plants, is related to factors such as seaweed phyllum, geographical origin, and seasonal, environmental and physiological variations (Mabeau & Fleurence, 1993). Yamamoto, Otsuka, Okazaki, and Okamoto (1979) have reported a positive correlation between each mineral element concentration and seaweed oceanic residence time. Mineral content also depends on the type of seaweed processing (Nisizawa et al., 1987;Yoshie, Suzuki, Shirai, & Hirano, 1994) and on the mineralization methods used (Fleurence & Le Coeur, 1993).

Seaweed mineral content is higher than that of land plants and animal products (Ito $&$ Hori, 1989; Ortega-Calvo et al., 1993). In most land vegetables, ash content ranges from 5 to 10 g/100 g dry weight (USDA, 2001), e.g. potato 10.4, carrot 7.1, and tomato 7.1. Sweet corn has a lower content (2.6%) , while spinach has a exceptionally high mineral content (20.4%) for a land plant.

^{0308-8146/02/\$ -} see front matter \odot 2002 Elsevier Science Ltd. All rights reserved. PII: S0308-8146(02)00171-1

Thus edible marine seaweeds may be an important source of minerals (Nisizawa et al., 1987), since some of these trace elements are lacking or very minor in land vegetables.

In view of the current increasing demand for seaweed products, and the few reports on minerals of edible seaweeds, the aim of this work was to determine the mineral content of several edible marine brown and red Spanish seaweeds by atomic absorption spectrophotometry.

2. Materials and methods

2.1. Raw material

Brown seaweeds: Fucus vesiculosus, Laminaria digitata (Kombu) and Undaria pinnatifida (Wakame) and red seaweeds: Chondrus crispus (Irish moss) and Porphyra tenera (Nori) were obtained from a local supplier (Algamar CB, Redondela, Pontevedra, Spain).

Commercial edible marine seaweeds were cut into small pieces and freeze-dried on a Virtis Benchtop 3L freeze-drier (Hucoa Erlöss, Madrid, Spain), then milled to a particle size of less than 1.0 mm and kept in airtight plastic bottles at room temperature until analysis.

Residual moisture content was determined by drying to a constant weight at 105° C in an oven. All determinations were performed at least in triplicate and data reported on a dry matter basis as mean values \pm standard deviation.

2.2. Ashes

Seaweed samples were incinerated in a digitally controlled Hobersal HD-230 furnace (Barcelona, Spain). Temperature was gradually increased to 550 \degree C and then maintained for 16 h. Ashes were quantified gravimetrically.

2.3. Sulphate

Sulphate was determined by the gelatin-barium chloride turbidometric method (Chaplin & Kennedy, 1986) with a Perkin-Elmer Lambda 12 UV-vis spectrophotometer. In brief, seaweeds (5 mg) were first hydrolyzed with 1 M HCl (1 ml) at $105 \degree$ C for 16 h. Then, samples were passed through a Whatman GF/A glass microfibre filter (7 cm diameter) and their volume made up to 2 ml with distilled water. Aliquots (0.2 ml) of the filtrate were taken and evaporated to dryness in SVL tubes at 40 \degree C under reduced pressure to remove HCl. Then, distilled water (0.2 ml) was added to each tube. Absorbance was measured at 500 nm and sulphate concentration in the samples calculated with a calibration curve of K_2SO_4 (50–200 µg SO_4^{2-}).

2.4. Minerals by flame atomic absorption spectrophotometry

Ashes were dissolved in nitric acid (analytical grade Merck, Germany) and passed through an ash-free, acidwashed filter paper (Albet No. 242, 9 cm diameter). Major mineral elements (Na, K, Ca, Mg) and trace elements (Fe, Zn, Mn, Cu) were determined in a Perkin Elmer 5100 PC atomic absorption spectrophotometer, equipped with single hollow cathode lamps for each element and an air-acetylene burner. Standards of mineral elements for flame atomic absorption spectrophotometry were obtained from Panreac (Panreac Quı´ mica SA, Barcelona, Spain).

3. Results and discussion

3.1. General

The mineralization method used to obtain ashes, has been shown to exert a significant influence on the end determination of minerals from seaweeds (Fleurence & Le Coeur, 1993). There is a risk of losses during ashing, due to volatilization or insolubilization of mineral elements. So in preliminary studies, seaweed samples were first incinerated at 550 °C for 16 h, and then at 900 °C for 2 h, as previously reported for several seaweeds (Fleury & Lahaye, 1991; Michel, Sahaye, Bonnet, Mabeau, & Barry, 1996; Bobin-Dubigeon et al., 1997). When ashes were further calcined at 900 \degree C, recovery was approximately three to six times lower (data not shown), consequently, ashing only at 550 \degree C for 16 h was selected.

3.2. Ashes and sulphate

Ashes and sulphate in seaweeds are shown in Table 1. Ash content was higher in brown (30.1–39.3%), than in red seaweeds $(20.6-21.1\%)$ and all the seaweeds contained sulphate, ranging from 1.3 to 5.9%. As mentioned above, ash content in most land vegetables is

Table 1

Ash and sulphate contents of edible brown and red seaweeds (g/100 g dry weight)

Seaweed		Ashes ^a	Sulphate ^b
Brown seaweeds	Fucus	30.10 ± 0.20	3.75 ± 0.04
	Laminaria	37.59 ± 0.40	1.33 ± 0.05
	Wakame	39.26 ± 0.24	1.43 ± 0.11
Red seaweeds	Chondrus	$21.08 + 0.12$	5.86 ± 0.44
	Nori	$20.59 + 0.16$	$2.37 + 0.13$

Mean values of triplicate determinations \pm standard deviation.

^a Incinerated at 550 $^{\circ}$ C 16 h.

^b Sulphate determined in 1 M HCl hydrolyzates with the gelatinbarium chloride spectrophotometric method.

usually much lower than in marine seaweeds, with an average value of 5–10 g/100 g dry weight (USDA, 2001). Sweet corn has a lower content (2.6%), while spinach has a exceptionally high mineral content (20.4%) for a land vegetable, similar to that of red seaweeds.

The ash values obtained fit well within the wide ranges, from 8 to 40% of algal dry weight, reported for seaweeds (Fleury & Lahaye, 1991; Ito & Hori, 1989; Mabeau & Fleurence, 1993; Ortega-Calvo et al., 1993). The amounts of ash obtained in the present study were in agreement with previous results (Rupérez $\&$ Saura-Calixto, 2001). Meanwhile, those for sulphate, as measured with the gelatin-barium chloride turbidometric method, were higher than the sulphate content determined by the AOAC gravimetric method (Rupérez $\&$ Saura-Calixto, 2001). These variations may reflect differences in the method of sulphate determination.

Mineral content has been shown to vary according to seaweed species, oceanic residence time, geographical place of harvest, wave exposure, seasonal, annual, environmental and physiological factors, type of processing and method of mineralization (Honya, Kinoshita, Ishikawa, Mori, & Nisizawa, 1993; Fleurence & Le Coeur, 1993; Mabeau & Fleurence, 1993; Nisizawa et al., 1987;Yamamoto et al., 1979;Yoshie et al., 1994).

Sulphate seems to be a typical component of marine algal polysaccharides, related to high salt concentration in the environment and to specific aspects of ionic regulation. Sulphate is derived from fucans in brown algae or from galactans in red ones. Such sulphated mucilages are not found in land plants (Kloareg & Quatrano, 1988).

Regarding nutritional value, seaweed dietary fibres are not digested by humans. Thus, sulphated algal polysaccharides are weakly fermented and poorly desulphated by colonic bacteria (Bobin-Dubigeon et al., 1997; Lahaye & Kaeffer, 1997; Michel et al., 1996). Apparently, seaweed dietary fibre polysaccharides retain their ionic groups throughout the digestive tract, suggesting that they are relatively innocuous regarding sulphate ion toxicity (Mabeau, 1995).

3.3. Minerals by atomic absorption spectrophotometry

Atomic absorption spectrophotometry determination of the ashes (Table 2) showed that these seaweeds contained high amounts of the macrominerals (8083–17,875 mg/100 g) and trace elements $(5.1–15.2 \text{ mg}/100 \text{ g})$ needed in human nutrition. It is difficult to compare the values obtained for algal mineral composition with data in the literature because, apart from variations due to the factors pointed out above, details on the mineralization method employed are often omitted. Mineral content in seaweeds was higher than the values reported for edible land plants (Indegaard & Minsaas, 1991; Ortega-Calvo et al., 1993). Macromineral contents of typical land vegetables (USDA, 2001), expressed for direct comparison as $Na + K + Ca + Mg$ in mg/100 g dry weight, are: carrots 3276; sweet corn 1347, green peas 1452; potato 6015; tomato 3429. Only the high macromineral value of spinach (9679), was comparable to that of seaweeds (Table 2).

Most of the algae showed a Na content (Table 2) relatively higher than the value reported for land vegetables (USDA, 2001). Nevertheless, Na/K ratios were below 1.5 in all the seaweeds studied (0.33–1.34), which is interesting from the point of view of nutrition, since the intake of sodium chloride and diets with a high Na/ K ratio have been related to the incidence of hypertension. For instance, Na/K ratios in olives and sausages are 43.63 and 4.89, respectively (Ortega-Calvo et al., 1993).

Of the land plants selected, trace element content in sweet corn $(Fe + Zn + Mn + Cu, 4.9 \text{ mg}/100 \text{ g})$ was similar to that of *Laminaria* (5.1 mg/100 g, Table 2) and spinach showed the highest trace element content (50.7 mg/100 g), even higher than Nori.

The levels of trace elements detected (Table 2) also fit within the ranges observed in previous reports on seaweeds (Mabeau & Fleurence, 1993; Ortega-Calvo et al., 1993). Most of the trace elements present in the algal biomass are heavy metals (As, Cd, Cu, Hg, Pb, Zn), but

Table 2

Major mineral and trace elements (mg/100 g dry weight) determined by atomic absorption spectrophotometry in edible brown and red seaweeds

Mineral	Brown seaweeds			Red seaweeds		
	Fucus	Laminaria	Wakame	Chondrus	Nori	
Na	$5469 + 60$	3818 ± 43	7064 ± 166	4270 ± 62	$3627 + 115$	
K	$4322 + 46$	11.579 ± 128	$8699 + 144$	3184 ± 0	$3500 + 71$	
Ca	$938 + 7$	1005 ± 5	931 ± 38	420 ± 22	390 ± 17	
Mg	$994 + 13$	$659 + 6$	1181 ± 34	$732 + 6$	$565 + 11$	
Fe	4.20 ± 0.17	3.29 ± 0.54	7.56 ± 1.13	3.97 ± 0.11	10.3 ± 0.41	
Zn	3.71 ± 0.37	1.77 ± 0.44	$1.74 + 0$	7.14 ± 0.13	2.21 ± 0.17	
Mn	5.50 ± 0.11	< 0.5	$0.87 + 0$	1.32 ± 0	2.72 ± 0	
Cu	< 0.5	${<}0.5$	${<}0.5$	< 0.5	< 0.5	
Total cations	$11,736 \pm 127$	17.066 ± 183	$17,885 \pm 383$	8618 ± 90.2	8097 ± 215	

Mean values of triplicate determinations \pm standard deviation.

their content is generally below the toxic limits allowed in several countries (Indegaard & Minsaas, 1991). In the USA, algal products have to comply with the following maximum limits: 45% ash, 40 ppm heavy metals (Food and Nutrition Board, 1981). Copper plus zinc content were below those values in all seaweeds, and Zn content $(1.74-7.14 \text{ mg}/100 \text{ g}, \text{Table 2})$ in marine seaweeds was also below the maximum amount allowed in macroalgae for human consumption in Japan and France (1.5–10 mg/100 g, respectively; Indegaard & Minsaas, 1991). Algal products would supplement the daily intake of some trace elements for adults: Fe, $10-18$ mg; Zn, 15 mg; Mn, 2.5–5 mg and Cu, 2–3 mg (Indegaard $\&$ Minsaas, 1991).

In summary, this study has shown an important mineral content in several edible marine Spanish seaweeds. Edible brown and red seaweeds could be used as a food supplement to help meet the recommended daily adult intakes of some macrominerals and trace elements.

Acknowledgements

This research work was supported by the Comisión Interministerial de Ciencia y Tecnología, CICYT Project ALI98–0830. Thanks are given to Mrs. I. Fernández-Conde and Mr. G. Guerrero for technical assistance.

References

- Bobin-Dubigeon, C., Hoebler, C., Lognoné, V., Dagorn-Scaviner, C., Mabeau, S., Barry, J.-L., & Lahaye, M. (1997). Chemical composition, physico-chemical properties, enzymatic inhibition and fermentation characteristics of dietary fibres from edible seaweeds. Science des Aliments, 17, 619–639.
- Chapman, V. J. & Chapman, D. J. (1980). Sea vegetables (algae as food for man). In Seaweeds and their uses (pp. 62–97). London: Chapman & Hall.
- Fleurence, J. (1999). Seaweed proteins: biochemical, nutritional aspects and potential uses. Trends in Food Science and Technology, 10, 25–28.
- Fleurence, J., & Le Coeur, C. (1993). Influence of mineralisation methods on the determination of the mineral content of brown seaweed Undaria pinnatifida by atomic absorption spectrophotometry. Hydrobiologia, 260/261, 531–534.
- Fleury, N., & Lahaye, M. (1991). Chemical and physico-chemical characterisation of fibres from Laminaria digitata (Kombu Breton): a physiological approach. Journal of the Science of Food and Agriculture, 55, 389–400.
- Food and Nutrition Board. (1981). Food chemical codex (3rd ed.). Washington DC: National Academy Press.
- Honya, M., Kinoshita, T., Ishikawa, M., Mori, H., & Nisizawa, K. (1993). Monthly determination of alginate, M/G ratio, mannitol and minerals in cultivated Laminaria japonica. Nippon Suisan Gakkaishi, 59, 295–299.
- Indegaard, M., & Minsaas, J. (1991). Animal and human nutrition. In M. D. Guiry, & G. Blunden (Eds.), Seaweed resources in Europe: uses and potential (pp. 21–64). Chichester: John Wiley & Sons Ltd.
- Indegaard, M., & Ostgaard, K. (1991). Polysaccharides for food and pharmaceutical uses. In M. D. Guiry, & G. Blunden (Eds.), Seaweed resources in Europe: uses and potential (pp. 169–183). Chichester: John Wiley & Sons Ltd.
- Ito, K., & Hori, K. (1989). Seaweed: chemical composition and potential uses. Food Review International, 5, 101–144.
- Jurković, N., Kolb, N., & Colić, I. (1995). Nutritive value of marine algae Laminaria japonica and Undaria pinnatifida. Die Nahrung, 1, 63–66.
- Kishi, K., Inone, G., Yoshida, A., Fuwa, H., Koishi, H., Koide, G., Miyoshi, T., Inone, T., Yoshida, M., & Omori, A. (1982). Digestibility and energy availability of sea vegetables and fungi in man. Nutrition Reports International, 26, 183–192.
- Kloareg, B., & Quatrano, R. S. (1988). Structure of the cell walls of marine algae and ecophysical functions of the matrix polysaccharides. Oceanographic Marine Biology Annual Reviews, 26, 259–315.
- Lahaye, M., & Kaeffer, B. (1997). Seaweed dietary fibres: Structure, physico-chemical and biological properties relevant to intestinal physiology. Science des Aliments, 17, 619–639.
- Mabeau, S. (1995). Conception and small scale production and nutritional evaluation of new dietary fibre ingredients from seaweeds and seaweed products. Project AAIR 0518, Dietary fibre from seaweed, F-FE 182/95.
- Mabeau, S., & Fleurence, J. (1993). Seaweed in food products: Biochemical and nutritional aspects. Trends in Food Science and Technology, 4, 103–107.
- Michel, C., Sahaye, M., Bonnet, C., Mabeau, S., & Barry, J.-L. (1996). In vitro fermentation by human foetal bacteria of total and purified dietary fibres from brown seaweeds. Br. J. Nutr., 71, 263–280.
- Nisizawa, K., Noda, H., Kikuchi, R., & Watanabe, T. (1987). The main seaweeds in Japan. Hydrobiologia, 151/152, 5–29.
- Ortega-Calvo, J. J., Mazuelos, C., Hermosin, B., & Sáiz-Jiménez, C. (1993). Chemical composition of Spirulina and eucaryotic algae food products marketed in Spain. Journal of Applied Phycology, 5, 425–435.
- Rupérez, P., & Saura-Calixto, F. (2001). Dietary fibre and physicochemical properties of edible Spanish seaweeds. European Journal of Food Research and Technology, 212, 349–354.
- USDA (2001). Agricultural research service. Nutrient Database for Standard Reference, Release 14.
- Yamamoto, T., Otsuka, Y., Okazaki, M., & Okamoto, K. (1979). The distribution of chemical elements in algae. In H. A. Hoppe, T. Levring, & Y. Tanaka (Eds.), Marine algae in pharmaceutical science (pp. 569–607). Berlin: Walter de Gruyter.
- Yoshie, Y., Suzuki, T., Shirai, T., & Hirano, T. (1994). Changes in the contents of dietary fibers, minerals, free amino acids, and fatty acids during processing of dry Nori. Nippon Suisan Gakkaishi, 60, 117–123.