Available online at www.sciencedirect.com
SCIENCE DIRECT
Talanta 66 (2005) 937–942
Talanta
www.elsevier.com/locate/talanta

Application of ultrasound-assisted acid leaching procedures for major and trace elements determination in edible seaweed by inductively coupled plasma-optical emission spectrometry

Raquel Domínguez-González, Antonio Moreda-Piñeiro, Adela Bermejo-Barrera, Pilar Bermejo-Barrera*

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, 15782-Santiago de Compostela, Spain

Received 28 July 2004; received in revised form 4 November 2004; accepted 17 December 2004
Available online 22 January 2005

Abstract

A new method using diluted reagents (nitric and hydrochloric acids and oxygen peroxide) and ultrasound energy to assist metals acid leaching with from edible seaweed was optimized. The method uses a first sonication at high temperature with hydrochloric acid as a previous stage to an ultrasound-assisted acid leaching with 7 ml of an acid solution containing nitric acid, hydrochloric acid and hydrogen peroxide at concentrations of 3.7, 3.0 and 3.0 M, respectively. Optimum conditions for the first sonication step were ultrasound energy at 17 kHz, sonication temperature at 65 °C, an acid volume of 2 ml, an hydrochloric acid concentration of 6.0 M and a sonication time of 10 min. It has been found that the first sonication stage at high temperature with hydrochloric acid is necessary to obtain quantitative recoveries for As, Ba, Fe and V. Otherwise quantitative recoveries were reached for the other elements investigated (Ca, K, Na, Mg, Cd, Cr, Cu, Mn, Ni, Pb and Zn). The repeatability of the ultrasound-assisted acid leaching method was around 10% for all elements. Adequate limit of detection and limit of quantification were reached by using inductively coupled plasma-optical emission spectrometry (ICP-OES) for measurements. The method resulted accurate after analysing several seaweed certified reference materials (IAEA-140/TM, NIES-03 and NIES-09). The method was finally applied to the multi-element determination in edible seaweed samples.

Keywords: Ultrasound-assisted acid leaching; Major and trace elements; Seaweed; Inductively coupled plasma-optical emission spectrometry

1. Introduction

Multi-element determination in biological solid samples requires commonly a prior sample pre-treatment stage. These treatments are based on wet decomposition procedures, most of the time acid digestion processes assisted by microwave energy, which use concentrated nitric acid, hydrochloric acid and/or oxygen peroxide as reagents [1]. These treatments lead to a total dissolution of the biological material except when containing insoluble substances such as silicates. Plant materials, and specially seaweed, present high silicate contents, and the use of hydrofluoric acid is needed to guarantee a total dissolution of the material [1–6]. However, the use of hydrofluoric acid presents several drawbacks such as corrosion of glass and quartz parts of instruments, the use of additional stages to destroy the excess of hydrofluoric acid and the special care needed because of its high corrosive and dangerous properties.

As alternative, the use of diluted acids to extract or leach trace elements from the biological matrices has been proposed by some authors. These procedures do not involve the total matrix sample destruction but the breakdown of the chemical bonds between the trace elements and the matrix sample constituents [7]. Acid leaching procedures can be assisted by ultrasound energy [8–11] in order to speed up the

---

* Corresponding author. Tel.: +34 600942346; fax: +34 981595012.
E-mail address: pbermejo@usc.es (P. Bermejo-Barrera).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.12.051

leaching process because of the induced cavitations process occurring in the liquid when applying ultrasound energy promotes an increase of pressure and temperature, which allow a high analyte transport from the solid particles to the liquid phase [12]. Because this high extracting efficiency, low acids concentrations can be used, implying a low reagents consumption and low wastes.

Because of the current interest on seaweed as natural or health food, the analysis and control of contaminants in such material is needed. This is important for trace elements because these aquatic plants can bio-accumulate high trace elements concentrations, which can be dangerous for Human. In addition, there are not European Union specific regulations concerning seaweed as a food staff and/or levels of potential contaminants, such as some trace elements, in seaweed.

The focus of the current work is the application of a previous ultrasound-assisted acid leaching procedure, which has been shown as adequate for the accurate determination of Ca, Cu, K, Mg, Mn, Na and Zn in seaweed [14], to extract other metals such as Al, As, Ba, Cd, Cr, Cu, Fe, Ni, Pb and V. Because of the lack of accuracy for some elements (Al, As, Ba, Fe and V) a previous treatment with hydrochloric acid was optimized in order to achieve accurate results for all elements.

2. Experimental

2.1. Instrumentation

Optima 3300 DV inductively coupled plasma atomic emission spectrometer (Perkin-Elmer, Norwalk, USA) equipped with an autosampler AS 91 (Perkin-Elmer) and a GemCone nebulizer on a cyclonic spray chamber. Raypa® Model UCI-150 ultrasonic bath with a power of 400 W, working frequencies at 17 and 35 kHz and programmable for temperature and time was from R. Espinar S.L. (Barcelona, Spain). Vibrating ball mill, Retsch (Haan, Germany), equipped with zircon cups (15 ml in size) and zircon balls (7 mm diameter) was used to pulverise dried seaweed samples. Centrifuge Centromix (Selecta, Barcelona, Spain) was used to separate solid and liquid phases. Panasonic domestic microwave oven (Osaka, Japan), programmable for time and microwave power from 100 to 900 W, was used for total digestion of samples. The low pressure poly(tetrafluorethylene) (PTFE) bombs were laboratory-made and hermetically sealed.

2.2. Reagents and standard solutions

Chemicals were of ultrapure grade, using ultrapure water, resistance 18 MΩ cm^{-1} (Millipore Co., Bedford, MA). Multi-element standard solutions were prepared by combining stock standard solutions (1000 or 10,000 g l^{-1}) supplied by Merck (Poole, Dorset, UK). Nitric acid 70.0% was supplied by Merck, while hydrochloric acid 37% and hydrogen peroxide 33% were from Panreac (Barcelona, Spain). The certified reference materials were IAEA-140/TM, *Fucus—Sea Plant Homogenate*, from the International Atomic Energy Agency and NIES-CRM-09, Sargasso, from National Institute of Environmental Studies.

2.3. Seaweed samples

Edible seaweeds were purchased by a local manufacturer as a 100 g dried product or as canned cocked seaweeds (around 40 g wet weight). The samples include five Atlantic seaweeds harvested in Galician coast (Northwest Spain): *Porphyra* and *Palmaria* (red seaweed) and *Undaria pinnatifida*, *Himanthalia elongata*, and *Laminaria ochroleuca* (brown seaweed). Canned cocked seaweeds were previously lyophilised at −40 °C for 2 weeks (LYPH-LOCK® 6 l freeze dry system, model 77530 from Labconco Corporation, Kansas City, USA). Seaweed samples were pulverised in a vibrating zircon ball mill for 45 min (power of 75%) and were kept into pre-cleaned polyethylene vials.

2.4. Microwave acid digestion procedure

Powdered seaweed samples were acid digested according with a microwave induced acid digestion procedure described elsewhere [13,14]: around 0.2 g and 2 ml of concentrated nitric acid were subjected to two microwave cycles at 330 W and 2 min inserting a 5 min cooling stage in between. After cooling in an ice-bath for 10 min, 1 ml of concentrated hydrogen peroxide was added and the bombs were irradiated twice at 360 W and 3 min, inserting a 5 min cooling stage in between too. Finally, acid digests were made up to 10 ml with ultrapure water and were kept into polyethylene vials at 4 °C before measurements. Because of the high silicon content in seaweeds, a non-soluble silicate was obtained in the acid digests after this treatment. All seaweed samples have been subjected to the microwave acid digestion procedure three or four times and R.S.D. values were lower than 5% for all elements investigated.

2.5. Ultrasound-assisted acid leaching procedure

Pulverised seaweed, about 0.2 g, were directly weighted into centrifuge tubes and 2 ml of 6.0 M hydrochloric acid was added. Since the ultrasonic energy in the Raypa® Model UCI-150 ultrasonic bath is generated in every spot of the surface, the placement of samples in the bath is not critical. Therefore, around six tubes were placed in the centre of the bath and a first sonication stage at 17 kHz and at 65 °C for 10 min using was carried out (Fig. 1). This step is needed in order to destroy cellular walls allowing a better leaching of some elements such as Fe [14] or As [13,15]. The solution was centrifuged at 3000 rpm for 10 min and the acid liquid phase was separated by decantation and it was reserved. According to Ref. [14], a volume of 7 ml of an acid/oxidising solution (3.7, 3.0 and 3.0 M of nitric acid, hydrochloric acid and hydrogen peroxide, respectively) was added and a second sonication

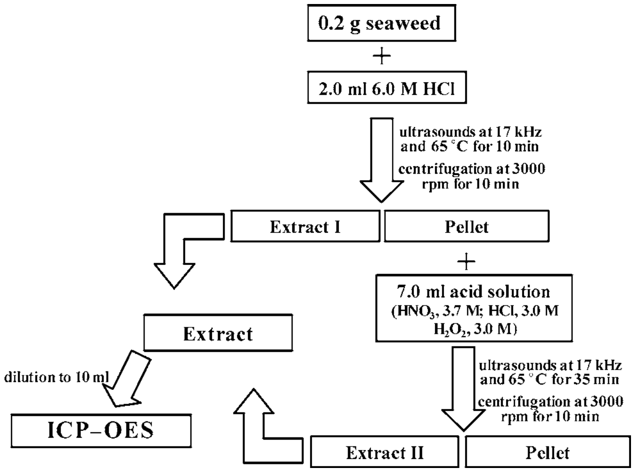

Fig. 1. Extraction scheme for ultrasound-assisted acid leaching of metals from seaweed.

stage at 17 kHz and 65 °C for 35 min (Fig. 1) was performed. After centrifugation (3000 rpm and 10 min), the acid liquid phase was separated by decantation and combined with the hydrochloric acid leachate. Finally, combined acid leachates were made up to 10 ml with ultrapure water. All seaweed samples have been subjected to the ultrasound-assisted acid leaching procedure three or four times and R.S.D. values were lower than 5% for all elements investigated.

2.6. *ICP-OES determinations*

Major elements (Ca, K, Mg and Na) were determined in the acid leachates by ICP-OES (radial configuration) using a dilution factor of 1:10. Trace elements (Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) were determined in the acid leachates by ICP-OES (axial configuration). Aqueous calibrations were performed to determine major elements (analyte concentration between 0 and 10 mg l^{-1}). However, the standard addition technique, covering analyte concentration ranges between 0 and 10 mg l^{-1} for Al, Cu, Fe, Mn and Zn; between 0 and 2 mg l^{-1} for As, Cd, Cr, Ni, V and Pb; between 0 and 0.2 mg l^{-1} for Ba, was used for trace elements determinations.

3. Results and discussion

3.1. *Effect of an hydrochloric acid pre-treatment before the ultrasound-assisted acid leaching*

According to Muñoz et al. [15], the use of a first hydrochloric acid treatment before trace metals extraction from seafood products is necessary. Membranes cells are disrupted by hydrochloric acid and mechanical stirring and quantitative total inorganic arsenic recoveries are reached from seafood products. Similarly, the use of a previous treatment with hydrochloric acid combined with ultrasound energy was found necessary to extract total arsenic [13] and iron and manganese [14] from seaweed. Therefore, the effect of a sonication stage at 17 kHz with a 6.0 M hydrochloric acid solution on the trace elements extraction from seaweed was studied as a previous step to the application of an ultrasound-assisted acid leaching procedure [14]. The sonication time was fixed in 10 min for all these experiments (Fig. 1) and experiments were carried out at 20 °C (room temperature) and at 65 °C. Fig. 2 shows the major and trace elements concentrations measured after the application of the ultrasound-assisted acid leaching procedure from Ref. [14] (coded as “without HCl treatment”), with the first hydrochloric acid sonication step at 20 °C (coded as “sonication at room temperature”) and with the first hydrochloric acid treatment at 65 °C (coded as “optimized method”). It can be seen that the amount of metal extracted for most of the elements are similar for method using the first hydrochloric acid sonication step (at 20 and 65 °C) and for the conventional method without the hydrochloric acid pre-treatment (ultrasound-assisted acid leaching method from Ref. [14]), except for Al, As, Fe and Zn. This assumption has been proved after statistical comparison (Cochran’C and Bartlett’s tests at a 95.0% to compare variances and ANOVA test to compare means) of both data sets. Therefore, Al, Fe and Zn acid leaching from seaweeds offers a similar behaviour than that previously reported for As [13], involving the use of a first hydrochloric acid sonication step before the ultrasound-assisted acid leaching process to assess quantitative results.

3.2. *Effect of the temperature water bath on the ultrasound-assisted acid leaching*

Recent studies have revealed that moderate temperature conditions combined with ultrasounds help to increase the metal releases from biological samples [8,11]. Thus, the use of a water-bath temperature of 90 °C combined with ultrasound energy at 35 kHz allows the quantitative extraction of selenium from mussel samples [11], quantitative recoveries whose cannot be reached by sonication at room temperature [16]. Therefore, the effect of temperature at the first hydrochloric acid treatment has been investigated by sonication different seaweeds samples at 17 kHz for 35 min and at 20 °C (room temperature) or at 65 °C. Fig. 2 shows that major (Ca, K, Mg and Na) and trace elements (Cu, Mn, Ni, Pb and Zn) are efficiently released when the first hydrochloric acid treatment is carried out at 20 °C (room temperature), but Al, As, Ba, Fe and V are not quantitatively leached from seaweed under these conditions. Again, Al, As and Fe need more drastic conditions than other major and trace elements to be leached from seaweed. In addition, Ba and V offer a similar leaching trends and it can be concluded that these elements could be stronger bound to seaweed matrix than other elements. Therefore, a first hydrochloric acid treatment at high temperature (65 °C) is necessary to reach a quantitative extraction for Al, As, Ba, Fe and V from seaweed.

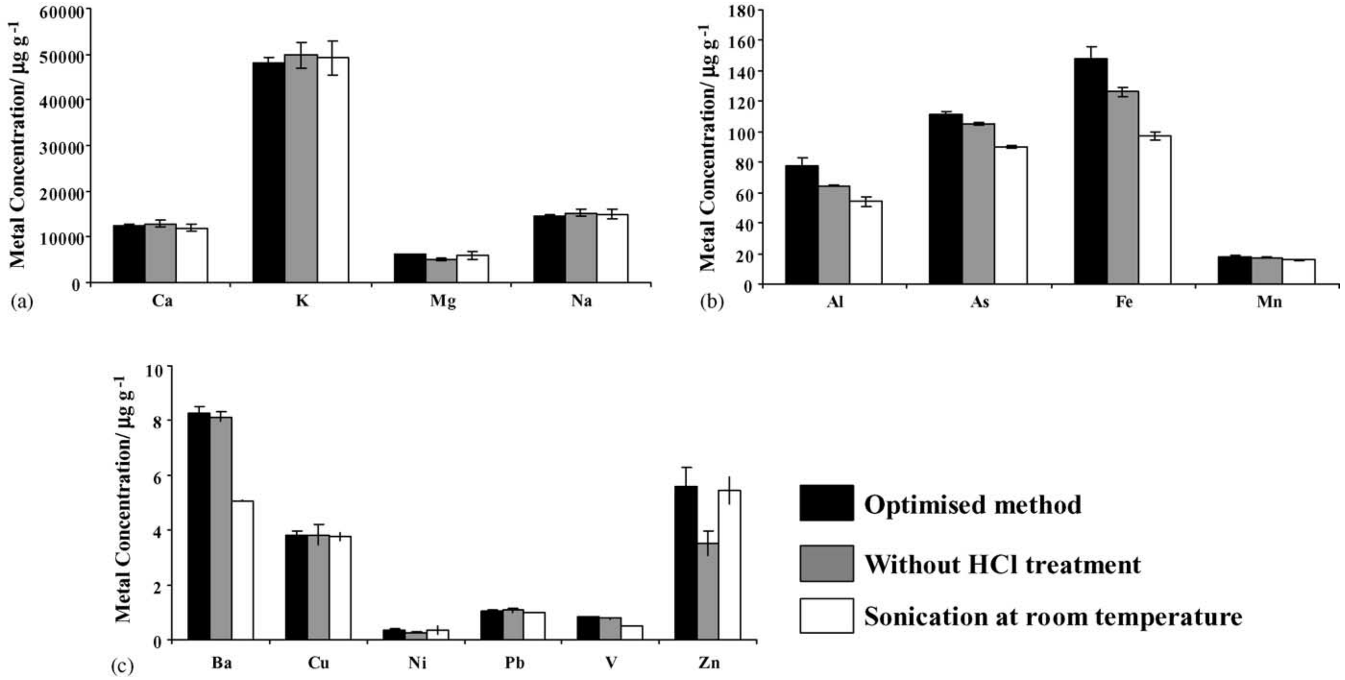

Fig. 2. Effect of a hydrochloric acid treatment and the sonication temperature on the acid leaching efficiency.

3.3. Analytical performances

The repeatability of the over-all procedure was assessed by analysing a seaweed sample which was subjected seven times to the optimised ultrasound-assisted acid leaching process. R.S.D.s are listed in Table 1. It can be seen good precision is achieved for all elements.

Table 1
LOD, LOQ and repeatability of the methods

	LOD[a] ($\mu g\,g^{-1}$)	LOQ[b] ($\mu g\,g^{-1}$)	R.S.D.[c] (%)
Al	0.65	2.18	9.0
As	0.63	2.10	11.6
Ba	0.01	0.05	3.2
Ca	0.92	3.06	4.5
Cd	0.02	0.08	1.3
Cr	0.12	0.39	8.6
Cu	0.30	1.00	4.6
Fe	0.11	0.38	5.0
K	17.03	56.76	8.3
Mg	0.13	0.43	7.6
Mn	0.01	0.04	2.7
Na	3.63	12.11	8.3
Ni	0.36	1.21	11.4
Pb	0.07	0.25	5.0
V	0.12	0.40	1.9
Zn	0.02	0.07	1.0

[a] LOD = 3 S.D./m (S.D.: standard deviation of 11 measurements of a blank; m: standard addition slope).

[b] LOQ = 10 S.D./m (S.D.: standard deviation of 11 measurements of a blank; m: standard addition slope).

[c] R.S.D. = S.D./mean (S.D.: standard deviation of seven determinations of a seaweed sample; mean: the mean seven determinations of a seaweed sample.

The limit of detection and limit of quantification are also listed in Table 1. It can be seen good values to determine major and trace elements in seaweed samples.

The accuracy of the method was studied by analysing three certified reference materials (IAEA-140/TM, *Fucus—Sea Plant Homogenate*, NIES-CRM-03, *Chlorella*, and NIES-CRM-09, *Sargasso*). Each reference material was subjected to the optimised ultrasound-assisted acid leaching procedure four times, and the elements were measured twice in each acid leachate. Similarly, the three certified reference materials were analysed after performing a microwave assisted acid digestion [13,14]. Tables 2 and 3 show the results obtained after analysing the acid leachates and the acid digest, respectively. It can be seen, after statistical comparisons (*t*-test), that good agreement with the certified/informative concentrations, for all elements except Al, Pb and V in all certified reference materials and for Cr in IAEA-140/TM have been obtained for acid leachates. However, good agreement with certified/informative concentrations has been obtained after using the HNO_3/H_2O_2 microwave assisted acid digestion. These results could be expected because since it was commented before, more drastic conditions for temperature and hydrochloric acid concentration were needed for Al and V, elements which appear to be the strongest bound to seaweed matrix.

3.4. Applications

The proposed method was applied to 11 edible seaweed samples: two Nori (*Porphyra*) samples, two Dulse (*Palmaria*) samples, two Wakame (*Undaria pinnatifida*) samples, two

Table 2
Analysis of certified reference materials after ultrasound-assisted acid leaching

	IAEA-140/TM (*Fucus*)		NIES-CRM-09 (*Sargasso*)		NIES-CRM-03 (*Chlorella*)	
	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})
Al	1184 ± 260[a]	283 ± 7	215[a]	103 ± 6	–[b]	<2.18[c]
As	44.3 ± 2.2	46.0 ± 0.6	115 ± 9	113 ± 1	–[b]	<2.10[c]
Ba	20.2 ± 8.9[a]	7.9 ± 0.1	–[b]	8.4 ± 0.3	–[b]	5.0 ± 0.1
Ca	12730 ± 1782	13224 ± 221	13400 ± 536	13563 ± 155	4900 ± 294	5025 ± 110
Cd	0.537 ± 0.027	0.550 ± 0.010	0.15 ± 0.02	0.14 ± 0.01	0.025[a]	<0.08[c]
Cr	10.4 ± 0.8	3.6 ± 0.2	0.2[a]	0.20 ± 0.04	–[b]	1.1 ± 0.1
Cu	5.05 ± 0.30	4.89 ± 0.13	4.9 ± 0.2	4.9 ± 0.1	3.5 ± 0.3	3.3 ± 0.1
Fe	1256 ± 38	1220 ± 9	187 ± 6	178 ± 3	1850 ± 92	1724 ± 31
K	31100 ± 2488	35353 ± 389	61000 ± 1830	73002 ± 523	12400 ± 620	10316 ± 5
Mg	9070 ± 907	9490 ± 883	6500 ± 325	6321 ± 82	3300 ± 198	3156 ± 78
Mn	56.1 ± 2.2	54.1 ± 0.1	21.2 ± 1.1	20.4 ± 0.5	69 ± 5	63 ± 1
Na	32000 ± 6720	31250 ± 2818	17000 ± 850	17829 ± 125	–[b]	<12.11[c]
Ni	3.79 ± 0.42	3.65 ± 0.04	–[b]	0.7 ± 0.1	–[b]	0.50 ± 0.06
Pb	2.19 ± 0.64	1.40 ± 0.02	1.35 ± 0.05	1.17 ± 0.04	0.6[a]	1.3 ± 0.1
V	3.67 ± 0.48	2.96 ± 0.02	1.0 ± 0.1	0.7 ± 0.1	–[b]	<0.40[c]
Zn	47.3 ± 1.9	46.8 ± 1.2	15.6 ± 1.2	14.2 ± 0.5	20.5 ± 1.0	19.7 ± 0.2

[a] Informative value.
[b] Not given.
[c] <LOQ.

Sea spaghetti (*Himanthalia elongata*) samples, two Kombu (*Laminaria ochroleuca*) samples, and a canned seaweed in brines sample.

Portions of around 0.2 g were subjected to the optimised ultrasound-assisted acid leaching procedure by triplicate and to a microwave assisted acid digestion (three times) too. Each acid leachate and acid digest was analysed twice, so the mean concentration reported for each sample is related to six independent determinations.

Table 4 lists the metals concentrations ranges for groups of samples according to their type (brown or red seaweed). It can be seen that metal concentrations ranges after ultrasound-assisted acid leaching and microwave assisted acid digestion are similar, even for Cr, Pb and V, metals for which lack of accuracy was observed when analysing certified reference materials. However, higher Al concentrations were obtained for acid digests than those obtained in acid leachates.

Table 3
Analysis of certified reference materials after HNO_3/H_2O_2 microwave assisted acid digestion

	IAEA-140/TM (*Fucus*)		NIES-CRM-09 (*Sargasso*)		NIES-CRM-03 (*Chlorella*)	
	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})
Al	1184 ± 260[a]	1220 ± 14	215[a]	209 ± 2	–[b]	<2.18[c]
As	44.3 ± 2.2	43.0 ± 0.3	115 ± 9	110 ± 1	–[b]	<2.10[c]
Ba	20.2 ± 8.9[a]	15.4 ± 0.1	–[b]	6.0 ± 0.1	–[b]	4.2 ± 0.1
Ca	12730 ± 1782	12901 ± 156	13400 ± 536	13677 ± 125	4900 ± 294	5032 ± 93
Cd	0.537 ± 0.027	0.561 ± 0.008	0.15 ± 0.02	0.13 ± 0.01	0.025[a]	<0.08[c]
Cr	10.4 ± 0.8	9.7 ± 0.3	0.2[a]	0.18 ± 0.03	–[b]	0.8 ± 0.1
Cu	5.05 ± 0.30	4.93 ± 0.03	4.9 ± 0.2	5.0 ± 0.1	3.5 ± 0.3	3.4 ± 0.1
Fe	1256 ± 38	1219 ± 17	187 ± 6	182 ± 1	1850 ± 92	1901 ± 33
K	31100 ± 2488	33404 ± 355	61000 ± 1830	70022 ± 445	12400 ± 620	12527 ± 183
Mg	9070 ± 907	9121 ± 541	6500 ± 325	6771 ± 64	3300 ± 198	3374 ± 84
Mn	56.1 ± 2.2	54.1 ± 0.4	21.2 ± 1.1	20.2 ± 0.2	69 ± 5	66 ± 1
Na	32000 ± 6720	32320 ± 2541	17000 ± 850	17750 ± 212	–[b]	<12.11[c]
Ni	3.79 ± 0.42	3.50 ± 0.08	–[b]	0.5 ± 0.1	–[b]	0.48 ± 0.03
Pb	2.19 ± 0.64	1.85 ± 0.05	1.35 ± 0.05	1.28 ± 0.04	0.6[a]	1.2 ± 0.1
V	3.67 ± 0.48	3.33 ± 0.15	1.0 ± 0.1	0.9 ± 0.1	–[b]	<0.40[c]
Zn	47.3 ± 1.9	46.3 ± 1.0	15.6 ± 1.2	14.7 ± 0.4	20.5 ± 1.0	19.6 ± 0.3

[a] Informative value.
[b] Not given.
[c] <LOQ.

Table 4
Metal concentration ranges, in $\mu g\, g^{-1}$, for different seaweed samples

	Brown seaweed: Kombu, Wakame and Sea spaguetti ($n = 6$)		Red seaweed: Dulse and Nori ($n = 4$)		Canned seaweed in brines[a] ($n = 1$)	
	Acid leaching	Acid digestion	Acid leaching	Acid digestion	Acid leaching	Acid digestion
Al	4.8–14.9	2.4–10.7	9.4–78.2	5.6–66.4	8.9 ± 1.4	6.3 ± 0.6
As	20.3–72.0	19.8–71.3	7.5–25.2	7.1–24.5	10.9 ± 0.2	11.1 ± 0.1
Ba	<0.05[b]–19.2	<0.05[b]–19.8	<0.05[b]	<0.05[b]	12.5 ± 0.3	12.1 ± 0.2
Ca[c]	0.6–1.0	0.8–1.1	0.2–0.5	0.2–0.6	1.4 ± 0.1	1.5 ± 0.1
Cd	<0.1[b]–1.6	<0.1[b]–1.3	<0.1[b]–0.2	<0.1[b]–0.3	1.0 ± 0.1	1.0 ± 0.1
Cr	<0.39[b]	<0.39[b]	<0.39[b]–0.60	<0.39[b]–0.80	<0.39[b]	<0.39[b]
Cu	1.3–3.2	1.4–3.6	3.4–6.1	3.0–6.6	2.3 ± 0.2	2.4 ± 0.2
K[c]	3.3–7.8	3.7–7.5	1.4–5.3	1.4–5.9	1.7 ± 0.2	1.5 ± 0.1
Fe	19.6–84.7	19.9–84.4	95.1–205.1	99.5–208.8	82.4 ± 2.6	84.3 ± 4.0
Mg[c]	3.3–6.6	3.3–6.7	0.6–1.8	0.7–1.8	2.2 ± 0.2	2.2 ± 0.1
Mn	2.9–59.4	2.9–60.3	18.8–22.1	18.2–22.9	22.6 ± 0.5	23.0 ± 0.2
Na[c]	2.9–6.9	2.4–6.7	0.6–1.0	0.6–1.2	6.9 ± 0.2	6.5 ± 0.3
Ni	<1.2[b]–2.6	<1.2[b]–2.5	2.7–3.7	2.5–3.5	1.7 ± 0.1	1.9 ± 0.2
Pb	0.4–0.9	0.5–1.0	0.6–1.4	0.7–1.4	1.1 ± 0.1	1.0 ± 0.1
V	<0.4[b]–3.8	<0.4[b]–3.9	6.2–32.1	6.3–33.1	3.6 ± 0.1	3.6 ± 0.1
Zn	10.6–71.2	10.4–71.3	48.8–158.9	46.6–158.5	44.9 ± 0.7	43.3 ± 0.8

[a] Sample analysed six times.
[b] <LOQ.
[c] Metal concentration in % (m/m).

4. Conclusions

The proposed method offers a rapid and efficient sample preparation method for the direct determination of major and trace elements in seaweed. The method avoids the use of hydrofluoric acid in conventional acid digestion to dissolve the relative high silicate contents in seaweed. In addition, since diluted acids are used and nitrous vapours formation are reduced, the method offers advantages such as low reagent cost and a low wastes, being this procedure an environmental friendly methodology. The use of a first treatment with hydrochloric acid combined with sonication at high temperatures (65 °C) increases metal recoveries for Al, As, Ba, Fe, V and Zn. However, lack of accuracy has been observed for Al, Cr, Pb and V when analysing certified reference materials, although, similar metals concentrations were observed for these elements, except for Al, when analysing several seaweed samples after the proposed ultrasound-assisted acid leaching and the microwave assisted acid digestion procedures.

Acknowledgements

The authors thank the “Secretaría Xeral de Investigación e Desenvolvemento–Xunta de Galicia” for financial support (research projects PGIDIT02RMA20301PR and PGIDIT02PXIB20901PR). Thanks to ALGAMAR (Redondela–Pontevedra–Spain) for providing edible seaweed samples.

References

[1] R. Chakraborty, A.K. Das, M.L. Cervera, M. de la Guardia, Fresenius J. Anal. Chem. 355 (1996) 99.

[2] M.A. Munilla, I. Gómez-Pinilla, S. Rodenas, M.T. Larrea, Analysis 23 (1995) 463.

[3] M.H. Norziah, C.Y. Ching, Food Chem. 68 (2000) 69.

[4] L. Campanella, G. Crescentini, P. Avino, A. Moauro, Analysis 26 (1998) 210.

[5] A. Jordanova, A. Strezov, M. Ayranov, N. Petkov, T. Stoilova, Water Sci. Technol. 8 (1999) 207.

[6] S. Farías, S. Pérez-Arisnabarreta, C. Vodopivez, P. Smichowski, Spectrochim. Acta B 57 (2002) 2133.

[7] P. Bermejo-Barrera, A. Moreda-Piñeiro, A. Bermejo-Barrera, Talanta 57 (2001) 906.

[8] P. Bermejo-Barrera, A. Moreda-Piñeiro, A. Bermejo-Barrera, J. Anal. At. Spectrom. 15 (2000) 121.

[9] A.V. Filgueiras, J.L. Capelo, I. Lavilla, C. Bendicho, Talanta 53 (2000) 433.

[10] C.C. Nascentes, M. Korn, M.A.Z. Arruda, Microchem. J. 69 (2001) 37.

[11] P. Bermejo-Barrera, O. Muñiz-Naveiro, A. Moreda-Piñeiro, A. Bermejo-Barrera, Anal. Chim. Acta 439 (2001) 211.

[12] J.L. Luque-García, M.D. Luque de Castro, Trends Anal. Chem. 22 (2003) 41–47.

[13] O. Muñiz-Naveiro, A. Moreda-Piñeiro, A. Bermejo-Barrera, P. Bermejo-Barrera, At. Spectrosc. 25 (2004) 79–87.

[14] N. Ladra-Ramos, R. Domínguez-González, A. Moreda-Piñeiro, A. Bermejo-Barrera, P. Bermejo-Barrera. Atom. Spectrosc. (2005) in press.

[15] O. Muñoz, D. Vélez, R. Montoro, Analyst 124 (1999) 601–607.

[16] H. El Azouzi, M.L. Cervera, M. de la Guardia, J. Anal. At. Spectrom. 13 (1998) 533.