Talanta 82 (2010) 1313–1317

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A simple ion chromatography method for inorganic anion analysis in edible seaweeds

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ARTICLE INFO

Article history:
Received 28 April 2010
Received in revised form 14 June 2010
Accepted 28 June 2010
Available online 24 July 2010

Keywords:
Seaweed
Ion chromatography
Anion
Sulphate
Chloride

ABSTRACT

A new, simple, fast and sensitive ion chromatography (IC) method, for the simultaneous analysis of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate in edible seaweeds was developed and reported for the first time. The validation of the analytical method was studied in terms of linearity, sensitivity, precision and accuracy. All standard calibration curves showed very good correlation between anion peak area and concentration ($r > 0.999$). Limits of detection and quantitation ranged between 0.002–0.05 mg/L and 0.01–0.1 mg/L, respectively and indicated the high sensitivity of the method. Relative standard deviation values of repeatability and inter-day precision for standard anions with the same sample were less than 2%. Anion recoveries ranged from 97 to 113% for chloride and from 87 to 105% for sulphate, respectively and showed the fairly good accuracy of the method. The method was applied to the analysis of inorganic anions in brown and red edible seaweeds. Brown seaweeds were characterized by higher chloride content up to 33.7–36.9%, while red seaweeds were characterized by higher sulphate content (45–57%). Sulphate content in seaweeds is related to the presence of sulphated polysaccharides of biological importance. The method developed was well applicable to mineral anion analysis in edible seaweeds and shows suitability and reliability of use in other food samples of nutritional importance.

1. Introduction

Seaweeds draw from the environment were they live, the sea, an incomparable wealth of mineral elements [1], some of which are essential for the proper functioning of the body. This rich array of essential nutrient minerals and trace elements, include mineral macronutrients such as sodium, calcium, magnesium, potassium, chlorine, sulphur and phosphorus; and micronutrients such as iodine, iron, zinc, copper, selenium, molybdenum, fluoride, manganese, boron, nickel and cobalt. Mineral fraction can account for up to 40% dry weight of some seaweeds [2], however, in some cases mineral content of seaweeds is recorded even higher than that of land plants and animal products [3]. Minerals in marine algae are attributed to ions associated with charged polysaccharides [4,5]. Specifically, edible brown and red seaweeds can be used as a food supplement to help meet the recommended daily intakes of some macrominerals and trace elements [6].

Sulphate and chloride are the main anions found in seaweeds. Sulphate may account for a 50% of the ashes [2], and it is an important constituent of charged polysaccharides in marine algae, related to high salt concentration in the environment and with specific functions in ionic regulation. Such sulphated mucilages are not found in land plants [7]. Sulphate is mainly derived from charged polysaccharides, such as fucan, alginate or laminaran in brown seaweeds or from agar and carrageenan (galactans) in red ones [6].

Physicochemical properties of dietary fibre in edible seaweeds have been related to the hydrophilic nature of the charged polysaccharides [2]. Sulphated polysaccharides from edible marine algae are not toxic for humans and, especially fucans and alginic acid derivatives, are known to exhibit different biological properties, such as: anticoagulant, anti-inflammatory, antiviral, or antitumoral activities [8–12]. As an attempt to find a substitute for heparin, the anticoagulant activity of sulphated polysaccharides from seaweeds has been the most researched property. Anticoagulant capacity has been shown to be related to sulphate content in fucans [13]. Also, sulphated polysaccharides from brown and red seaweeds have been reported to exhibit antioxidant capacity *in vitro* and potentially could be used as natural antioxidants by the food industry [14].

Many different methods have been reported in the literature for the analysis of mineral cations and anions in water and in plant materials. Flame atomic absorption spectrophotometry has been traditionally used for cation determination either in water or in

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Abbreviations: IC, Ion chromatography; RSD, Relative standard deviation; *r*, correlation coefficient; LOD, limit of detection; LOQ, limit of quantitation.

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0039-9140/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.talanta.2010.06.062

vegetable ashes [6,15–18]. Regarding anions, many methods have been developed which are in most cases specific for the separate analysis of every single anion. The Association of Official Analytical Chemists (AOAC, 2005) [19] and the American Public Health Association (APHA, 1998) [20] defined individual methods, which have been traditionally used, for the determination of chloride, fluoride, nitrate, sulphate and phosphorus in water. Since then, there have been many efforts to improve the utilization of these methods. In this way, potentiometry with ion-selective electrodes (ISE) seems to be the most popular and convenient method for fluoride determination [21]; Volhard method is a classical way to determine chloride in food [22]; while the automated ascorbic acid colorimetric method is more extensively used for phosphate determination in water and soil [23]. However, some of these methods suffer from many interferences with other anions.

Also, sulphate ions are measured using several direct and indirect analytical principles, including volumetric, gravimetric, colorimetric and turbidimetric methods. Currently, volumetric [24], colorimetric [25] and gravimetric methods for sulphate in water [19a] are not widely used because they are time consuming and require a skilled person to determine the end point of the analysis. Turbidimetric method is a well known quantification technique for sulphate analysis based on the precipitation of sulphate ions as insoluble barium sulphates [19b], which was improved for the determination of sulphate in plants and soils [26] and also used in seaweeds [6].

A comparative study of sulphate quantification methods, i.e. turbidimetric, ion chromatography (IC) and inductively coupled plasma atomic emission spectrometry (ICP-AES) indicates clearly that the widely used turbidimetric method is limited by its quantification range and suffers from interference of nitrate ions, while IC method shows a higher precision and lack of interferences in quantifying sulphate [27].

From its inception in 1975 [28], IC is currently a well-established technique in analytical chemistry for the separation and determination of inorganic anions. Because the most common mode of detection has been conductivity, this technique was usually applied to the determination of common anions (fluoride, chloride, nitrate and sulphate). Recent developments such as the use of higher capacity columns, larger loop injection, and more complex detection schemes have increased its utilization in a variety of areas. IC analysis of anionic and cationic species in plant materials has already been reported [29–32], using different sample preparation techniques and detection methodologies. IC is a direct way to determine sulphate concentration; moreover, this chromatographic method also permits in a single run the simultaneous determination of most anions like: fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate.

In view of the nutritional relevance to determine accurately mineral anion content, especially sulphate in edible seaweed and other food resources, and the usefulness of ion chromatography for the aqueous determination of ions, the aim of the present study was to develop a new, simple, fast and sensitive ion chromatography method for the simultaneous analysis of main anions in seaweeds, where no complex handling of the sample is required except for the preparation of ashes and filtration.

2. Material and methods

2.1. Reagents and standards

Deionized water from Millipore Milli-Q (18.2 MΩ cm, equipped with a Millipack 0.22 μm filter) was used for the preparation of solutions. Eluent solution was prepared by dissolving appropriate amounts of sodium carbonate (Na_2CO_3, Merck) and sodium hydrogen carbonate ($NaHCO_3$, Merck) powders in Milli-Q water and degassing in an ultrasonic bath for 10 min. Accurate weighing of chemicals was performed on a Boeco BBC 22 model (Boeco, Germany) analytical balance.

Standard solutions of fluoride, chloride, nitrate, phosphate and sulphate were prepared by appropriate dilution of their anion standard stock Fluka (Sigma–Aldrich, Buchs, Switzerland) solution of analytical grade (1000 mg/L, TraceCERT®) for IC to obtain the desired concentrations of each analyte. Composition of commercial standard anions is described as follows: Fluoride Standard, 1000 mg/L F^- in water, prepared with high purity NaF and water *Trace*SELECT®Ultra. Chloride Standard, 1000 mg/L Cl^- in water, prepared with high purity NaCl and water *Trace*SELECT®Ultra. Nitrate Standard, 1000 mg/L $NO_3{}^-$ in water, prepared with high purity $NaNO_3$ and water *Trace*SELECT®Ultra. Phosphate Standard, 1000 mg/L $PO_4{}^{3-}$ in water, prepared with high purity Na_2HPO_4 and water *Trace*SELECT®Ultra. Sulphate Standard, 1000 mg/L $SO_4{}^{2-}$ in water, prepared with high purity Na_2SO_4 and water *Trace*SELECT®Ultra. Moreover, standard solutions containing 25, 50, 75 and 100 mg/L of chloride and sulphate anions were prepared for the recovery assay.

2.2. Instrument and ion chromatographic conditions

A Metrohm Advanced compact ion chromatographic instrument (IC-861 model, Metrohm AG, Switzerland) controlled using Metrodata IC Net 2.3 software and attached to an Advance Sample Processor (IC-838) with an injection Valve Unit (IC-812) with a 20 μL sample loop was used in all analyses. The instrument was also equipped with a Pump (IC-818), an Eluent Degasser (IC-837) and a Liquid Handling Unit (IC-833) with a 0.45 μm filter that required a minimal volume of 10 mL for the samples. Detection was performed with a Conductivity Detector (IC-819) Advanced from Metrohm.

Separation was performed in a Metrosep A Supp 5–250 column (250 × 4 mm, 5 μm particle size). The carrier material was an anion-exchange polymer of polyvinyl alcohol with quaternary ammonium groups. All measurements were carried out at 32 °C (column temperature) under the following elution conditions: 3.2 mM sodium carbonate/1 mM sodium hydrogen carbonate at 0.70 mL/min as mobile phase, prepared as previously described. In order to adjust the baseline to 15 μS/cm, 50 mM sulphuric acid solution and ultrapure water (Milli-Q) were used for automatic chemical suppression.

Under the working conditions all anions were separated completely and total analysis time was 28 min. Anions in samples were identified by the coincidence of their retention times with those of commercial standard anions. Peak areas were utilized for quantitative analysis.

2.3. Validation of IC method

2.3.1. Linearity and sensitivity

The external standard calibration method used was based upon commercial Fluka standard solutions (1000 mg/L) and appropriate dilutions in ultrapure water. Calibration curves of different anions were prepared in seven levels evenly distributed from: 1 to 120 mg/L for chloride and sulphate, 0.75 to 90 mg/L for nitrate and phosphate, 0.2 to 24 mg/L for bromide, and 0.02 to 2.4 mg/L for fluoride and nitrite.

In order to check the sensitivity of the method under the working conditions used, the limits of detection (LOD) and quantitation (LOQ) were studied. LODs were calculated as the concentration corresponding to three times the peak height of the baseline noise (signal-to-noise ratio equals 3); whereas LOQs were set as 10 times the noise height (signal-to-noise ratio equals 10).

Table 1
Summarized calibration data of different anions in standard solution by IC.

Analyte	Range (mg/L)	Regression equation	Correlation coefficient (r)	LOD (mg/L)	LOQ (mg/L)
Fluoride	0.02–2.4	$y = 1.12899x$	0.99934	0.002	0.01
Chloride	1–120	$y = -4.33317e^{-5}x^2 + 1.21667x$	0.99965	0.002	0.01
Nitrite	0.02–2.4	$y = 32.8006x$	0.99971	0.052	0.17
Bromide	0.2–24	$y = 3.66138x$	0.99995	0.006	0.02
Nitrate	0.75–90	$y = 2.49096x$	0.99903	0.004	0.01
Phosphate	0.75–90	$y = 4.97956x$	0.99904	0.008	0.03
Sulphate	1–120	$y = -22.1121e^{-5}x^2 + 2.0793x$	0.99908	0.003	0.01

IC = Ion chromatography; y = concentration (mg/L); x = area (μS/cm × sec).
LOD = limit of detection; LOQ = limit of quantitation. LOD and LOQ were determined at a signal to noise ratio of about 3 and 10, respectively.

2.3.2. *Precision*

The precision of the IC method was assessed in terms of repeatability and intermediate (inter-day) precision by analyzing three replicate determinations on the same day and two determinations on two different days with the same sample of anion standards. Only most common anions in seaweeds were taken under consideration (fluoride, chloride, nitrate, phosphate and sulphate). Random concentrations of each analyte were prepared. The relative standard deviation (RSD) percentage of individual measurements was determined and expressed for intra-day precision and for inter-day precision. Also, RSD (%) corresponding to retention time, peak height and peak area were determined. To consider a good precision of the method, RDS values must be less than 5%.

2.3.3. *Accuracy*

To study the reliability and suitability of the IC method, recovery experiments were carried out. Recovery percentage was obtained by measuring anion content in one brown (*Laminaria*) and in one red alga (*Mastocarpus*), before and after the addition of four different concentrations (25, 50, 75 and 100 mg/L) of chloride and sulphate standard solutions. Each test was repeated three times. For this assay we only focused on these two anions because of their quantitative importance in each type of algae. Experimental values found were compared with the corresponding theoretical concentration.

2.4. *Sample material*

The brown seaweeds (Phaeophyta) *Himanthalia elongata* (L.) S.F. Gray (sea spaghetti), *Laminaria saccharina* (L.) J.V. Lamouroux (sweet Kombu) and *Bifurcaria bifurcata* R. Ross; and the red seaweeds (Rhodophyta) *Mastocarpus stellatus* (Stackhouse) Guiry and *Gigartina pistillata* (S.G. Gmelin) Stackhouse were obtained from a local supplier (Porto-Muiños, Cambre, Coruña, Spain). Marine algae were cleaned from epyphytes and sand, washed with tap running water, dried and milled to less than 1.0 mm particle size before analysis. Residual moisture content was determined by oven drying to a constant weight at 105 °C.

2.5. *Preparation of seaweed sample for anion analysis by IC*

Generally, ash content is the percentage of inorganic matter in a sample, and so, it can be used to analyze anion or cation content. To determine ash content, seaweed samples (0.5 g) were incinerated in a digitally controlled Hobersal HD-230 muffle furnace (Barcelona, Spain) at 550 °C for 16 h and weighed. Ash content was calculated and expressed as a percentage of the seaweed sample dry weight. Just before injection, ashes were milled with pestle and mortar and an aliquot (25 mg) dissolved in 50 mL Milli-Q water. To separate particulate matter, filtration was performed through Whatman No. 44 ashless cellulose filter (3 μm particle size, 110 mm diameter). Then all samples were appropriately diluted in ultrapure water and adjusted to a final volume of 10 mL to give an approximate concentration of 100 mg/L, poured to auto-sampler polyethylene tubes and analyzed by ion chromatography.

2.6. *Statistical analysis*

All determinations were performed at least in triplicate. Data were expressed as mean values ± standard deviations and reported on a dry matter basis. Relative standard deviation (RSD) percentage was calculated as standard deviation/mean value.

3. Results and discussion

3.1. *Validation of IC method*

3.1.1. *Linearity and sensitivity*

The linearity of the IC method was evaluated for the following anions: fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate (Table 1). The calibration curves showed a linear relationship (linear through zero) between the peak area and concentration over a wide range of concentrations for fluoride, nitrite, bromide, nitrate and phosphate. In order to adjust more properly to the whole and wider working range (1–120 mg/mL), chloride and sulphate presented a quadratic relationship (quadratic through zero) in their calibration curve.

Calibration data of different anions as summarized in Table 1, showed a good correlationship between peak area (x) and concentration (y, mg/L), with a correlation coefficient $r > 0.999$ for all analytes under the IC working conditions used.

The LODs results showed that the high sensitivity of IC method was obtained for all anions with values between 0.002 and 0.05 mg/L (Table 1). Also the LOQs values (0.01–0.1 mg/L), corresponding to the lowest level on the calibration curve that could be determined with appropriate precision and accuracy under the experimental conditions, confirmed the high sensitivity of the method.

3.1.2. *Precision and accuracy*

RSD (%) of repeatability was below 2.1% and RSD (%) of inter-day was below 1.4%, which indicated that the IC method has both good repeatability and inter-day precision (Table 2). Besides, assays of repeatability for retention times, peak heights and peak areas were carried out and results are shown in Table 3. Likewise, RSD (%) values were less than 2% and illustrated the good precision of the analytical method.

To determine the accuracy, ash solutions of *Laminaria* and *Mastocarpus* spiked with four different concentrations of chloride and sulphate standards were used. Recovery values amounted to 97.5–113% for chloride and 87.6–105% for sulphate (Table 4). Closeness of the results to 100% confirmed the fairly good accuracy of the IC method.

Table 2
Precision of the IC method.

	Repeatability ($n = 3$)			Inter-day precision ($n = 2$)		
Analyte	Prepared (mg/L)	Found (mg/L)	RSD (%)	Prepared (mg/L)	Found (mg/L)	RSD (%)
Fluoride	1	1.0 ± 0.0	0.2	1	1.0 ± 0.0	0.6
Chloride	50	49.4 ± 0.3	0.6	50	49.4 ± 0.3	0.5
Nitrate	10	8.4 ± 0.0	0.1	10	8.4 ± 0.1	0.9
Phosphate	6	5.9 ± 0.1	2.1	6	5.9 ± 0.1	1.4
Sulphate	50	49.0 ± 0.1	0.1	50	49.2 ± 0.4	0.8

Data are mean values ± standard deviation.
IC = Ion chromatography; RSD = Relative standard deviation.

Table 3
Repeatability ($n = 3$) of retention time, peak height and peak area.

Analyte	Prepared (mg/L)	Retention time (min)	RSD (%)	Peak height	RSD (%)	Peak area	RSD (%)
Fluoride	1	6.13	0.4	1.87	1.64	18.23	0.8
Chloride	50	9.51	0.2	68.76	1.19	832.74	0.9
Nitrate	10	16.59	0.3	2.82	1.25	67.44	0.5
Phosphate	6	21.33	0.3	0.84	0.68	23.53	1.4
Sulphate	50	25.42	1.1	16.22	1.73	496.43	0.6

Peak height = μS/cm; Peak area = μS/cm × sec.
RSD = Relative standard deviation.

Table 4
Recovery ($n = 3$) of the IC method.

Seaweed	Chloride in sample (mg/L)	Added chloride (mg/L)	Found (mg/L)	Recovery (%)	Sulphate in sample (mg/L)	Added sulphate (mg/L)	Found (mg/L)	Recovery (%)
Laminaria	36.6 ± 0.2	25	63.2 ± 0.5	108.2 ± 0.4	5.3 ± 0.1	25	29.6 ± 0.2	100.7 ± 0.7
		50	92.4 ± 0.4	108.6 ± 0.2		50	57.5 ± 0.3	105.3 ± 0.5
		75	119.6 ± 1.0	108.6 ± 0.7		75	85.6 ± 0.7	103.3 ± 0.6
		100	145.8 ± 0.7	107.1 ± 0.6		100	113.2 ± 1.0	105.8 ± 0.7
Mastocarpus	3.4 ± 0.1	25	28.8 ± 0.1	113.7 ± 0.2	55.5 ± 0.7	25	83.7 ± 0.7	105.0 ± 1.6
		50	56.0 ± 0.5	107.9 ± 1.0		50	105.6 ± 1.0	100.8 ± 1.6
		75	84.3 ± 1.7	109.4 ± 2.0		75	135.8 ± 4.4	102.0 ± 3.3
		100	100.5 ± 0.5	97.5 ± 0.5		100	137.8 ± 0.6	87.6 ± 0.1

Data are mean values ± standard deviation; IC = Ion chromatography.

3.2. *Application of IC method to seaweed analysis*

Differences in composition between brown and red seaweeds related to their polysaccharide composition are well known. Red seaweeds are mostly composed of sulphated galactans, such as agar and carrageenans, while brown seaweeds are composed of alginates, fucans, and laminarans [8,2,33]. Sulphate seems to be a typical component of marine algal polysaccharides, mostly derived from fucans in brown algae or from galactans in red ones. Therefore, differences in seaweed polysaccharides are translated into differences in anion composition. Fig. 1 shows a typical ion chromatogram for different standard anions and seaweed samples showing these differences. All anions in the samples were separated completely.

Ash and anion content in seaweeds are shown in Table 5. Ash content ranged from 24.9 to 36.4% algal dry weight, with the lowest value for the red alga *Mastocarpus* and the highest for the brown alga *Himanthalia*. Ash content in most land vegetables, with an average value of 5–10 g/100 g dry weight [34], is usually much lower than in marine algae. The ash values obtained fit well within the wide ranges, from 8 to 40% of algal dry weight, reported for seaweeds [3–5]. Also these values are in agreement with previous results [2,6].

Total anions content (% ash dry weight, Table 5) was lower for brown (40.6–48.9%) than for red seaweeds (55.4–61.7%). Besides, differences in relative anion abundance between brown and red seaweeds were found (Table 5, Fig. 1). Thus, brown seaweeds were characterized by a higher chloride content (33.7–36.9%), while red ones by a higher sulphate content (45–57%). These sulphate values agree with those reported previously by the AOAC gravimetric method [2] and by the gelatin-barium chloride spectrophotometric method [6,14] applied to seaweed samples, showing the characteristic difference in composition between brown and red seaweeds. In this way, this pattern agrees with that found in Hawaiian seaweeds [35] with a higher sulphate content in red (2–8% dry weight) than in brown algae (1–2% dry weight). Also, other red seaweeds, such as *Grateloupia lithophila* in the Gulf of Mannar (India),

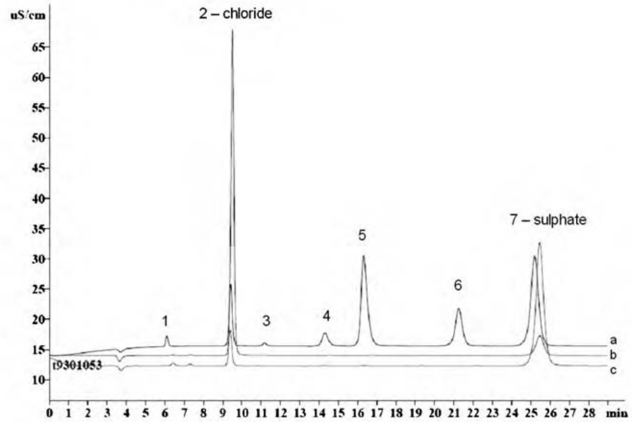

Fig. 1. A typical ion chromatogram for different samples: (a) standard solution of anions, (b) *Laminaria saccharina* (brown seaweed), (c) *Mastocarpus stellatus* (red seaweed). Identified peak anions: (1) fluoride; (2) chloride; (3) nitrite; (4) bromide; (5) nitrate; (6) phosphate; (7) sulphate.

Table 5
Ash and anion content in edible seaweeds by IC.

Anion[a]	Brown seaweeds			Red seaweeds	
	Himanthalia	*Bifurcaria*	*Laminaria*	*Mastocarpus*	*Gigartina*
Ash[b]	36.4 ± 0.2	34.3 ± 0.2	34.8 ± 0.1	25.0 ± 0.1	34.6 ± 0.5
Fluoride	0.1 ± 0.0	0.3 ± 0.0	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.0
Chloride	37.0 ± 1.1	33.7 ± 0.2	34.8 ± 0.5	4.1 ± 0.1	9.9 ± 0.7
Nitrite	nd	0.1 ± 0.0	nd	nd	nd
Bromide	nd	0.1 ± 0.0	nd	0.1 ± 0.0	0.1 ± 0.0
Nitrate	0.2 ± 0.1	0.2 ± 0.0	0.1 ± 0.1	0.2 ± 0.0	0.1 ± 0.0
Phosphate	0.1 ± 0.0	nd	0.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
Sulphate	11.6 ± 1.2	13.5 ± 0.7	5.5 ± 0.5	57.1 ± 0.8	45.1 ± 1.0
Total anions	48.9 ± 0.3	47.8 ± 0.2	40.6 ± 0.2	61.7 ± 0.2	55.4 ± 0.3

Data are mean value of triplicate determinations ± standard deviation. nd: not detected.

[a] Anion content expressed as % ash dry weight.

[b] Ash content expressed as % algal dry weight.

show higher sulphate values (162.8 mg/g algal dry weight), than the brown ones (0.88–61 mg/g algal dry weight) [36].

Chloride content in seaweeds may be related to the water salinity of the sea where they live [37], and can vary from one sea to another and with depth. Red seaweeds use to live in deeper waters with lower salinity levels that could explain the reason why they seem to have much lower chloride contents than brown seaweeds (Table 5). Moreover, mineral content has been shown to vary according to seaweed species, oceanic residence time, geographical place of harvest, seasonal, annual, environmental and physiological factors [1,5,38].

Besides chloride and sulphate, other minor anions were estimated (Table 5). Small amounts of fluoride, nitrate and phosphate were found in all the seaweeds. The brown seaweed *Bifurcaria* also presented trace amounts of nitrite and bromide, but no phosphate. Moreover, red seaweeds also exhibited trace amounts of bromide.

4. Conclusion

A simple, fast and sensitive ion chromatography method for the individual anion determination in edible seaweeds was developed. The brown and red edible seaweeds studied presented a rich array of inorganic anions. Chloride and sulphate were the main anions in brown and red seaweeds, respectively. The presence of sulphate is of especial relevance since it seems to play an important role in the biological properties of sulphated polysaccharides. This ion chromatography method showed good precision, accuracy, sensitivity and a lack of interference when applied to the anion analysis of seaweeds. This method could also be applied, with a similar preparation of the ashes, to the anion determination in other food samples of nutritional importance.

Acknowledgements

This research work was supported by the Spanish Ministerio de Ciencia e Innovación, Project AGL2008-00998ALI. Thanks are given to the algal supplier Porto-Muiños (Coruña, Spain) and to E. de Vega-Matallanos and I. Alvarez-Acero for IC technical assistance.

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