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Total arsenic, inorganic arsenic, lead and cadmium contents in edible seaweed sold in Spain

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Abstract

Total arsenic, inorganic arsenic, lead and cadmium contents were determined in 112 samples of seaweed preparations sold in Spain (seaweed packed in plastic or cardboard box, seaweed in the form of tablets and concentrates, foods containing seaweed, and canned seaweed). The concentration ranges found, expressed in mg/kg, dry weight, were: total As (0.031–149), inorganic As (<0.014–117), Pb (<0.050–12.1) and Cd (<0.003–3.55). For all the contaminants there were failures to comply with legislated values. In particular, all the samples of *Hizikia fusiforme* exceeded the inorganic As limit established in some countries, and a considerable number of species exceeded the Cd limit set by international regulations. With respect to food safety, consumption of 3 g/day of the samples analysed could represent up to 15% of the respective Tolerable Daily Intakes (TDI) established by the WHO. The situation is especially alarming for intake of inorganic As from *H. fusiforme*, which can be three times the TDI established.

Keywords: Lead; Cadmium; Arsenic; Inorganic arsenic; Edible seaweed

1. Introduction

In Western countries, the use of seaweed has traditionally concentrated on the extraction of compounds used by the pharmaceutical, cosmetics and food industries (production of agar, alginates, carrageenan, etc.) (Mabeau and Fleurence, 1993; Caliceti et al., 2002). In recent decades there has been an increase in direct consumption of seaweed as food, partly because of the nutritional (Mabeau and Fleurence, 1993; Darcy-Vrillon, 1993) and therapeutic (van Netten et al., 2000) benefits that these products provide. The mean intake of seaweed in Western countries is far from equalling that of Eastern countries, estimated for the Japanese population as 3.3 g dry seaweed per day (Darcy-Vrillon, 1993), but we must not forget the existence in all countries of extreme consumers, such as those who follow a macrobiotic diet.

From a nutritional point of view, seaweeds are interesting because of their high content of dietary fibre (33–50%), rich in soluble fractions with hypocholesterolemic and hypoglycemic effects (Mabeau and Fleurence, 1993; Jiménez-Escrig and Sánchez-Muniz, 2000). They are a source of proteins, with an amino acid composition of nutritional interest (Fleurence, 1999; Wong and Cheung, 2000). Minerals also attain considerable levels (8–40%), so that seaweed could be used as a food supplement in order to reach the recommended daily intakes of some macrominerals and trace elements (Rúperez, 2002). Finally, because of their low lipid content, 1–2%, they constitute a negligible energy source (Darcy-Vrillon, 1993). On the other hand, seaweed has a high metal pollution accumulation capacity. This reason it has been used as a bio-indicator for marine environment contamination (Riget et al., 1997), and there are studies on heavy metal contamination in different species of environmental and commercial importance (Hou

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and Yan, 1998; Sánchez-Rodríguez et al., 2001; Caliceti et al., 2002). Metal contamination is an aspect that can condition the safety of edible seaweeds as a food, but there are very few studies on inorganic contaminants in commercially available seaweed preparations (Norman et al., 1987; Ortega-Calvo et al., 1993; Munilla et al., 1995; van Netten et al., 2000; Hsu et al., 2001; Almela et al., 2002).

France, the USA, Australia and New Zealand have established specific regulations for toxic elements in edible seaweed (Mabeau and Fleurence, 1993; ANZFA, 1997). Other countries, such as Spain, do not legislate specifically for seaweed. At present, the European Community has not fixed maximum contents of contaminants in seaweed (Official Journal of the European Communities, Regulation (EC) No 466/2001).

The edible seaweeds sold in Spain come from regions in the north of the country or are imported from Japan, China, Korea and Chile. Existing data on contents of heavy metals and arsenic in edible seaweed sold in Spain (Ortega-Calvo et al., 1993; Almela et al., 2002) show that several samples do not comply with existing legislation. The cited studies provided a first approach to evaluating the food safety of seaweeds, but they are not sufficiently extensive in terms of number of samples and periodicity of sampling to permit characterization of the products to which the consumer has access. The aim of the present study is to evaluate the food safety, in terms of total arsenic, inorganic arsenic, Pb and Cd contents, of an extensive, representative range of edible seaweeds sold in Spain in various forms: dried seaweed, seaweed tablets and concentrates, seaweed incorporated in other foods (noodles, hamburgers, pizzas, soups, biscuits, etc.) and canned seaweed. We also wish to provide a database for future legislative enforcements.

2. Materials and methods

2.1. Instruments

Pb and Cd were determined by graphite furnace atomic absorption spectroscopy (GFAAS) with longitudinal AC Zeeman (AAnalyst 600, Perkin–Elmer, Madrid, Spain), equipped with a transversely heated graphite atomizer and a built-in, fully computer-controlled AS-800 autosampler (Perkin–Elmer). Pyrolytic graphite coated tubes with an inserted L'vov platform were used. Total and inorganic As were determined with an AAS model 3300 (Perkin–Elmer) equipped with an autosampler (AS-90, Perkin–Elmer) and a flow injection hydride generation system (FIAS-400, Perkin–Elmer).

Other equipment used included a domestic microwave oven (Optiquick DUO, Moulinex, Spain) with a maximum power of 900 W, a sand bath (PL 5125, Raypa, Scharlau, S.L., Spain), a muffle furnace equipped with a Eurotherm Controls 902 control program (K 1253, Heraeus, Spain), a mechanical shaker (KS 125 Basic, IKA Labortechnik, Merck Farma y Química, Spain) and an Eppendorf 5810 centrifuge (Merck).

2.2. Reagents

Commercial standard solutions (1000 mg L^{-1}) of As(V), Pb and Cd were used (Merck). Deionized water (18.2 MΩW cm) was used for the preparation of reagents and standards. All chemicals were of at least *pro analysis* quality or better. All glassware was treated with 10% v/v HNO_3 for 24 h, and then rinsed three times with deionized water before use.

2.3. Samples

A total of 112 samples were analysed: 52 samples were seaweed packed in plastic or cardboard box, 11 seaweed tablets and concentrates, 28 foods containing seaweed and 21 canned seaweed.

The products, which came from Spain, Chile, China, Korea and Japan, were purchased in shops in the city of Valencia (Spain) during the year 2002. The products with a high humidity content, e.g. canned seaweed, were freeze-dried and then crushed to a fine powder in a mill. The samples sold in dried form were only crushed in a mill. All samples were stored in previously decontaminated twist-off flasks and kept at 4 °C until analysis.

2.4. Total arsenic determination

Dry ashing mineralization and quantification by flow injection-hydride generation atomic-absorption spectrometry (FI-HG-AAS) were employed (Almela et al., 2002). Samples (0.25 g) were treated by 2.5 mL of ashing aid suspension (20% w/v $MgNO_3$ + 2% w/v MgO) and 5 mL of nitric acid (50% v/v). The mixture was evaporated to dryness and mineralized at 450 °C with a gradual increase in temperature. The white ash was dissolved in 5 mL 6 M HCl, reduced with 5 mL of reducing solution (5% w/v KI and 5% w/v ascorbic acid) and made up to 25 mL with 6 M HCl. The analytical conditions used for arsenic determination by FI-HG-AAS were the following: loop sample 0.5 mL; reducing agent 0.2% (w/v) $NaBH_4$ in 0.05% (w/v) NaOH, 5 mL min^{-1} flow rate; HCl solution 10% (v/v), 10 mL min^{-1} flow rate; carrier gas argon, 100 mL min^{-1} flow rate; wavelength 193.7 nm; spectral band-pass 0.7 nm; electrodeless discharge lamp system 2; lamp current setting 400 mA; cell temperature 900 °C.

Calibration standard solutions of As(III) were prepared from a reduced standard solution of As(V), using a mixture containing 5% (w/v) KI and 5% (w/v) ascorbic acid as reducing solution. Triplicate analyses were performed for each sample. The limit of detection for total As was 0.025 mg/kg dry weight (dw).

2.5. Inorganic arsenic determination

Analysis was performed by acid digestion, solvent extraction FI-HG-AAS (Almela et al., 2002). Deionized water (4.1 mL) and concentrated HCl (18.4 mL) were added to the samples (0.5 g) and the mixture was left overnight. After reduction by HBr (2 mL) and hydrazine sulphate (1.5% w/v, 1 mL), the inorganic arsenic (i-As) was extracted into chloroform (3 × 10 mL) and back-extracted into 1 mol L^{-1} HCl (2 × 10 mL). For the determination of i-As in the back-extraction phase 2.5 mL of ashing aid suspension (20% w/v $MgNO_3$ + 2% w/v MgO) and 10 mL of concentrated HNO_3 were added. The mixture was evaporated to dryness and then treated in the same way as for total As (dry ashing FI-HG-AAS). Calibration standard solutions of As(III) were used. Triplicate analyses were performed for each sample. The limit of detection for inorganic As was 0.014 mg/kg dw.

2.6. Cadmium and lead determination

Analysis was performed by wet digestion GFAAS (Almela et al., 2002). The sample (0.20 g) was placed in a high pressure poly(tetrafluoroethylene) (PTFE) vessel, and 2 mL of 65% HNO_3 and 1 mL of 35% H_2O_2 were added. The vessel was sealed with the screw cap and placed inside the microwave oven. Samples were irradiated at a 700 W power setting for 3 cycles of 1 minute. After digestion, the vessel was cooled, filtered and diluted with water to a final volume of 25 mL. The furnace programme [temperature (°C)/ramp time (s)/hold time (s)] employed for Cd determination was: drying (90 °C/10 s/20 s; 120 °C/10 s/20 s; 130 °C/5 s/40 s; 300 °C/5 s/5 s); pyrolysis (500 °C/10 s/20 s); cooling (20 °C/10 s/20 s); atomization (1400 °C/0 s/5 s); cleaning (2450 °C/1 s/5 s). For the determination of Pb the same furnace programme was used, with the