Journal of Food Composition and Analysis 53 (2016) 49–60

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

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

Original research article

Element content and daily intake from dietary supplements (nutraceuticals) based on algae, garlic, yeast fish and krill oils—Should consumers be worried?

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ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form 15 August 2016
Accepted 19 September 2016
Available online 19 September 2016

Keywords:
Krill oil
Fish oil
Essential elements
Non-essential elements
Garlic
Food supplement
Algae
Food composition
Food analysis

ABSTRACT

The element content of sixty seven food supplements falling into five different categories was determined with an Agilent 8800 Triple Quadrupole ICP-MS and the maximum daily intake calculated. The determined elements were: Rb, Cs, Mg, Ca, Sr, Ba, V, Cr, Mn, Fe Co, Cu, Zn, Mo, Se, I, Br, B, Al, As, Cd, Sb and Pb. The majority of supplements contained significantly less essential elements than the recommended daily intake. Exceptions were two algae based products leading to a very high iron intake. The use of 3 other algae based products would result in increased iodine intake. Of the non-essential elements determined the intake of inorganic arsenic from all supplements was below the limit set by ANSI 173, but several algae based and one garlic based supplement contained levels of inorganic arsenic above the limit set in China for food supplements. Generally garlic, fish oil and krill oil based products pose little risk of inadvertent increased intake of essential and non-essential elements. Algae based products can lead to intakes above the recommended limits for specific elements and generally contain higher amounts of all elements. None of the tested food supplements poses a direct risk to healthy adults.

1. Introduction

Dietary supplements are used by an estimated 50% of the population through the western world; out of these, an estimated 8–25% use botanical and herbal supplements (Geshwin et al., 2010; Genuis et al., 2012; Garcia-Alvarez et al., 2014). The market for food supplements increased significantly in the last decades. In 2005 the market size in the EU was estimated to be 5 billion €; the estimate for the USA was 20 billion $ in 2010 (Gershwin et al., 2010). Dietary supplements include vitamin and mineral supplements and plant and animal based products. Marketed as food supplements, they have to comply with laws applicable to food, but not drugs. In the US, the main applicable regulation for dietary supplements is the Dietary Supplement Health and Education Act (DSA) of 1994 and follow-on legislation like 21 CFR Part 111 (Gershwin et al., 2010). Within the EU they have to comply with Directive 2002/46/EC and follow-on legislation like 2006/37/EC. Both regulations deal mostly with production, permitted ingredients and labelling issues. The laws regulating metal contamination of food are also applicable to food supplements within the EU and the US. The American Institute for Standards has developed maximum levels for certain elements in food supplements (ANSI, 2010). The area of dietary supplements is not regulated by the laws governing the production of drugs (Pharmacopeia). In the US, supplements do not need approval by the FDA (2015), but production facilities need to be registered by the FDA, and cGMP regulation must be followed. Claims on labels in the US are not allowed to include statements concerning treatment of disease or conditions, but are allowed if supported by inconclusive evidence (FDA, 2009). Within the EU, it is required that any health claims are substantiated by scientific evidence (EC, 2002, 2015b).

For this study, out of the several thousand individual products available over the counter in the USA and UK, 67

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http://dx.doi.org/10.1016/j.jfca.2016.09.008
0889-1575/

products containing the main ingredient algae, garlic, yeast, fish or krill oil were randomly chosen based on availability (market survey). Three out of the 67 studied food supplements were fortified with minerals or trace elements according to their label. All others are recommended either to increase intake of poly-unsaturated fatty acids (fish and krill oils) or to increase intake of phytochemicals thought to be beneficial to health, e.g., allicin in garlic.

During this study the aim was to determine the total element content of a variety of essential and non-essential elements in these dietary supplements using ICP-MS/MS. The determined content was used in conjunction with the maximum daily dose recommended by the manufacturers to calculate maximum daily intake resulting from use of these supplements. Calculated consumption was compared to the recommended daily allowance (RDI) or adequate intake (AI) for essential elements and minimal risk levels (MRL) for non-essential elements (where such levels have been defined). The maximum permitted levels were taken from NSF International Standard/American National Standard 173 (ANSI, 2010), United States Pharmacopeia (USP) (USP, 2015), European and Australian food/food supplement legislations (ANZ, 2015; EC, 2015a), MRL values were found in publications of the Agency for Toxic Substances and Disease Registry and the integrated Risk Information System (IRIS) of the U.S. Environmental Protection Agency (EPA) (IRIS, 2015) for the relevant elements. In addition to total arsenic levels, the level of inorganic arsenic was estimated using hydride-generation (HG) ICP-MS/MS without chromatography, since total arsenic does not reflect the toxicological potency of this element.

2. Materials and methods

2.1. Samples

In total, sixty seven dietary supplements were used (details: Table S1). Seven commercially available products based on either marine algae (kelp or fucus, n = 3), single cell algae chlorella (n = 1) or spirulina (n = 3) were purchased in the UK or California. Ten garlic-based products containing dried garlic (n = 7) or garlic extract (n = 3) and two yeast-based products, one for use as a selenium supplement and the other a commercial food product (Marmite™), were also sourced. Additional 19 pure krill oil supplements and 30 fish oil supplements (fish oil without elemental additives n = 28) were purchased in the UK or California.

2.2. Quality controls and statistical analysis

The following certified reference materials were analysed alongside the samples: NIST1568a (Rice) Standard Reference Material 1568b Rice Flour and RM8415 (Whole Egg Powder) Reference Material 8415 Whole Egg Powder both from the National Institute of Standards and Technology (NIST, Gaithersburg, USA), ERM-BCR–211 (Rice), BCR-402 (White Clover) and BCR-062 (Olive Leaves) from the Institute for Reference Materials and Measurements (Geel, Belgium), DORM-3 (Fish Protein Dogfish Muscle Certified Reference Material for Trace Metals), DOLT-2 (Dogfish Liver Certified Reference Material for Trace MetalsDogfish Liver), TORT-2 (Lobster Hepatopancreas Reference Material for Trace MetalsLobster Hepatopancreas) and DOLT-4 (Dogfish Liver Certified Reference Material for Trace MetalsDogfish Liver) from the National Research Council of Canada, Seronorm urine blank from SERO (Norway) and IAEA-140 (Trace Elements and Methylmercury in Seaweed) from the International Atomic Energy Agency (Vienna, Austria). Results for the different CRM's are given in Table S3 and S4.

2.3. Chemicals

Water (18.2 MΩ cm) provided from a MilliQ water purification system (Millipore, UK) was used throughout this work. Nitric acid (≥69.0%, TraceSELECT®) was purchased from Fluka (Switzerland), hydrogen peroxide (≥30%, analytical reagent grade) and hydrochloric acid (32% laboratory grade) were from Fisher Scientific (Loughborough, UK) as was the ammonia (25% p.a.). Triton-X100 was from BDH (UK). Calibration standards were prepared from 10 mg/kg multi element standard AccuTrace® (AccuStandard®, New Haven, USA), and 1000 mg/kg B, Br, I, Sb and Mo single element standards (High-Purity Standards, USA).

2.4. Sample preparation

Ten tablets or 10 capsules of each individual sample were weighed (whole tablet or content of capsule and additionally capsule shell of powdered samples) and pooled. The tablets were ground and homogenized with a mortar and pestle. Capsules with a powdered, paste or oil-like content were homogenized. Liquids were used directly after homogenization. All samples were stored at room temperature in 15 mL polypropylene (PP) tubes (Corning® Ltd, UK) prior to use.

Open or closed vessel microwave digestion (Mars5, CEM Microwave Technology Ltd, Buckingham, UK) was used for matrix digestion, all samples were digested and measured in triplicate. Open vessel digestion was used for algae and garlic based (not garlic oil) supplements. For these, a portion (100 mg weighed to 0.1 mg) of sample or CRM was placed in PP tubes. One mL HNO_3 was added and samples were pre-digested overnight, the hydrogen peroxide (2 mL) was added to open vessel digests. Samples were heated to 95 °C for 30 min. After cooling the samples were diluted with water to 50 g.

Closed vessel digestion was used for oil-based supplements using Mars5 Microwave digestion system following the recommended procedure of CEM. For this, a portion (100 mg weighed to 0.1 mg) of sample or CRM was placed in the Teflon vessels and 10 mL conc. HNO_3 was added. The vessels were closed and heated to 180 °C for 30 min. After cooling the samples were diluted with water to 50 g. Multi element standards were prepared in water containing 10% HNO_3 (v/v) (closed vessel digestion) or 1% HNO_3 (v/v) (open vessel digestion), the calibration range was from 0.1 μg/kg to 100 μg/kg. Rhodium and germanium (each 10 μg/kg in 1% (v/v) HNO_3) were used as internal standards and added on-line in each case.

Iodine and bromine were determined in alkaline extracts. A portion (100 mg weighed to 0.1 mg) of sample was mixed with 10 g of a solution containing 1% (v/v) ammonia and 0.1% Triton X-100 and homogenized. Algae, garlic and yeast samples were centrifuged after a 24 h extraction period to remove solid particles. Fish and krill oils were only homogenized. Standards were made up in the same solvent. Tellurium (10 μg/kg in the same solvent) was added on-line as internal standard.

Extraction for arsenic speciation (inorganic arsenic): Samples (100 mg weighed to 0.1 mg) were mixed 10 mL of a solution containing with 2% HNO_3 (v/v) or HCl (v/v, for fish and krill oils) and 3% H_2O_2 (v/v) and extracted using microwave assisted extraction as described by Petursdottir et al. (2014). After cooling, the samples were weighed again and centrifuged. The supernatant was used for the determination of inorganic As by HG-ICP-MS/MS.

2.5. ICP-MS/MS

For the determination of the total element content of dietary supplements, an Agilent 8800 Triple Quadrupole ICP-MS (ICP-MS/MS, Agilent Technologies, UK) equipped with a Scott-type spray chamber and a MicroMist concentric glass nebulizer (Glass