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Investigation of chemical modifiers for the direct determination of arsenic in fish oil using high-resolution continuum source graphite furnace atomic absorption spectrometry

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ABSTRACT

High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) has been applied for the development of a method for the determination of total As in fish oil samples using direct analysis. The method does not use any sample pretreatment, besides dilution with 1-propanole, in order to decrease the oil viscosity. The stability and sensitivity of As were evaluated using ruthenium and iridium as permanent chemical modifiers and palladium added in solution over the sample. The best results were obtained with ruthenium as the permanent modifier and palladium in solution added to samples and standard solutions. Under these conditions, aqueous standard solutions could be used for calibration for the fish oil samples diluted with 1-propanole. The pyrolysis and atomization temperatures were 1400 °C and 2300 °C, respectively, and the limit of detection and characteristic mass were 30 pg and 43 pg, respectively. Accuracy and precision of the method have been evaluated using microwave-assisted acid digestion of the samples with subsequent determination by HR-CS GF AAS and ICP-MS; the results were in agreement (95% confidence level) with those of the proposed method.

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1. Introduction

Arsenic is a trace element, which has a great impact on human health. Even at low concentration, As and its compounds may result in various diseases, among them, serious disorders of the central nervous system, peripheral vascular and cardiovascular diseases and skin cancer [1]. The human body might be exposed to As from water, soil, air, and mainly through food [2,3], where seafood usually has the highest concentration of As. Obviously, fish and shellfish products, such as fish oils, may have a high concentration of As compounds as well, since it can be bio-accumulated in fatty tissue [3]. Some products, such as nutritional supplements, are manufactured by further concentrating the crude fish oil, and the control of the different process streams is very important in order to monitor the removal of contaminants, such as As. The concentration of total As in omega-3 fish oil is included in monographs of organizations such as the United States Pharmacopoeia ($< 0.1\ \mu g\ g^{-1}$ As), and monitored worldwide by industrial and commercial organizations.

Fat is an important source of calories and energy. It is very rich in fatty acids, which can be saturated, monounsaturated, or polyunsaturated. In the case of fish oil, the predominant fatty acids are the polyunsaturated omega-3 acids with four to six double bonds, including the relevant eicosapentaenoic acid (EPA) and docosahexenoic acid (DHA) [4,5]. The fat may still be source of different long and intermediate chain fatty acids, which are not produced by the human organism [6]. On the order hand, because of the nonpolar property of fatty tissues, they are great accumulators of organic compounds, among them arsenolipids, such as arsenic fatty acids (AsFA) [7], arsenic hydrocarbons (AsHC) [7,8] and arsenosugar phospholipids [9,10] besides other arsenical compounds, which might affect human health. The arsenolipids in the form of AsHC were tested to be toxic at the in-vivo and the in-vitro level and the cytotoxicity of the AsHCs was comparable to that of arsenite [11].

Different methodologies were developed for the determination of As in raw fish oil and concentrates using inductively coupled plasma optical emission spectrometry (ICP OES) [11], inductively coupled plasma mass spectrometry (ICP-MS) [12,13] and hydride

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generation atomic absorption spectrometry (HG AAS) [14–16]. However, these methods require a sample pretreatment, usually procedures involving microwave-assisted digestion [17] or microwave-induced combustion (MIC) [18]. Atomic absorption spectrometry (AAS) using graphite furnace (GF) atomization is widely employed for the determination of As in different samples [19–21]; however, in the case of oil samples or fish tissues, some negative effects were found. Zmozinski et al. [22], reported the determination of As in seafood and fish using GF AAS and palladium as a chemical modifier. The authors observed that arsenobetaine (AsB) was not detected under these conditions due the low pyrolysis temperature (about 600 °C), at which AsB was not decomposed.

The goal of this work was to develop a strategy for the determination of arsenic in fish oil samples using high-resolution continuum source GF AAS (HR-CS GF AAS), with view of its application in an industrial company, where sample turnaround time, low reagent consumption and relative ease of instrumental operation are very relevant factors. Different permanent and conventional chemical modifiers have been evaluated in order to prevent losses of As independent of its form and/or oxidation state when submitted to the heating program. The results found by the developed method have been compared with those obtained by ICP-MS after sample digestion to ensure the accuracy of the method for routine application in fish oil samples.

2. Materials and methods

2.1. Instrumentation

A high-resolution continuum source atomic absorption spectrometer Model contrAA 600 (Analytik Jena AG, Jena, Germany), with transversely heated graphite tube atomizer was used in all measurements. The instrument is equipped with a 300 W xenon short-arc lamp, operating in a hot-spot mode, which emits a high-intensity continuous spectrum within the wavelength range from 189 to 900 nm. The optical compartment consists of a prism pre-monochromator and an echelle grating monochromator (high-resolution double monochromator), and a linear charge-coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution [23]. The As measurements were carried out at 193.696 nm, using the integrated absorbance of three pixels (peak volume selected absorbance, PVSA, $A_{\sum 3,int}$).

Pyrolytically coated graphite tubes with a PIN platform (Analytik Jena, Part no. 407-A81.025) were used throughout the work. The optimized temperature program used for all determinations with HR-CS GF AAS is shown in Table 1.

The measurements using ICP-MS were carried out with a Model Elan 6000 inductively coupled plasma mass spectrometer (Perkin-Elmer Sciex, Thornhill, Canada). The operating parameters of the ICP-MS instrument are listed in Table 2. Argon with a purity of 99.996% from White Martins (São Paulo, Brazil), was used as plasma and nebulizer gas.

Table 1
Temperature program for the determination of As by HR-CS GF AAS. An argon gas flow of 2.0 L min^{-1} was used in all stages, except in the atomization stage, where the gas flow was interrupted.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)
Drying 1	110	50	20
Drying 2	130	50	20
Pyrolysis	1400	50	10
Atomization	2300	3000	5
Cleaning	2400	1000	4

Table 2
Operational parameters used for ICP-MS.

Radio frequency potential		1100
Gas flow (L min^{-1})		
	Main	15.0
	Auxiliary	1.0
	Nebulizer	0.96
Cones		
	Sampler/skimmer	Pt
Signal measurement		Peak hopping
Readings for replicates		50
Replicates		3
Dwell time (ms)		50
Auto lens mode		On
Detector voltages (V)		
	Pulse	1600
	Analogic	−2260
	Dead time (ns)	50
	Detector operation mode	Dual
Monitored isotopes	^{75}As	

2.2. Reagents and reference materials

Ultrapure water with a resistivity of 18 MΩ cm was obtained from a Model Mega ROUP (Equisul, Pelotas, Brazil) purification system and used for the preparation of the standard solutions and dilution. A stock standard solution of 1000 mg L^{-1} As, as 4-hydroxy 3-nitrobenzenearsenic acid (Roxarsone, ROX), 4-aminobenzenearsenic acid (p-arsanilic acid, p-ASA), arsenate, arsenite, dimethyl arsenic acid (DMA), and monomethyl arsenic acid (MMA) were obtained from (Sigma-Aldrich, Brazil). Ruthenium and Ir (Sigma-Aldrich) solutions of 1000 mg L^{-1} were used as permanent chemical modifiers whereas palladium (Fluka) was used as conventional chemical modifier in solution.

The fish oil samples were obtained from Golden Omega S.A. (Arica, Chile), corresponding to different processes of oil purification following: Sample A-Raw fish oil (origin South Pacific Ocean: Peruvian anchovy *Engraulis ringens* and Chilean mackerel *Trachurus murphyi)*; Sample B-Cleaned fraction (rich in omega-3); Sample C-Waste fraction (dilute omega-3); and Sample D-Final product.

2.3. Procedure in HR-CS GF AAS

Approximately 0.5 g of each sample (A–D), was diluted in 5 mL of 1-propanole in order to reduce the viscosity of the samples. The 1-propanole solvent was proposed by Chaves et al. [24] for the determination of Ca, Cu, Fe, K, Mg, Na, P, S and Zn in biodiesel and vegetable oils via ICP OES and its application for fish oil was found to be a good choice. Aliquots between 10 and 30 μL were transferred to the platform of the graphite tube, previously treated with a total of 400 μg (10 injections of 40 μL containing 40 μg [25,26]), of Ru or Ir permanent chemical modifier. Then 10 μL of Pd solution were added over the sample or standard and submitted to the temperature program.

2.4. Microwave-assisted digestion

For comparison, the samples have been prepared using microwave-assisted acid digestion using a TOPwave laboratory microwave oven (Analytik Jena) with contact-free temperature and pressure control in each of the eight digestion vessels. The oil samples were weighed (about 0.3 g) and transferred to the PTFE vessels of the microwave oven; a mixture of 5.0 mL of concentrated nitric acid and 3.0 mL of 30% hydrogen peroxide was added and the digestion was started using the heating program shown in Table 3. All digestions were carried out in triplicates and

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