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Development of a fast screening method for the direct determination of chlorinated persistent organic pollutants in fish oil by high-resolution continuum source graphite furnace molecular absorption spectrometry

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ABSTRACT

The occurrence of persistent organic pollutants (POPs), mainly organochlorine pesticides and polychlorinated biphenyls, was directly associated with several diseases and environmental endocrine disrupting. In the aquatic environment, POPs can accumulate in fish lipoid tissues due to their high hydrophobicity, and become this way one of the main sources of human exposure to POPs through the consumption of fish meat and oil as Omega-3 source. Chlorine might serve as a proxy for the presence of POPs, and a fast screening of chlorine in a complex matrix, such as fish oil, could provide substantial information about the contamination with POPs. Therefore, a method has been developed in this work for the determination of total chlorine in fish oil samples via molecular absorption of the strontium mono-chloride molecule in the gas phase using high-resolution continuum source graphite furnace molecular absorption spectrometry. The effect of zirconium as permanent chemical modifier in the pyrolysis and vaporization stages was optimized in order to avoid the need for any kind of sample preparation prior to the determination of total chlorine, using just a dilution with 1-propanol. The accuracy has been evaluated using micro-coulometric titration after sample combustion, and the values were statistically in agreement (95% confidence level) between both techniques. The method has been applied for the determination of total chlorine in five different fractions of a commercial pooled marine fish oil sample collected from the Pacific Ocean, where the majority of the fish is Peruvian anchovy (*Engraulis ringens*), two commercial oils from Brazil and three Omega-3 supplements acquired in Germany. The limit of detection of the procedure is 1.8 ng Cl absolute or 0.9 μg g^{-1} Cl in the fish oil. The time required for a single determination is less than 5 min, and less than 15 min for a triplicate determination.

1. Introduction

Chlorine has a huge importance in human health and may be present in several matrices with very different degrees of complexity. Some of the chlorine compounds, known as “organochlorines”, are a class of the “Persistent Organic Pollutants” (POPs) and have properties of accumulation in lipid-rich tissues and sediments (Merib, Nardini, & Carasek, 2014). Therefore, the bioaccumulation of chlorine in fish tissues in aquatic systems emerges as a possible contamination, once fish is an important component of the diet of many people around the world. In addition, the oil obtained from fish is a source of energy and calories, a mixture of colorants, steroids, glycids, phospholipids and fatty acids, where

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polyunsaturated Omega-3 fatty acids can be found, predominantly with four to six double bonds (Pereira et al., 2016).

During the industrial processes leading to the purification of the raw fish oil and concentration of the Omega-3 fatty acids, the concentration of the organochlorine compounds is lowered to meet regulatory specifications, relying on chromatographic methods for the individual quantification of compounds or classes of compounds in the final product. However, the level of complexity and cost required for such determinations, including sample preparation steps, precludes their application in the quality control of an industrial laboratory. Considering that most of the regulated POPs contain chlorine in their molecules, the determination of total chlorine in the oil with little or no sample preparation can be envisaged as an excellent tool in a manufacturing environment.

Usual monitoring methods are gas chromatography with mass spectrometric detection (GC-MS) and to a lesser extent high performance liquid chromatography electron spray ionization mass spectrometry (HPLC-ESI-MS). Both techniques are molecular-specific and are useful if detailed information about the nature of the chlorinated compounds is needed. However, they are often used for target analysis and not giving the total sum of all chlorinated compounds since they are hidden amongst hundreds of other organic compounds, which are in much higher concentrations. Additionally, due to the use of chromatographic separation the sample throughput is not high, leaving alone the need for sample preparation steps.

A variety of methods was proposed to determine chlorine in different matrices, including classical procedures, such as gravimetric or volumetric analysis, ion-chromatography and ion-selective electrode potentiometry (Flores et al., 2008; Mello et al., 2013; Peng, Wu, Lai, Xiao, & Li, 2012; Smith, McMurtrie, & Galbraith, 1977). However, these techniques often require a sample digestion prior to analyte determination, including Schöniger oxidation (Flores, Barin, Mesko, & Knapp, 2007), alkaline fusion (Blackwell, Cave, Davis, & Malik, 1997), pyrohydrolysis (Duarte et al., 2013) or microwave-induced combustion (Flores et al., 2007, 2008). Plasma-based techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS) are not usually employed for the determination of chlorine. In the case of ICP OES, the wavelengths of this element are situated in the vacuum-UV (<200 nm), making it difficult to separate the analytical signal from the noise, unless a purged monochromator is used (Welz et al., 2009). On the other hand, the ionization is also very low due to the high ionization potential of Cl (12 eV) in an argon-based plasma.

Eliminating sample preparation as much as possible from the analytical protocol avoids or at least reduces the risk of contamination and analyte losses, is less time consuming, and often improves the limit of detection. However, only a few analytical techniques have shown some capacity for the determination of chlorine with relative sensitivity and accuracy, mainly for complex matrices, using direct determination. Among these techniques are electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) (Antes et al., 2013; Gois, Pereira, Welz, & Borges, 2014; Gois, Pereira, Welz, & Borges, 2015), laser induced plasma spectrometry (LIPS) (Kaski, Häkkänen, & Korppi-Tommola, 2004), X-ray fluorescence spectrometry (XRF) (Doyle, Saavedra, Tristão, Nele, & Aucélio, 2011), and more recently also high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS) (Bechlin, Ferreira, & Gomes Neto, 2017; Enders et al., 2016; Guarda et al., 2017; Heitmann, Becker-Ross, Florek, Huang, & Okruss, 2006; Nakadi, da Veiga, Aramendia, Garcia-Ruiz, & Resano, 2015; Ozbek & Akman, 2016; Pereira et al., 2014, 2015; Welz, Vale, Pereira, Castilho, & Dessuy, 2014). The last technique is a very robust tool with a high tolerance for complex matrices due to the use of a graphite tube furnace, which makes possible the analysis of liquids, slurries and solid samples. It often permits to skip sample preparation, making this technique an interesting alternative for the determination of chlorine.

For MAS, bands of diatomic molecules that exhibit a pronounced rotational fine structure can be formed in the graphite tube vaporizer employing a molecule-forming reagent and can be monitored for quantitative determination (Welz et al., 2009). The successful application of HR-CS GF MAS is correlated with the continuum radiation source coupled to a high-resolution double monochromator and a linear charge-coupled device (CCD) array detector providing a resolution of $\lambda/\Delta\lambda \approx 175{,}000$, which makes possible the use of the entire spectral region (190–900 nm) for analytical measurement at high resolution (Welz, 2004; Welz et al., 2014). The diatomic molecules formed in the gas phase should have dissociation energies higher than 400 kJ mol^{-1} to ensure their stability at the temperatures of the pyrolysis and vaporization stages, and avoid formation of competitive molecules (Butcher, 2013).

The goal of this work was to develop a fast and simple procedure for the direct determination of chlorine in fish oil samples via the SrCl molecule using HR-CS GF MAS, so that a screening for all organochlorine compounds in a fish oil sample becomes feasible. The method describes the use of strontium carbonate solution as the molecule-forming reagent and Zr as permanent chemical modifier, investigating different parameters, such as pyrolysis and vaporization temperatures in relation to matrix components that could interfere directly with the stability of the molecule.

2. Experimental

2.1. Instrumentation

All measurements have been made using a high-resolution continuum source atomic absorption spectrometer Model contrAA 600 (Analytik Jena AG, Jena, Germany). It is equipped with a transversely heated graphite tube atomizer and a xenon short-arc lamp as the radiation source, with emits a spectral continuum between 190 and 900 nm. The spectrometer consists of a high-resolution double monochromator, equipped with a prism pre-monochromator for pre-dispersion of the radiation and an echelle grating monochromator for the high resolution. The analytical signal is detected using a CCD array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution (ca. 1.5 p.m./pixel at 200 nm).

Chlorine has been determined via the molecular absorption of SrCl (Pereira et al., 2014), which has been measured at 635.862 nm (Fig. 1) using the integrated absorbance of three pixels (peak volume selected absorbance, PVSA, $A_{\Sigma 3,int}$) (Heitmann, Welz, Borges, & Lepri, 2007). All measurements were carried out using pyrolytically coated graphite tubes with PIN platform (Analytik Jena Part No. 407-A81.025) and a sample volume of 20 μL injected with a micropipette. Argon 99.996% (Air Liquid, Florianópolis, Brazil) was used as a purge and protective gas. The optimized temperature program used for all determinations with HR-CS GF MAS, is shown in Table 1.

Chlorine was also determined by micro-coulometric titration after sample combustion in a Cl analyser (Model Multi EA® 5000 elemental analyser, Analytik Jena), using Ag/AgCl and Pt electrodes. Fish oil samples were weighed and introduced directly into the combustion tube by a solid sample introduction system (Model Multi-matrix sampler MMS 5000, Analytik Jena), using a quartz boat (40 × 9 mm, Part No. 402–889.674, Analytk Jena). The operational conditions of the Cl analyser were used as recommended by the manufacturer: furnace temperature: 1050 °C, time for second