



Development and feasibility of emulsion breaking method for the extraction of cadmium from omega-3 dietary supplements and determination by flow injection TS-FF-AAS



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ABSTRACT

In the present study a new method for the determination of Cd^{2+} in omega-3 dietary supplement employing extraction induced by emulsion breaking (EIEB) and thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) was described. The method was based on the formation of a water-in-oil emulsion by the addition of extractor solution constituted by 3.54% (m/v) Triton X-114 and $1.16 \text{ mol L}^{-1} \text{ HNO}_3$ in the oil sample and further breaking of this emulsion by heating. Two well-defined phases were formed and the acid aqueous one containing the extracted cadmium ions was analyzed by TS-FF-AAS using a flow injection system. Different parameters that exert influence on the extraction efficiency of Cd^{2+} were optimized by means of chemometric tools. The limits of detection and quantification were found to be 2.5 and 8.3 ng g^{-1} , respectively using a calibration curve made in aqueous medium. The accuracy of the proposed method was assured by good agreement with the results achieved by microwave-assisted acid digestion procedure without statistical differences (confidence interval of 95%) and by spiking the samples with known concentrations of $50 \text{ ng g}^{-1} \text{ Cd}^{2+}$. The content of Cd^{2+} in the samples was varied from 37.3 up to 54.5 ng g^{-1} .

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1. Introduction

Fatty acids present in the majority of the oil matrix samples are organic compounds formed by a hydrocarbonated chain and by carboxylic groups that are normally bounded with glycerol forming triacylglycerides classified as mono, di or triglycerides [1]. The nature of the hydrocarbonated chain defines the fatty acids as saturated or unsaturated compounds, which in turn can be monounsaturated or polyunsaturated fatty acids (PUFA) [2]. Omega-3 polyunsaturated fatty acids, more specifically the EPA (cis-5, 8, 11, 14, 17 – eicosapentaenoic acid) and DHA (cis-4, 7, 10, 13, 16, 19 – docosahexaenoic acid) are fatty acids essential to the human health and known to exert beneficial effects in cardiovascular diseases, reducing blood triacylglycerol levels, and blood pressure and in the inflammatory process, preventing platelet aggregation [3]. However, the amounts of EPA and DHA produced by the human body through conversion of α -linoleic acid is very low and this deficiency can be remedied by the consumption of natural food products, such as fish,

sardine, salmon and other alternative sources such as marine microalgae or by the ingestion of omega-3 gelatin capsules available commercially [4,5].

Nevertheless, the chemical quality of edible oils plays an important role in human health and is commonly evaluated by means of concentration of peroxidase, fatty acid composition and by the presence of trace metals, since it affects the stability of oil matrix, catalyzing oxidative reactions that result in the formation of toxic products [6–8]. The contamination of heavy metals into the oil matrix occurs usually from its extraction process or from outer sources to the production process, such as bleaching, hardening, refining and deodorization. In addition, these samples present high levels of carbon and lipid contents and can cause serious spectrometric interferences during measurements for most analytes, leading to inaccurate determinations [9,10]. Thus, the determination of trace elements in edible oil samples has become a major challenge in the field of analytical chemistry. Some spectroanalytical techniques, such as Flame Atomic Absorption Spectrometry (FAAS), Electrothermal Atomic Absorption Spectrometry (ETAAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES), have been very popular techniques for the elemental analysis of oil samples, due to their high selectivity and suitable sensitivity and precision. However, the reliable analysis of oil samples by these techniques requires previous sample

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treatment to avoid matrix effect and to minimize possible interferences [6].

In order to overcome these drawbacks, different sample preparation procedures, among them, microwave-assisted digestion and some extraction methods have been proposed in order to eliminate the possible interferences. The microwave-assisted digestion is one of the most common methods and widely used in the preparation of oil samples for inorganic analysis [11–13]. Nevertheless, this procedure requires a relatively long time of analysis besides needing careful temperature control to avoid loss of volatile metals [14]. Alternatively, extraction methods have been employed due to the use of less aggressive reagents, lower time of analyses and the use of aqueous standards for calibration. The procedures that involve the formation of emulsion and microemulsion have received great attention in the last years. Microemulsion, composed by a mixture of oil–water stabilized by means of a surfactant agent and an organic solvent, presents high stability, facility in its preparation, as well as other desirable features for direct measurement, such as low viscosity and high sample throughput. Although the use of microemulsion offers some advantages over procedures that involve dilution with organic solvent and some emulsion systems, since they allow the use of aqueous solutions for calibration instead of expensive organometallic standards, this method can be applied only when atomic spectrometry techniques are used [14–17]. Similarly, detergent-less microemulsion has also been proposed to separate and preconcentrate metals from edible oils followed by ICP-MS detection [18], ICP OES [19] and FAAS [20]. In this case, a homogeneous system containing both the aqueous phase and the liquid organic phase resulting in a homogenous and long-term stable three-component solution is formed when a co-solvent is used [16,21]. Furthermore, the determination of metals at trace levels in oil samples with minimal manipulation and high reliability using microextraction as dispersive liquid–liquid microextraction (DLLME) and ultrasound-assisted single-drop microextraction (UA-SDME) have gained increasing popularity in recent years [22,23]. The main features of DLLME include the low volume of the extractor phase, which in turn makes it possible to achieve high enrichment factor and the high sample throughput [22, 24,25]. In a similar way, the use of ultrasonic energy has also been exploited for metal extraction from different oil samples [8,22,26]. Trindade et al. [27] reported the use of ultrasound assisted liquid–liquid extraction for determination of Cu, Fe, Ni and Zn in edible oil samples using the High-resolution Continuum Source Flame Atomic Absorption Spectrometry (HR-CS-FAAS). Herein, the amounts of studied metals were in agreement with data obtained from a comparative method (wet digestion) using ICP OES.

Recently some papers have been reported in the literature regarding the use of extraction induced by emulsion breaking (EIEB) for the extraction of metals from oil samples with posterior determination by atomic spectrometric techniques [7,9,10,17]. This procedure is based on the formation and breaking of emulsions prepared by a mixture of oil sample and aqueous phase containing nitric acid and surfactant. During the emulsion breaking, in which the aqueous phase is separate from the oil phase by heating or centrifugation, the analyte is transferred to the aqueous phase. This method has shown to be effective, quick, simple, reliable and excellent when compared with other procedures previously reported. Currently, there is no record in the literature regarding the feasibility of using EIEB for extraction of metals in fish oil capsules with further determination through flow injection thermospray flame furnace atomic absorption spectrometry (FI-TS-FF-AAS). According to the aforementioned, the present work describes the development of a simple, inexpensive and sensitive method for Cd^{2+} determination in omega-3 dietary supplement at trace levels using the EIEB associated with TS-FF-AAS, employing external calibration with aqueous standards. The optimization of experimental parameters that exert influences on emulsion breaking procedure was performed by means of factorial design. The accuracy of the present method was checked by means of comparison between EIEB and the microwave-assisted acid digestion procedure.

2. Experimental

2.1. Apparatus

The determination of Cd^{2+} in the solutions (extracts and standard solutions) was carried out with a Shimadzu AA 7000 flame atomic absorption spectrometer (Kyoto, Japan) equipped with a hollow cathode lamp for cadmium, operated at 8.0 mA and wavelength set at 228 nm. Background correction was performed with a deuterium lamp. For this analysis, the flame was composed of a mixture of acetylene and air at a flow rate of 1.8 L min^{-1} and 15.0 L min^{-1} , respectively. The thermospray apparatus was composed of a 99% Ni tube (Camacam, Brazil) with length of 10 cm and 2.5 cm i.d., containing 6 holes of 2.5 cm i.d. and a 0.5 mm i.d. ceramic capillary tube (99.7% of Al_2O_3) (Friatec, Mannheim, German). The sample introduction and further transports towards the nickel tube were done with the aid of a home-made injector commutator made of Teflon® (PTFE, polytetrafluoroethylene) and a peristaltic pump (ICP-08 model, Ismatec, Switzerland). The emulsion breaking was induced by heating using a thermostatic bath (Marconi, Piracicaba, Brazil) operating at $88 \text{ }^\circ\text{C}$. The total digestion of the fish oil (omega-3 dietary supplement) samples was performed with a Milestone Ethos One microwave oven (São Paulo, Brazil) equipped with 50.0 mL Teflon® vessels.

2.2. Reagents and solutions

All solutions used in this work were prepared in purified water using a Milli-Q purification system (Millipore, Bedford, MA, USA) (resistivity higher than $18.2 \text{ M}\Omega \text{ cm}$). Before use, all laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution, in order to avoid any metal contamination. After that, it was rinsed thoroughly with ultrapure water and dried. A standard Cd^{2+} solution of 1.0 mg L^{-1} was prepared from a stock standard Cd^{2+} solution of 1000.0 mg L^{-1} (Merck, Darmstadt, Germany) using appropriate dilutions. Hydrogen peroxide (35%, v/v) and nitric acid (65%, v/v), used in the digestion procedure, were supplied from Merck (Darmstadt, Germany) and Sigma Aldrich (St. Louis, MO, USA), respectively. Triton X-114 and Triton X-100 solutions (Acros Organics, St. Louis, USA) were prepared by dissolving suitable masses of surfactant (according to the experiment) in 25.0 mL of HNO_3 solution with the desired concentration established according to the multivariate experiment.

2.3. General procedure of extraction induced by emulsion breaking (EIEB)

The extraction of Cd^{2+} from the capsule of omega-3 dietary supplements (fish oil) was performed through the EIEB procedure using optimized conditions from multivariate analysis. The procedure is based on formation of stable water-in-oil emulsions, which is obtained by vigorous mixing of 1.0 mL of fish oil (approximately 0.94–0.96 g) with 500.0 μL of a solution containing Triton X-114 (10.6%, m/v) and 3.5 mol L^{-1} HNO_3 in a capped polyethylene flask of 15.0 mL. The final concentration of Triton X-114 and HNO_3 was found to be 3.54% (m/v) and 1.16 mol L^{-1} , respectively. Afterwards, the flasks containing the emulsions were transferred to a thermostatic water bath at $88 \pm 1 \text{ }^\circ\text{C}$ and kept until breaking of the emulsion, for approximately 10 min. As a result of emulsion breaking, two well-separated phases were formed: (i) the upper organic phase containing the omega-3 and (ii) the aqueous lower phase rich in acid-surfactant and Cd^{2+} ions. Finally, the lower aqueous phase was collected with the aid of a micropipette and 200 μL was inserted in a loop through a flow injection system. The sample was then transported towards the TS-FF-AAS system using 1.0 mol L^{-1} HCl /ethanol (1:1, v/v) as carrier and peak height was taken as the analytical response. In order to examine the influence of factors that affect the extraction procedure of Cd^{2+} from omega-3 dietary supplements (brand 3), a 2^4 full factorial design was employed. The factors, type and concentration of surfactant, HNO_3 concentration and temperature of the thermostatic bath were evaluated and the maximum (+) and minimum (–) levels studied are depicted

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