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Determination of cadmium and lead in edible oils by electrothermal atomic absorption spectrometry after reverse dispersive liquid–liquid microextraction



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ABSTRACT

The dispersive liquid–liquid microextraction of edible oils with a low volume of an acidic solution in the presence of isopropyl alcohol allows cadmium and lead to be completely separated into the aqueous phase. After centrifugation, the metals are determined by electrothermal atomization atomic absorption spectrometry using a palladium salt for chemical modification in the heating cycle. Using a 10 g oil sample, the enrichment factor is 140, which permits detection limits of 0.6 and 10 ng kg⁻¹ for cadmium and lead, respectively. The results agree with those obtained after sample mineralization. Data for the cadmium and lead levels for 15 samples of different characteristics are given.

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1. Introduction

Edible oils play an important role in human nutrition worldwide, and so the development of analytical procedures to check their chemical quality is of great practical interest. In addition to the major components and minor compounds that affect both their nutritional quality and sensorial properties, edible oils contain very small quantities of metals. Monitoring the presence of these low concentrations is of some relevance since, besides the toxic nature of some of these metals, they may affect certain oxidation reactions that will result in the formation of toxic compounds [1].

Along with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), especially in the electrothermal atomization mode (ETAAS), can be considered a suitable analytical technique for this purpose because of its wide availability and good sensitivity. The sample can be diluted with an organic solvent or even directly introduced into the corresponding spectrometer [2–6]. In this way, sample handling

is minimal, although the complexity of the matrix may sometimes hinder measurements. Other alternatives using AAS or ICP techniques are based on solid phase extractions [7,8], or the use of emulsions [9–11], among others [12]. To completely avoid the difficulties caused by the oil matrix, the most common strategy is to mineralize the samples by means of a dry [13] or, preferably, wet digestion procedure [14–18]. However, the dissolution stage means that the detection limit is worsened and the risk of analyte loss or contamination is increased. For these reasons, a number of studies dealing with oil extraction in aqueous acidic solutions have been reported. Complete extraction in a short time requires that the contact surface between the phases be large [19,20], for which reason approaches such as mechanical stirring at low temperatures [20,21] or ultrasounds [13,22,23], sometimes in the presence of complexing agents [24–26], have been proposed. An interesting strategy, related with the approach studied herein, is that recently proposed based on the extraction induced by emulsion breaking although the enrichment factors reported are low [27–30].

Whatever the method used, it is clear that the determination of low concentrations of metals in edible oils is a difficult task and that the difficulty increases as the analyte concentration decreases. This is the case of lead and cadmium, which, while ubiquitous, tend to be present at very low concentrations in oils. The European Union has fixed the maximum level of lead at 100 ng g⁻¹ while, to the best of our knowledge, no particular threshold for cadmium

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exists. The levels reported for lead and cadmium in edible oils vary over a wide range [6,7,9,10,15,16,28,31–33]. In the case of some edible oils manufactured with strict quality control, the concentrations of lead and cadmium may be even lower than 1 ng g^{-1} , which poses an analytical challenge since the detection limits reported for lead in edible oils are 0.8 [32], 166 [33] and 4 ng g^{-1} [6], as measured by ICP-MS, ICP-AES and ETAAS, respectively. As regards cadmium, the detection limits reported are 1.5 [32], 44 [33] and 0.4 ng g^{-1} [34], respectively, for the same techniques.

Combining the high sensitivity of ETAAS with microextraction techniques would permit the determination of concentrations below 1 ng g^{-1} with minimal manipulation and high reliability. Dispersive liquid–liquid microextraction (DLLME), introduced by Rezaee et al. [35], has gained increasing popularity in recent years because of its speed and the high preconcentration that is achieved. A great number of the DLLME analytical procedures reported to date have dealt with water analysis or relatively simple matrices. However, recent reviews have shown that the technique also provides excellent results when dealing with complex matrices such as foods [36,37].

In this paper we report studies to develop very sensitive procedures for lead and cadmium determination in edible oils based on DLLME followed by ETAAS measurement. DLLME is carried out in a reverse mode, a way of operation already proposed by Hashemi et al. [38], since a low volume of aqueous phase is used to extract a relatively high volume of organic phase (the oil sample [39]) in the presence of isopropyl alcohol to form a dispersion [40]. The result is an analytical procedure that provides detection limits at the same (or even better) level as ICP-MS but using ETAAS, which is available in most laboratories.

2. Materials and methods

2.1. Instrumentation

All the measurements were carried out using an atomic absorption spectrometer (model 800, Perkin-Elmer, Shelton, USA) equipped with a Zeeman-effect background corrector and a transversely heated graphite tube atomizer. The samples were pipetted manually into the atomizer. Pyrolytic graphite platforms inserted in pyrolytically coated tubes were provided by the same manufacturer. The inert gas was argon flowing at 250 mL min^{-1} . Cadmium and lead hollow cathode lamps (Perkin-Elmer) were used as the radiation sources. The instrumental parameters are summarized in Table 1.

A 50 W ultrasound bath (ATU, Valencia, Spain) of 0.7 L capacity was used for the ultrasonic treatment. The samples were digested with a Multiwave 3000 microwave digestion system (Anton Paar, Austria).

2.2. Reagents and samples

Pure water obtained with a Millipore system (Millipore, Bedford, MA, USA) was used exclusively. To minimize contamination, polypropylene vessels were used to store the solutions. All plastic vessels were washed with 1% (v/v) concentrated nitric acid solution, and then water. Cadmium (II) and lead (II) standard solutions (1000 mg mL^{-1}) were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ (Aldrich, St. Louis, MO 63103, USA), respectively. Appropriate working standard solutions were obtained by dilution. A 0.5 mol L^{-1} solution of ammonium pyrrolidine dithiocarbamate (APDC) was prepared by dissolving the compound (Sigma-Aldrich Chemie GmbH, Germany) in high purity methanol. Solutions (1 mol L^{-1}) of 1-octyl-3-methylimidazolium chloride ($[\text{C}_8\text{MIm}]\text{Cl}$) and lithium bis(trifluoro-methylsulfonyl) imide ($[\text{Li}][\text{NTf}_2]$), (from IOLITEC, Heilbronn, Germany) were prepared by dissolving 1.15

and 1.43 g, respectively, in 50 mL of water. A 0.2 mol L^{-1} aqueous solution of Triton X-114 (1,1,3,3-tetra-methylbutyl)phenyl-polyethylene glycol from Sigma was also used. All the other chemicals used were from Fluka. A solution containing 2 g L^{-1} palladium was used for chemical modification in the heating program. Solid-phase cartridges HLB (6 mL and 200 mg) were obtained from Supelco (Bellefonte, PA).

Eight samples of oil were acquired in local supermarkets. The samples were labeled as olive, olive pomace, sunflower, maize, soy, avocado, walnut and macadamia. Five samples, namely F8020 (fish oil from menhaden), 74380 (fish liver oil from *Gradus morrhua*), 85067 (sesame oil from *Sesamum indicum*), P1244 (peanut oil) and C8267 (corn oil), were obtained from Sigma. Nutritional supplements marketed in the form of pills as fish oil (salmon and cod) were acquired in a specialized outlet.

2.3. DLLME procedure for cadmium and lead determination in oils

A 10 g oil sample was placed in a conical centrifuge tube and heated to 80°C . After adding $300 \mu\text{L}$ of a 4:1 isopropyl alcohol:3% v/v nitric acid solution, the tube was shaken for a few seconds, and then introduced into the ultrasounds bath at 80°C for 3 min. The mixture was centrifuged at 4000 rpm for 15 min. A $30 \mu\text{L}$ fraction of the aqueous phase recovered ($67 \pm 1 \mu\text{L}$) was injected into the electrothermal atomizer and the heating program given in Table 1 was applied. When maximum sensitivity was not considered necessary, the injection volume was decreased to $10 \mu\text{L}$ to carry out duplicate measurements of each analyte in a single microextraction experiment. Calibration was carried out by submitting sunflower oil samples spiked with lead and cadmium solutions prepared in isopropyl alcohol to the same procedure (final concentration ranges 2–40 and 30–900 ng kg^{-1} for cadmium and lead, respectively).

On the other hand, the samples were mineralized using a microwave oven. To this effect, 0.6 g fractions were taken and digested with a solution containing concentrated hydrogen peroxide (3 mL) and nitric (5 mL) and hydrochloric acid (0.5 mL). A two-stage temperature control program was used as suggested by the oven manufacturer. A 1400 W power was first applied with a 15 min ramp and then held for 10 min. Next the power was switched off and the vessels cooled for 15 min. The liquids were finally made up to 25 mL. For comparison purposes after mineralization of the samples, and for the additional studies carried out to check the nature of the lead and cadmium compounds, an already reported procedure based on the formation and extraction of an ionic liquid was used. In short, the procedure [41] involves 10 mL of aqueous sample, to which 0.2 mL of a 0.5 mol L^{-1} APDC solution is added, followed by 0.1 mL of a $[\text{C}_8\text{MIm}]\text{Cl}$ solution, 0.2 mL Triton X-114 solution and 0.1 mL of a $[\text{NTf}_2]\text{Li}$ solution. After centrifuging, the organic phase recovered is submitted to ETAAS and the lead and cadmium signals are obtained. A detailed explanation is given elsewhere [41].

3. Results and discussion

3.1. Optimization of the DLLME conditions

The main characteristics that have led to the wide acceptance of DLLME in the analytical laboratory are the fact that it uses a low volume of extractant phase to achieve a high enrichment factor and the speed of the process; hence, all the experiments had this double goal.

DLLME is used here in the opposite way to which it is normally used since the sample to be extracted was of an organic nature while the extractant was an aqueous phase. A large number of

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