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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.

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 $Cd(NO_3)_2 \cdot 4H_2O$ and $Pb(NO_3)_2$ (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 ($[C_8MIm]Cl$) and lithium bis(trifluoro-methylsulfonyl) imide ($Li[NTf_2]$), (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 μL 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 μL fraction of the aqueous phase recovered (67 ± 1 μL) 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 μL 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 $[C_8MIm]Cl$, solution, 0.2 mL Triton X-114 solution and 0.1 mL of a $[NTf_2]Li$ 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

Table 1
Instrumental parameters and experimental conditions for Pb and Cd determination in the DLLME extracts.

Parameter	Lead	Cadmium
Lamp current (mA)	14	4
Wavelength (nm)	283.3	228.8
Spectral band width (nm)	0.7	
Atomizer type	Platform	
Injected sample volume (μL)	30	
Chemical modifier	40 μg Pd	
Calibration graph (ng kg^{-1})	30–1000	2–40
Acceptor phase (μL)	300 (75% isopropyl alcohol+25 % of 3 % HNO_3 v/v solution)[a]; 150 ($[C_8MIm]Cl$)+150 ($Li[Tf_2N]$)[b]	
Donor phase (g)	10 g[a]; 10 mL[b]	
Enrichment factor	146	140
Limit of detection in oil (ng kg^{-1})	10	0.6
RSD (%) (n=20)	3.5	4.0

Furnace heating program

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold (s)
1: Dry	130	5	20
2: Dry	350	20	30
3: Ash	600	10	30
4: Atomization[cd]	1600 (Pb); 1300 (Cd)	0	4
5: Clean	2600	0	3

Sequence for lead and cadmium determination

A	Pipette 20 μl of the modifier and run step 1 and 2
B	Inject the sample and run the entire program

[a] Reverse DLLME procedure.
[b] Only for the direct DLLME procedure using ionic liquid.
[c] Flow of argon stopped.
[d] Reading step.

experiments were carried out, in which 10 g oil samples were extracted with solutions of different acidity levels containing variable proportions of methanol, ethanol, isopropyl alcohol, acetone or acetonitrile as disperser solvent. After centrifugation, aliquots of the extracts were injected into the electrothermal atomizer, and the cadmium and lead signals were obtained. As can be seen in Fig. 1, which depicts a part of the results obtained for cadmium, maximum signals were achieved using isopropyl alcohol mixed with a slightly acidic nitric acid solution. Similar results were found for lead and so this alcohol was selected as the disperser agent. It was experimentally found that when volumes of this chemical exceeding 400 μL were used excessive time was required for centrifugation.

The maximum volume of liquid that can be injected in the electrothermal atomizer used is 30 μL and so, to obtain maximum sensitivity and to carry out the measurements in duplicate, the volume of the aqueous phase recovered after centrifugation must not be too low. The experimental results demonstrated that for 10 g oil samples, the most suitable volume for the dispersive solution was 300 μL of a mixture containing diluted nitric acid (75 μL of a solution containing 3% v/v concentrated acid) and isopropyl alcohol. In this way, the volume recovered by centrifugation was 67 ± 2 μL. Note that this low proportion of nitric acid is not harmful to the pyrolytic coating of the atomizer.

On the other hand, it should be noted that the viscosity of the oils hinders dispersion, and so the effects of ultrasounds and temperature were studied to speed up the process. No significant differences were observed when ultrasounds were applied by means of a probe or by a simple ultrasound bath. Since the bath facilitates sample heating, it was used for the remaining experiments. Fig. 2 shows the results for experiments in which both the temperature of the bath and the time of treatment with ultrasounds were varied. Provided that the bath was maintained at 80 °C, a 3-min treatment sufficed to obtain the maximum signal

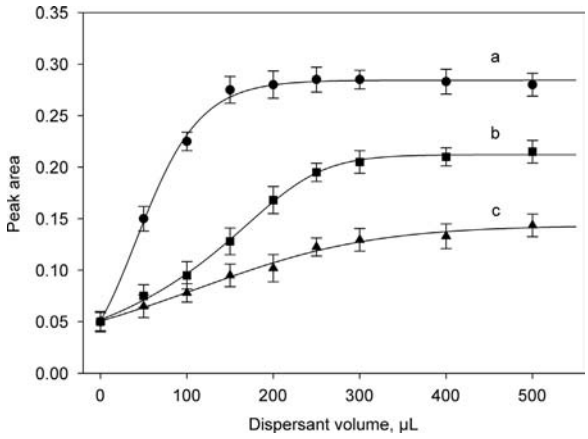

Fig. 1. Effect of the dispersant on the analytical signal of cadmium. Maize oil (42 ng kg^{-1}) was used as the sample and 15 μL of the extract were injected. The rest of the conditions were those specified as optimal. Curves a–c correspond to isopropyl alcohol, ethanol and methanol, respectively. Vertical bars indicate the relative standard deviation (n=3).

for lead. The same behavior was observed when the analytical signal of cadmium was measured.

3.2. Optimization of the furnace heating program

The heating program was optimized in the usual way by studying the ashing-atomizing graphs for both analytes. Pyrolytic atomizers coated with a tungsten salt as a permanent modifier [42] were first assayed, but better sensitivity and a longer atomizer lifetime were achieved when a palladium salt was used as chemical modifier. The experiments showed that 600 °C was the most suitable ashing temperature for both analytes, while analytical

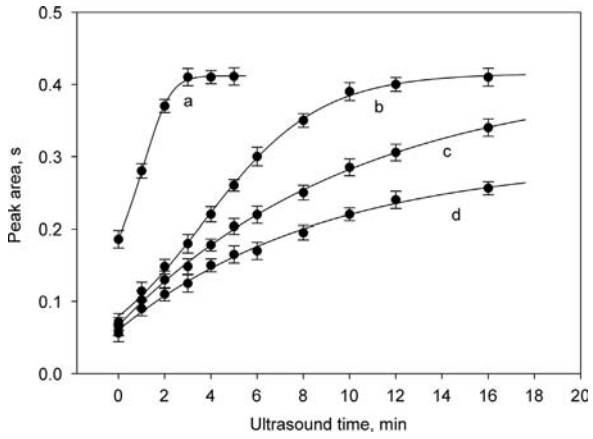

Fig. 2. Effect of the temperature of the ultrasound bath and the duration of the treatment on the analytical signal of lead. Olive oil (0.64 ng g^{-1}) was used as the sample and 30 μL of the extract was injected. The rest of the conditions was those specified as optimal. Curves a–d correspond to 80, 65, 45 and 20 °C, respectively. Vertical bars indicate the relative standard deviation (n=3).

signals were maximal when 1300 °C and 1600 °C were used as the atomization temperatures for cadmium and lead, respectively.

To achieve the highest sensitivity, a 30 μL aqueous extract was injected in the atomizer. This meant that the chemical modifier (20 μL of a palladium salt) could not be injected subsequently because of platform overflow. For this reason, as described in the recommended procedure, the sequence used for the heating cycle was begun by first injecting the modifier solution and then, after drying, the aliquot of the sample before the total heating cycle. The background signals obtained were very low for the two analytes. The heating cycle given in Table 1 also contains the slight modifications used in a procedure involving an ionic liquid, which was only used for verification purposes, as outlined below.

3.3. *Analytical figures of merit. Results for oil samples*

Using the optimized experimental conditions, a high preconcentration effect was achieved for both analytes. The enrichment factors obtained experimentally were practically identical for both analytes, namely 140 and 146 for cadmium and lead, respectively. A linear relationship between the analytical signal and the cadmium and lead concentrations in the oil samples was verified in the 2–40 ng kg^{-1} and 0.03–1 ng g^{-1} range, respectively. Based on the criterion of three times the standard error from the calibration graphs, the limits of detection were calculated to be 0.6 and 10 ng kg^{-1} for cadmium and lead in the oil, respectively. Using the heating program given in Table 1, the characteristic masses were calculated as 1.4 and 30 pg for cadmium and lead, respectively. The reproducibility of the measurements was estimated from 10 microextraction experiments, ten for each analyte, each extract being measured in duplicate. No significant differences between the analytes were observed, the relative standard deviations being 4% and 3.5% for cadmium and lead, respectively.

The results obtained when the optimized procedure was applied to 15 samples of differing nature are shown in Table 2. As can be seen in the data reported, the levels found were extremely low, and their measurement was only possible due to the high preconcentration achieved in the DLLME process. The concentration of lead in the three nutritional supplements was higher than in the rest of the samples but below the maximum permitted level (100 ng g^{-1}). As far as we know, there is no particular regulation for cadmium concentration in these samples for which, notwithstanding, very low values were recorded.

Table 2
Results for lead and cadmium determination in edible oils.

Oil sample	Metal content found			
	Proposed procedure		Microwave digestion[d]	
	Pb (ng g^{-1})	Cd (ng kg^{-1})	Pb (ng g^{-1})	Cd (ng kg^{-1})
Olive[a]	0.64 ± 0.03	160 ± 5	< LOD	164 ± 8
Olive pomace[a]	0.78 ± 0.04	205 ± 6	< LOD	201 ± 7
Sunflower[a]	0.06 ± 0.02	12 ± 4	< LOD	< LOD
Maize[a]	0.25 ± 0.02	42 ± 5	< LOD	< LOD
Soy[a]	0.32 ± 0.02	35 ± 5	< LOD	< LOD
Avocado[a]	0.61 ± 0.03	48 ± 5	< LOD	< LOD
Walnut[a]	1.68 ± 0.05	39 ± 5	1.53 ± 0.07	< LOD
Macadamia[a]	1.57 ± 0.05	72 ± 6	1.59 ± 0.07	75 ± 6
Fish oil[b]	0.54 ± 0.04	21 ± 4	< LOD	< LOD
Fish liver oil[b]	0.89 ± 0.05	32 ± 5	< LOD	< LOD
Sesame[b]	1.32 ± 0.05	43 ± 5	1.38 ± 0.07	< LOD
Peanut[b]	0.65 ± 0.04	81 ± 6	< LOD	87 ± 8
Corn[b]	0.78 ± 0.05	52 ± 5	< LOD	< LOD
Salmon[c]	5.06 ± 0.08	126 ± 7	5.12 ± 0.09	120 ± 9
Cod-1[c]	5.02 ± 0.08	158 ± 7	4.96 ± 0.09	162 ± 7
Cod 2[c]	3.90 ± 0.07	119 ± 6	3.97 ± 0.08	123 ± 6

[a] Commercial samples acquired in supermarkets.
[b] Laboratory products (Sigma).
[c] Nutritional supplement marketed as pearls.
[d] The solutions obtained after mineralization were analyzed by the procedure of Ref. [41].

A large number of experiments were carried out to verify the reliability of these data and to check that the amounts reported corresponded to the total present in the oil samples. First, an oil sample was submitted to the reverse DLLME procedure; the aqueous extract was discarded, while the organic phase, after filtering to remove the small amount of water still present, was again submitted to the reverse DLLME process. No signal due to cadmium or lead was found when the aqueous extract obtained in the second extraction was submitted to ETAAS. These experiments were repeated for two more samples, leading to the same conclusion that extraction was complete, although the possibility of very small quantities of non-extractable lead or cadmium compounds cannot be discarded. Additionally, recovery experiments were carried out by spiking the samples at two levels, namely 0.01 and 0.02 ng g^{-1} for cadmium and 0.2 and 0.4 ng g^{-1} for lead. The recoveries (three experiments at each level) were 98 ± 5% and 101 ± 4% for cadmium and lead, respectively.

Finally, to check the reliability of the data, all the samples were mineralized by treatment in a microwave oven to measure the total content of both elements in an alternative procedure. In this respect, it should be noted that the mineralization stage means the analytes are diluted, so that the concentration in the solutions finally obtained may be below the detection limits of ETAAS or even ICP-MS in some cases. To partly overcome this and to obtain valid results for comparison, the aqueous solutions obtained after mineralization were analyzed by a completely different DLLME process based on the *in situ* formation of an ionic liquid, the reliability of which has recently been reported [41]. As can be seen in Table 2, there was an agreement between the values obtained using the two procedures, as demonstrated by a non-parametric Wilcoxson test, which showed the absence of significant differences at the 95% confidence level. It should be noted that, although the sensitivity of these two DLLME procedures was similar, some samples could not be analyzed after the microwave treatment because of the strong dilution effect inherent in the mineralization stage. The advantage of the reverse DLLME procedure is that it does not require sample mineralization.

The above data confirm that the extraction of both lead and cadmium from oils to the aqueous phase could be considered as

complete, and suggest the analytes were in an inorganic or easily available form. To confirm this, a large number of experiments were carried out in which oil samples mixed with hexane were passed through HLB solid phase cartridges. The successive elution of the cartridges, first with hexane, then with ethanol and finally with a 3% v/v nitric acid solution allowed three fractions, corresponding to non-polar, medium-polar and highly polar fractions, to be obtained. The levels of cadmium and lead in the three fractions were measured in triplicate for the 15 samples studied using the procedure already reported [41]. The results, which, for simplicity, are not included in Table 2, showed that the two metals were present exclusively in the third fraction, while the concentrations found agreed with those obtained by the optimized reverse DLLME procedure.

4. Conclusions

The determination of low concentrations of cadmium and lead in edible oils does not require the samples to be mineralized. Dispersive microextraction with a small volume of a slightly acidic aqueous solution allows both metals to be completely separated from the organic phase. The high enrichment factor inherent in the microextraction process, together with the sensitivity of ETAAS, results in an extremely sensitive analytical procedure with detection limits that are better than those achieved by ICP-MS. The data obtained for a variety of edible oil samples indicate that both cadmium and lead are present in an easily available form.

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