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Multielemental analysis of oils and animal fat by using deep eutectic solvents assisted by an aerosol phase extraction procedure

Ana Torres [a], Ismael Romero [a], Raquel Sánchez [a], Ana Beltrán [a], Gabriela Guillena [b], José-Luis Todolí [a,*]

[a] Analytical Chemistry, Nutrition & Food Sciences Department, University of Alicante, PO Box 99, E-03080 Alicante, Spain
[b] Organic Chemistry Department, University of Alicante, PO Box 99, E-03080 Alicante, Spain

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ABSTRACT

In the present study, thirteen elements (Ag, Al, Ba, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb) have been extracted from used cooking oils, olive oils and animal fat. Either inductively coupled plasma optical emission spectrometry (ICP-OES) or tandem mass spectrometry (ICP-MS/MS) have been chosen as detection techniques. Due to the difficulty of directly introducing highly viscous organic samples into the spectrometer, a fast dispersive liquid – liquid aerosol phase extraction (DLLAPE) method has been selected to isolate the analytes from the sample matrix. The DLLAPE is based on the generation of an aerosol from the extracting phase with the help of a pneumatic nebulizer. This high velocity aerosol impacts and penetrates in the liquid sample. Consequently, the liquid – liquid exchange surface area becomes high, thus leading to high extraction yields. A hydrophilic deep eutectic solvent (DES) consisting of choline chloride and ethylene glycol (1:2 mass ratio) has been selected as the extracting solvent. Prior to undertaking the experiments, the extraction method has been evaluated in terms of precision under suitable conditions. In comparison with conventional methods based on sample digestion, sample dilution and shot analysis or extraction assisted by vortex agitation, the DLLAPE shows several advantages, because it is faster, and it provides lower limits of detection than the reference methodologies. The procedural limits of quantification for the determined elements with the DLLAPE in ICP-OES were 0.046 (Ag), 0.396 (Al), 0.013 (Cd), 0.033 (Cr), 0.040 (Cu), 0.20 (Fe), 0.026 (K), 0.026 (Li), 0.33 (Mg), 0.013 (Mn), 2.64 (Ni) and 0.53 (Pb) mg kg^{-1}. Meanwhile, pLOQ in ICP-MS/MS lowered by roughly one order of magnitude. The accuracy of the aerosol phase extraction method has been evaluated through the determination of the recoveries for four representative analytes (Ca, Cu, Mg and Ni) from spiked real samples. For these elements, recovery has taken values of (100 ± 20)%. Moreover, a comparison of the multielemental concentration obtained with conventional methods (*c.a.*, sample dilution and shot ICP analysis and liquid-liquid extraction using a vortex agitator) against that measured with the DLLAPE has been carried out. Multiemelemental concentrations have been obtained for real samples and the found levels have been similar to those encountered in previously published works.

Introduction

Biomass-based biorefineries are crucial contributions to circular economy [1]. On this subject, the use of food wastes as substrates for biofuel production is of great relevance. However, to optimize the biorefinery production and product safety, the quality of the raw matter should be thoroughly controlled. The increasing demand for novel biodiesel precursors, for instance, strongly forces the development of new analytical methods to assess the quality of the final product [2]. Among these raw materials, one can find edible and used cooking oils as well as solid animal fat.

Metals may be harmful components present in edible oils [3] and the biofuel finally obtained. In general terms, metals are present in vegetal oils as they come from the soil, fertilizers, the production process or the oil storage and transport [4]. Some metals, such as Cd, Cr and Pb, are toxic for human consumption at a given concentration and cannot be degraded in the human body [5]. Meanwhile, others induce side reactions. Thus, for instance, the presence of Cu, Fe, Mg or Mn give rise to the catalysis of oxidation reactions that promote the oil degradation [3, 6]. Besides these issues, when present in biofuel precursors, some metals

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* Corresponding author.
E-mail address: jose.todoli@ua.es (J.-L. Todolí).

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above certain levels may exclude their application to biofuel production [2]. These species are also responsible for catalyst poisoning and fouling and their presence in biofuels may degrade the engine performance. The presence of metals in biofuels can be a result of their use as additives because the properties of some of them as anti-knocking, anti-icing or detergents, among others. Once in the biofuel, metals may cause environmental concerns, as they are pollutants [7,8] thus degrading the quality of marine ecosystems, for instance [9].

Therefore, metals determination in oils and fats is of capital importance in order to assess their use and applicability for biofuel production as well as from the point of view of edible oil consumption. However, there are some difficulties associated to the determination of these elements in the mentioned samples: *(i)* they are present at very low concentrations (µg L^{-1}); *(ii)* there are limited certified reference materials; and *(iii)* they may contain several organic compounds depending on its origin and treatment [10]. Therefore, a sensitive and robust enough technique must be applied to carry out the determination of metals and metalloids in this type of samples. In addition, it is necessary to develop analytical procedures able to remove matrix effects caused by the components of edible as well as used cooking oils and fats.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS) appear as the most appropriate techniques to perform multielemental determinations in oils and fats [11]. Unfortunately, their direct analysis cannot be performed by using conventional liquid sample introduction systems, because these specimens are highly viscous and, hence, very difficult to turn out into an aerosol. Several methodologies have been proposed to overcome this problem. Virtually all of them involve a previous sample treatment such as sample dilution with an appropriate solvent [12], digestion at high temperature in presence of acids [13] or emulsification in an aqueous medium [14]. Dispersive liquid-liquid (micro)extraction (DLLE or DLLME) emerges as an efficient method for the multielemental analysis of oils [15]. According to this methodology, an appropriate extracting solution, immiscible with the sample, is dispersed in the specimen. As the liquid-liquid exchange surface is high, the analyte migration to the extracting solution takes place rapidly and efficiently. The dispersion is achieved by several ways [2] such as addition of a dispersing agent, use of ultrasounds or agitation [16].

Commonly, DLLME methods require from a dispersing reagent (*e.g.*, isopropyl alcohol [17], nitric acid [18]), they are time consuming and rather difficult to be automatized. To overcome these problems, an alternative based on the generation of an aerosol from the extracting solution and its introduction into the sample has been described [19]. This is the so-called dispersive liquid-liquid aerosol phase extraction (DLLAPE). So far, it has been applied to the analysis of water [12], biodiesel [20] and edible oil samples [21]. The versatility of the method has allowed to apply it to the efficient extraction and further quantification of organic compounds as well as metals and metalloids. Obviously, the DLLAPE does not require from any dispersing reagent, the analysis time can be shortened by a factor close to one order of magnitude with respect to conventional liquid-liquid extraction methods and it can be easily automatized. The extracting agents used in previous studies performed with the DLLAPE on oil samples have been mostly mixtures of water and methanol either in the presence or absence of nitric acid.

An interesting approach as extracting media in metal liquid-liquid extraction applications are the so-called deep eutectic solvents (DES) [22]. The use of DES for the multielemental analysis of liquid samples has been previously described in the literature. DES are composed of a donor and acceptor of hydrogen which combine through strong interactions leading to eutectic mixtures, that have a melting point much lower than the ideal, referred to as the eutectic point. Due to their enhanced donating and accepting properties, DES can be applied as extracting agents. Furthermore, these extracting media meet some advantages over conventional solvents since they have a low toxicity, they are renewable and contain biodegradable components. Unlike several extracting solutions, DES have a high thermal stability. Furthermore, their synthesis is simple and cost effective and they are promising solvents that fulfill the Green Chemistry principles. For all the mentioned advantages, DES are becoming widely accepted in the analytical laboratories [23].Until now, deep eutectic solvents have been used to determine metals in medicines [24], drugs [25], environmental samples [26] wine [27] or edible oils [28], among other applications. Although promising, the use of DES, or natural DES, as extracting agents has not been generally extended in the analytical laboratories [29]. Besides, the number of elements extracted and determined in the previously published studies is limited to 2–6.

The goal of the present study was, thus, to apply the DLLAPE as a liquid-liquid extraction procedure in which a hydrophilic DES, consisting of a mixture of choline chloride and ethylene glycol, was used. In previous studies, the use of the DLLAPE with methanol containing extracting solutions promoted the rapid evaporation of a significant fraction of these solutions before their mixing with the sample [22]. Note that, as an aerosol was generated at the exit of a pneumatic nebulizer, the solvent evaporation proceeded faster than in condensed phase. The low volatility of the DES used mitigated this drawback. Thus, for a giving nebulization time, the analyte extraction efficiency increased, because a higher amount of solvent was available for the analyte extraction. The method was applied to extract and detect several elements in edible olive oils as well as used cooking oils and an animal fat sample. The reference procedures were: *(i)* the sample dilution with xylene and the further introduction into an ICP-OES; and *(ii)* the agitation of the mixture sample-DES with the help of a vortex and multielemental determination by means of inductively coupled plasma tandem mass spectrometry (ICP-MS/MS).

Experimental

Reagents and samples

Choline chloride (98%, Alfa Aesar, Germany, NºCAS 67–48–1) and ethylene glycol 99%, (Labkem, Spain, Nº CAS 107–21–1) were used as components of the DES. Ultrapure water supplied by a three-step ion-exchange system, Milli-Q, fed by reverse osmosis, Elix 3, both from Millipore (El Paso, TX) was used throughout, whereas *n*-hexane suitable for HPLC (>95%, Merck) was used for sample dilution.

An ICP multielement standard solution (Merck IV) containing 100 mg of element kg^{-1} was used to prepare the standards by serial dilution with the selected DES. With the aim of performing experiments with spiked solutions, an organic standard containing 23 different elements at 1000 mg kg^{-1} (Conostan, SCP Science, Canada) was taken.

A total of twelve samples were analyzed. Table 1 summarizes their codification and main characteristics.

Instrumentation

Two axially viewed inductively coupled plasma optical emission

Table 1
List of samples analyzed.

Code	Sample	Origin
BV	Olive oil; cultivar: Blanqueta	Bottled
AV	Olive oil; cultivar: Alfafarenca	Bottled
AP	Olive oil; cultivar: Alfafarenca	Pressed
MV	Olive oil; cultivar: Manzanilla	Bottled
MP	Olive oil; cultivar: Manzanilla	Pressed
UO1	Used cooking oil	Corn oil
UO2	Used cooking oil	Tall oil
UO3	Used cooking oil	Colza oil
UO4	Used cooking oil	Tall oil
UO5	Used cooking oil	Colza oil
AG	Fat	Animal origin
CO	Oil	Carinata oil

spectrometers, ICP-OES (Optima 7300 DV PerkinElmer ICP-OES spectrometer, Uberlingen, Germany and Agilent, 720 Model, CA, USA) and an Agilent 8900 ICP-QQQ inductively coupled plasma tandem mass spectrometer (ICP-MS/MS) instrument (Agilent Technologies, CA, USA) were used to take the analytical signals. The operating conditions of both instruments are summarized in Table 2.

Drop size distributions of the aerosols generated by the nebulizer were obtained by means of a laser Fraunhofer diffraction system (model 2600c; Malvern Instruments, Malvern, Worcestershire, U.K.). The sizer was equipped with a 63 mm focal length lens, which enabled the system to measure droplets with diameters included within the 1.2 − 118 µm range and provided the aerosol liquid volume fraction for a set of 31 diameter intervals (bands), thus giving rise to the complete volume drop size distribution. The nebulizer tip was set at 30 mm from the lens and 15 mm from the laser beam center.

Liquid-liquid extraction and reference methods

The experimental setup required to perform the DLLAPE has been described elsewhere [12,13]. Droplets generated from the extracting solution having a given initial velocity penetrate the sample thus leading to the interaction of the two phases involved in the extraction process. Moreover, the gas at the exit of the nebulizer creates turbulences and agitation of the mixture containing the two immiscible phases. Both phenomena promote the analyte extraction.

In the present study, 1 g of oil was weighed in a 5 mL polypropylene tube, 1 mL of hexane was added, and the tube was weighed again. The nebulizer gas and liquid flow rates were set by using a mass flow controller (58,505, Brooks Instruments, Hatfield, PA, EEUU) and a peristaltic pump (Perimax, Spetec, Ending, Alemania), respectively. The DES liquid flow rate was set at 1 mL min^{-1}. A pneumatic concentric nebulizer (Model TR-30-A2, Meinhard, Golden, CO, EEUU) dispersed the extracting solution into fine droplets that were directed against the surface of the solution contained in the plastic tube. Once the nebulization ceased, the tube containing the sample, hexane and the extracting solution was weighed to measure the mass of extracting solution trapped by the sample. The tubes were left stand for 30 s. Afterward, the DES deposited at the bottom of the extraction tube was taken with a pipette and inserted into a new open metal-free polypropylene tube.

A dilution and shot ICP-OES analysis methodology was taken as reference. Xylene was the chosen solvent, and the samples were 1:20 diluted prior to their direct introduction into the ICP-OES Perkin-Elmer instrument. Because of the plasma degradation induced by the introduction of xylene, a small sample volume (*i.e.*, 5 µL) was injected into an air carrier stream and, thus, a transient signal (peak) was obtained whose height was directly related with the analyte concentration in the sample. An external calibration was applied in which the standards were prepared in xylene. Experimental details are given in ref. [30].

Table 2
Operating conditions of ICP-OES and ICP-MS/MS instruments.

Variable	ICP-OES (Perkin-Elmer)	ICP-OES (Agilent)	ICP-MS/MS
RF Power (kW)	1.4	1.4	1.6
Plasma flow (L min^{-1})	15	15	15
Auxiliary flow (L min^{-1})	1	1.5	1
Nebulizer flow (L min^{-1})	0.5	0.7	0.4
Liquid flow (mL min^{-1})	0.03	1.0	0.4
Replicates	6	5	5
	Element/Wavelength, nm		Nuclide
	Ag I 328.068		^{7}Li
	Al I 167.019		^{39}K
	Ba II 455.403		^{55}Mn
	Cd II 214.439		^{58}Fe
	Cr II 267.716		^{60}Ni
	Cu I 327.395		^{107}Ag
	Fe II 238.204		^{111}Cd
	K I 766.491		^{138}Ba
	Li I 670.783		^{208}Pb
	Mg II 280.271		
	Mn II 257.610		
	Ni II 231.604		
	Pb II 220.353		

The ICP-OES instrument allowed the determination of elements at the sub-mg kg^{-1} level. However, some samples contained analytes whose concentration was below this level. Therefore, an alternative method was used in which 1 g of sample was weighed in the extraction tube and 2 mL of the DES were added. Then, the mixture was shaken with a vortex system for 5 min. After shaking, fifteen minutes were left to allow for complete phase separation. The DES fraction was collected by using a pipette and directly introduced into the ICP-MS/MS spectrometer.

Results and discussion

DES selection and aerosol phase extraction conditions

The DLLAPE method involved the addition of a given volume of hexane to the oil samples. It was observed that, due to the action of the nebulizer gas, a 24% of the mass of this solvent could leave the sample through evaporation. Therefore, with this method, all the samples were weighed before and after the extraction.

As regards the extracting solution, a rather low viscosity DES was required within the frame of the present study. This was mandatory to achieve a continuous and stable aerosol production regime. Furthermore, the drop size distribution of the generated aerosol had to contain fine droplets to increase the interfacial surface area thus giving rise to a fast and efficient extraction of the different analytes. Moreover, the solvent had to be compatible with the plasma. Among the different possibilities, a choline chloride : ethylene glycol (1:2) mixture was chosen. This solvent has been previously used in fuels desulfurization and de-aromatization [31]. Changes in the plasma thermal state caused by the introduction of the mentioned DES were monitored by obtaining the Mg(II) to Mg(I) net emission intensity ratio [32]. It was verified that the values of this ratio found in presence of the deep eutectic solvent were not significant different to those measured for a plain water solution, thus suggesting that neither degradation nor enhancement of the plasma performance were produced.

Additionally, it was observed that the prepared DES provided high emission signals for analytes such as Cr, Fe and Mg, that were present as contaminants. Consequently, all the standards had to be prepared in the deep eutectic solvent.

Finally, some of the critical DLLAPE variables were set at values close to the optimum ones according to previous studies [14]. Thus, for instance, the initial distance from the nebulizer nozzle to the solution surface was 1.5 cm. The nebulizer liquid and gas flow rates, in turn, were set at 1 mL min^{-1} and 0.3 L min^{-1}, respectively. These values were chosen because, on the one hand, they provided a mass of the DES solution close to the diluted oil mass in a reasonable period of time and, on the other hand, the aerosol droplets velocity was not excessively high, thus avoiding sample losses from the extraction tube. The selected nebulization conditions led to a continuous aerosol production.

Drop size characterization

To verify whether the generated aerosol was appropriate to achieve an efficient and fast extraction of the analytes, its drop size distribution was measured at the exit of the nebulizer. Fig. 1 shows the accumulated volume drop size distributions for a plain water solution and the used DES. According to this plotting, a shift of the curves towards the left indicated that the aerosols became finer. It may be observed that the choline chloride : ethylene glycol (1:2) mixture provided aerosols slightly coarser than water. For a given set of pneumatic nebulization

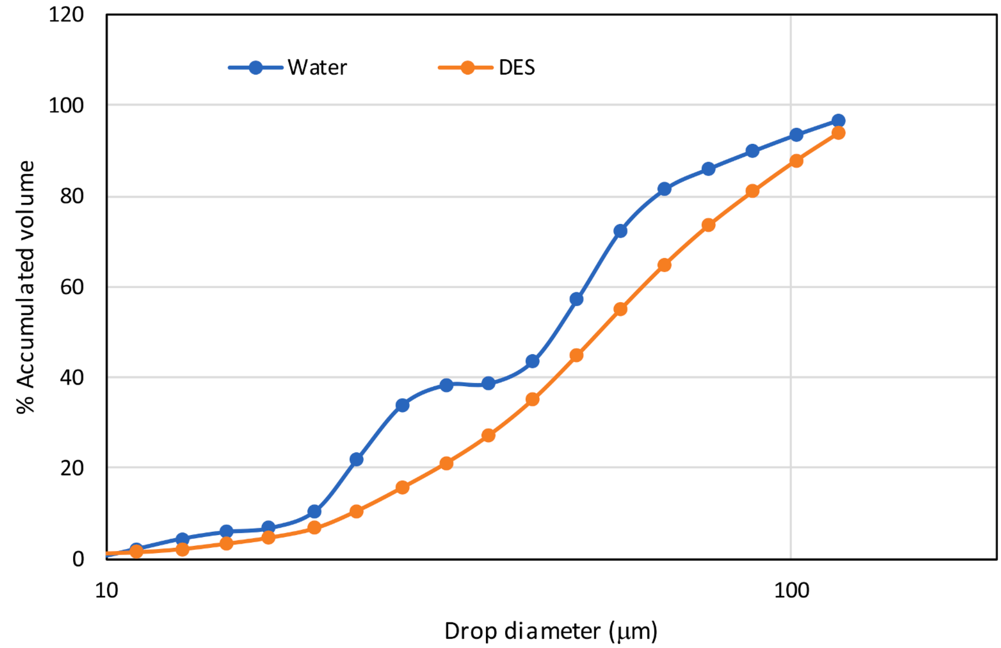

Fig. 1. Accumulated volume drop size distributions of the aerosol generated by the pneumatic concentric nebulizer for the selected DES and water.

conditions, the solution physical properties precluding the characteristics of the aerosols are mainly the surface tension and the viscosity. At 25 °C, surface tension of the employed DES was lower than that for water (*i.e.*, 48.0 and 72.8 mN/m, respectively) [33]. This promoted the generation of finer aerosols for the former solvent, because the lower the surface tension, the lower the amount of energy required to generate a droplet. However, viscosity was much higher for the DES than for water (*i.e.*, 37 and 1 cP at 25 °C for the DES and water, respectively) [34,35]. An increase in this property leads to a dampening in the instabilities generated on the liquid surface during the nebulization process and, hence, induces the generation of coarse droplets. The impact of surface tension on the aerosol generation was, thus, counterbalanced by that of the increased viscosity thus giving rise to slightly coarser aerosols in the case of the DES than for water.

From the data in Fig. 1, it was verified that the aerosol generated from the DES contained droplets whose diameters were in between 2.19 and 118 µm. This range corresponded to the drop diameters found in the case of the so-called emulsions [36]. Therefore, because of its thermodynamic instability, once generated, the emulsion was rapidly broken, and the phases could be easily separated.

The sizer provided additional parameters such as the specific surface area that corresponded to the total liquid surface area generated per liquid volume unit. It was found that, when using the DES, this parameter was 0.18 m^2 cm^{-3}. Therefore, a significant liquid-liquid exchange area was generated and, hence, the extraction could proceed in an efficient way.

Effect of the extraction time

In order to test the influence of the extraction time on the analyte

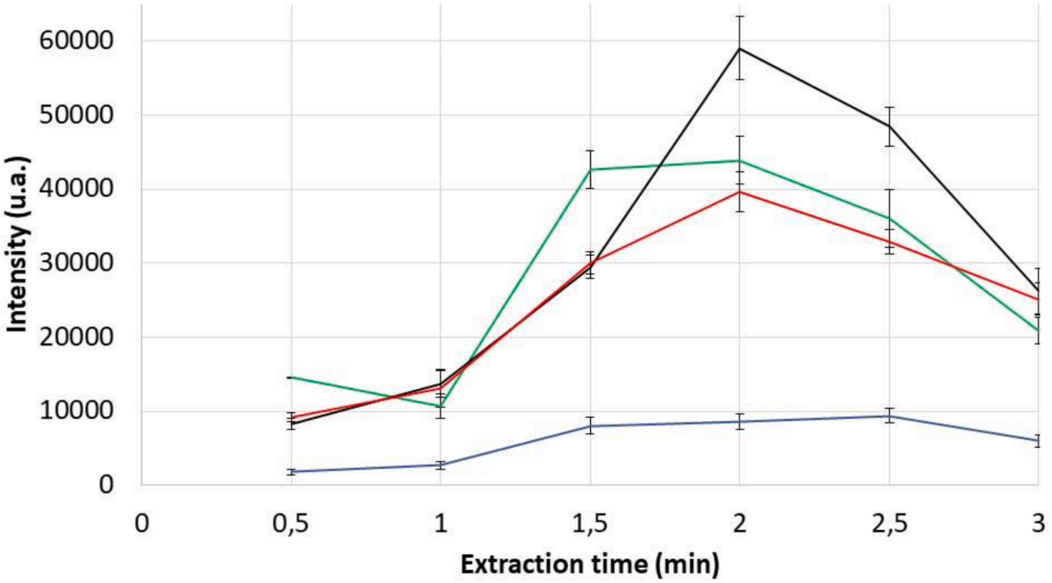

Fig. 2. ICP-MS/MS ionic intensity *versus* the DLLAPE extraction time for several nuclides. Green line: ^{60}Ni; blue line: ^{107}Ag; black line: ^{138}Ba; red line: ^{208}Pb. Sample: Carinata oil: CO. Error bars correspond to the standard deviation obtained from five extraction replicates.

extraction efficiency, the ICP-MS/MS signal was measured for each one of the assayed times. The obtained results are summarized in Fig. 2 for four different nuclides. It was first verified that the selected DES was able to extract some of the elements of interest. Besides, the maximum signal was achieved at extraction time of 2 min. Similar results were encountered for elements such as Cu and Zn. An increase in the extraction time in the case of the DLLAPE was associated to an increase in the total mass of extracting solution used, thus increasing the analyte extraction yield. However, when the volume of the extracting solution became excessively high, the signal decreased because of the analyte dilution and the losses of solution as the tube became full.

A different study was performed in ICP-OES to extend the extraction study to a total of 13 analytes. A used cooking oil sample (AU1, see Table 1) was spiked at 2 mg kg^{-1} with a multielemental organic certified solution containing alkaline, alkaline earth, transition metals (monovalent and di-valent), tri-valent metals and heavy metals (Ag, Al, Ba, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Ni and Pb). It was observed that, for the selected elements, an extraction time of around 2 min provided the maximum ICP-OES emission signal. This experiment also helped to verify that the DLLAPE was an appropriate method for multielemental analysis of oil samples both in ICP-OES and ICP-MS/MS.

From the obtained data, it was concluded that a 2 min extraction time was appropriate. This gave rise to an extractant to sample ratio (R) close to 4, that warrantied the extraction of almost the totality of the analyte mass while minimized the impact of the sample dilution on the analytical signal. This extraction time was in contrast with the optimum value found in previous works with an extracting solution containing water and methanol at 1:1 ratio (*i.e.*, 1.5 min) [14]. This was mainly due to the characteristics of the aerosols generated. In fact, it was found that the aerosols were finer for solutions containing methanol than for the DES (lower surface tension and viscosity for the former solution). As a result, the exchange liquid surface area was lower in the latter case and, hence, a slightly longer extraction time was required.

Analytical performance of the DLLAPE

A precision study was undertaken by performing sixteen consecutive extraction of independent sample aliquots. The RSD (%) values found for the different elements are summarized in Table 3. To evaluate the contribution of the detection to the RSD, two different ICP-OES spectrometers were used under optimized conditions.

In general terms, the achieved results were acceptable (*i.e.*, RSD ≤ 10%). Nevertheless, some elements did not follow this rule. Thus, for instance, results for Fe, Li and Mg were, in some cases, higher than this value. Furthermore, these elements were those for which high blank signals were registered (Table 3). In any case, these metals could be determined in the samples of interest.

Table 3
RSD (%, $n = 16$) using the DLLAPE with a DES as extractant solution and the two ICP-OES spectrometers.

Element/ wavelength (nm)	ICP1 [*]	ICP2 [#]	Blank signals for the DES ICP2/ cps	Blank signals for ultrapure water ICP2/ cps
Ag 328.068	5	3	420	250
Al 167.019	10	3	19	28
Ba 455.403	4	-[&]	730	770
Cd 214.439	5	6	37	31
Cr 267.716	4	20	150	70
Cu 327.395	4	7	160	110
Fe 238.204	14	12	1020	60
K 766.491	-[&]	7	1680	1960
Li 670.783	7	-[&]	46,100	50,700
Mg 279.553	17	6	23,900	1680
Mn 257.610	5	7	220	110
Ni 231.604	5	4	38	38
Pb 220.353	6	-[&]	60	34

[*] Agilent system (see Experimental section).

[#] Perkin-Elmer system (see Experimental section).

[&] Not detected.

To test the reliability of the DLLAPE, once the extraction was completed, a second extraction was done on the residual sample. No analytical signals distinguishable from the blank were encountered in the DES extracts for Ag, Al, Ba, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Ni and Pb, that meant that the first extraction was complete for these elements.

Furthermore, a recovery study was performed in which the Conostan® multielemental standard was added to the UO1 sample so that the spiked concentration of Ca, Cu, Mg and Ni was 2 mg kg^{-1}. The DLLAPE was applied to the spiked sample and the analysis of the extracts was done by means of external calibration using multielemental standards prepared in the DES. The DLLAPE was also applied to the UO1 non-spiked sample, and the elemental concentration was obtained through external calibration as well. Recovery (R) was calculated according to the following equation:

$$R = \frac{Concentration\ spiked\ UO1 - Concentration\ non\ sipked\ UO1}{2} \times 100 \tag{1}$$

The obtained recoveries for the four tested elements were included in the range (100 ± 20)% that also provided an indication of the good accuracy of the DLLAPE when a DES was used as extracting agent.

Recoveries were also determined for other elements. However, the obtained values were significantly lower than 100%. Thus, for Ag, Al, Ba, Cd, Cr and Fe, the respective values were: 22, 30, 35, 11, 34 and 30%. These results could be likely linked to the fact that the chemical form of these elements in the stock solution was not compatible with the solvent employed. It should be noted that, according to the literature, the behavior of trace metals or organometallic substances may depend on their chemical form [37]. Therefore, more hydrophobic DES should be tested in order to extract non-polar organometallic compounds. Finally, Li and K were not present in the Conostan® stock solution used and signals for Pb were extremely low.

For all the aforementioned reasons, the concentrations found with the DLLAPE were compared against those provided by conventional methods based on the sample dilution prior to its analysis and vortex agitation liquid-liquid extraction using the selected DES as extracting solution.

Comparison of the DLLAPE with the dilution and shot analysis through ICP-OES

To evaluate the efficiency of DLLAPE when using DES, three used cooking oils (UO) were analyzed and the concentrations obtained were compared against those provided by a conventional method consisting of the sample dilution with xylene and direct introduction into an ICP-OES system.

Table 4 summarizes the obtained concentrations according to the two studied methods. The gray cells correspond to those situations in which both methods provided similar concentrations according to the Fisher test (α=0.05; n_1=6 and n_2=5). Black figures highlight the data for which, unlike the dilution method, the DLLAPE provided quantitative results. This was due to the lower detection limits that were provided by the latter procedure because the dilution factor was lower than that for the reference method. Note that with the conventional method, all samples were diluted with xylene by a factor 1:20 (sample:xylene). Meanwhile, with the DLLAPE procedure, the sample dilution factor was 1:2 (sample:DES). This fact contributed to obtain lower LODs with the extraction method as compared to the dilution and shot procedure. Finally, the numbers in red indicated those situations for which the DLLAPE and the extraction methodology afforded significantly different concentrations. According to the data shown in Table 4, only for 3 out of 24 evaluated situations, both methods provided significantly different elemental concentrations.

Table 4
Multielemental concentrations (mg kg^{-1}) found with the DLLAPE and with a conventional method based on the sample dilution and shot analysis through the Perkin-Elmer ICP-OES.

Element	UO2		UO4		UO5	
	DLLAPE	Dilution and shot analysis	DLLAPE	Dilution and shot analysis	DLLAPE	Dilution and shot analysis
Al	0.40 ± 0.08	0.47 ± 0.09	1.03 ± 0.08	1.2 ± 0.2	1.03 ± 0.06	1.1 ± 0.2
Cd	0.26 ± 0.06	0.29 ± 0.14	0.29 ± 0.03	0.35 ± 0.03	0.27 ± 0.04	2.01 ± 0.09
Cr	0.12 ± 0.03	0.11 ± 0.02	0.484 ± 0.003	0.10 ± 0.02	0.486 ± 0.006	0.35 ± 0.03
Fe	0.16 ± 0.04	0.20 ± 0.05	0.39 ± 0.06	0.28 ± 0.08	0.39 ± 0.02	7.4 ± 0.2
Mg	0.65 ± 0.03	< 0.02	1.21 ± 0.3	1.29 ± 0.14	0.81 ± 0.02	0.85 ± 0.10
Mn	0.29 ± 0.06	< 0.013	0.32 ± 0.04	0.25 ± 0.07	0.29 ± 0.04	0.26 ± 0.06
Ni	0.27 ± 0.06	< 0.18	0.30 ± 0.05	< 0.18	0.27 ± 0.03	< 0.18
Pb	0.29 ± 0.07	< 1.2	0.33 ± 0.06	< 1.2	0.27 ± 0.05	< 1.2

It is worth mentioning that the sample dilution factor required with the DLLAPE (*i.e.*, 2) was ten times lower than that needed in the case of the dilution and shot analysis procedure. Therefore, the limits of quantification were lower for the DLLAPE procedure. In the present work, the procedural limit of quantification, pLOQ, was calculated (Table 5).

The pLOQ was calculated according to:

$$pLOQ = \frac{10\, s_b}{S}\, DF \qquad (2)$$

where s_b was the standard deviation corresponding to 10 consecutive blank measurements, S was the sensitivity defined as the slope of the calibration line and DF was the effective sample dilution factor (*i.e.*, 20 in the case of the dilution and shot analysis method and 2 for the DLLAPE).

The obtained results are summarized in Table 5 for the three spectrometers used. It may be verified that, in the case of the Perkin-Elmer instrument the DLLAPE methodology afforded pLODs from roughly 1.3 to 10 or even higher depending on the element and the spectrometer used.

Table 5
Procedural limits of quantification (pLOQ) found in ICP-OES as well as in ICP-MS/MS.*.

Element	pLOQ Perkin-Elmer mg kg^{-1}	pLOQ Agilent mg kg^{-1}	pLOQ Perkin-Elmer dilution & shot analysis mg kg^{-1}	pLOQ ICP-MS/MS mg kg^{-1}
Ag	0.05	0.06	n.d.	0.0024
Al	0.4	0.08	0.2	n.d.
Ba	n.d	n.d.	0.2	0.011
Cd	0.013	0.12	0.6	0.001
Cr	0.033	0.11	0.11	n.d.
Cu	0.040	0.012	0.11	0.004
Fe	0.20	0.13	0.20	n.d.
K	0.03	0.03	n.d.	0.017
Li	0.03	0.020	n.d.	0.0016
Mg	0.3	0.033	0.04	n.d.
Mn	0.013	0.073	0.05	0.004
Ni	0.13	3	0.3	0.004
Pb	0.53	5	1.3	0.002

[*] pLOQ correspond to the analyte concentration that could be actually determined with a 95% confidence level in the original sample.

Comparison of the DLLAPE with a conventional vortex agitated extraction method in ICP-MS/MS for trace analysis

The results found with the method based on the aerosol phase extraction were also compared against those provided by a vortex shaker. The detector selected in this case was the ICP-MS/MS instrument, because it provided extremely low limits of detection. Note that, for the oils selected (AU6, AG and CO), the concentration in the sample for most of the elements was below the limit of detection provided by the ICP-OES instrument.

To compare both methods, the concentration found by applying the DLLAPE was divided by that measured according to the vortex-based method. Obviously, a value of 1 in this parameter indicated results were similar. According to Fig. 3, considering the error bars and with a 20% tolerance (see dashed lines in Fig. 3), the concentrations did not depend on the method selected, thus highlighting the good accuracy of the DLLAPE.

It was interesting to notice that Ba concentrations found with the DLLAPE method agreed with those given by the reference method (Fig. 3). Thus, it was verified that the aerosol phase extraction could be considered as a good protocol for the quantification of this element as well. It was also remarkable that, because and ICP-MS/MS was used, elements not detected by ICP-OES (*e.g.*, Li, Pb, Ni with the conventional dilution and shot analysis procedure) were quantified. This permitted to verify that, also for these elements, similar results could be obtained with the DLLAPE and a conventional extraction method.

In contrast, with the ICP-MS/MS employed, nuclides such as ^{52}Cr, ^{56}Fe and ^{24}Mg were not determined, because of the existence of spectral interferences caused by $^{12}C^{15}N^{+}$, $^{40}Ar^{12}C^{+}$, $^{40}Ar^{16}O^{+}$ and $^{12}C^{12}C^{+}$, respectively. Besides, ^{27}Al was interfered by $^{12}C^{15}N^{+}$ or $^{13}C^{14}N^{+}$, among other ions [38]. This problem could be overcome by properly optimizing the instrumental reaction – collision cell conditions. However, this was out of the scope of the present study, because the main interest was focused on the applicability of the DLLAPE for the multielemental extraction in oily samples.

Analysis of real oil samples through ICP-OES

As mentioned before, a total of ten real samples were analyzed through ICP-OES. The results are shown in Table 6. The data corresponding to olive oils were compared against those published in the literature obtained through digestion (see Table 7). It may be observed that most of the determined elements (Table 6) lied within the ranges defined by published studies.

Some of the elements present in the samples analyzed were considered in official regulations as they may have hazardous effects. Thus, for instance, according to the Spanish regulation, Cu maximum level in vegetal oils is 0.4 mg kg^{-1} [39]. European regulations establish the same level for this element in fats and virgin oils, whereas in the particular case of olive oil, a 0.1 mg kg^{-1} maximum level is established [40]. Copper is commonly used as pesticide even in organic olive production [41]. Therefore, this element is often determined in oil samples. Long term exposure to this element above this concentration may cause skin, eyes, nose and throat irritation as well as kidney and liver affections. As it may be observed from Table 6, the levels found for this element did not surpass the maximum values, although for samples labelled as MP and AP, Cu concentrations were slightly above those dictated by the European regulation for olive oils. Interestingly, by considering the Cu concentration for used cooking oils, it was clearly seen that the level of this element was far above those provided for olive edible oils. This fact suggested that Cu could be incorporated to the oil during the cooking process either from the processed foods or from the metallic components in contact with oil.

Lead is another element considered in several regulations regarding oils and fats [38,39]. In those instances, the maximum permitted value is 0.1 mg kg^{-1}. This element may cause severe health problems such as

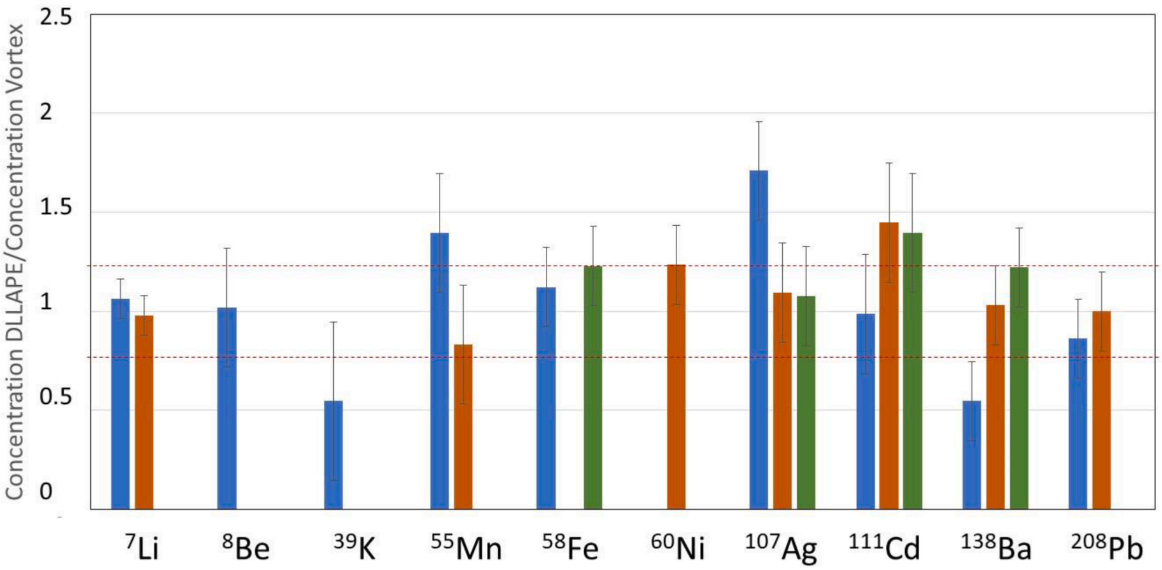

Fig. 3. Concentration found with the DLLAPE divided by that found with the vortex method for a used cooking oil (blue, UO6), animal fat (orange, AG) and Carinata oil (green, CO). Error bars correspond to the expanded confidence intervals for the analytical concentrations.

Table 6
Analytical concentration (mg kg^{-1}) of the different oil samples tested.[*].

Sample code					
Element	MP	AP	BV	MV	AV
Al	0.522 ± 0.011	0.49 ± 0.04	0.42 ± 0.07	0.383 ± 0.017	0.373 ± 0.018
Ba	0.120 ± 0.005	0.109 ± 0.013	0.099 ± 0.018	0.091 ± 0.010	0.090 ± 0.009
Cr	0.156 ± 0.04	0.147 ± 0.010	0.13 ± 0.02	0.117 ± 0.003	0.117 ± 0.010
Cu	0.13 ± 0.03	0.114 ± 0.011	0.099 ± 0.013	0.085 ± 0.002	0.082 ± 0.006
Fe	0.17 ± 0.02	0.158 ± 0.015	0.15 ± 0.04	0.139 ± 0.005	0.139 ± 0.015
Mg	0.4 ± 0.4	0.22 ± 0.080	0.15 ± 0.09	0.160 ± 0.015	0.107 ± 0.012
Mn	0.385 ± 0.008	0.36 ± 0.03	0.30 ± 0.04	0.277 ± 0.009	0.26 ± 0.02
Ni	0.39 ± 0.05	0.33 ± 0.03	0.29 ± 0.04	0.257 ± 0.006	0.247 ± 0.015
Pb	0.46 ± 0.09	0.36 ± 0.11	0.31 ± 0.05	0.278 ± 0.009	0.26± 0.02
Sample code					
Element	UO1	UO2	UO3	UO4	UO5
Al	0.84 ± 0.07	0.40 ± 0.08	0.96 ± 0.08	1.03 ± 0.08	1.03 ± 0.06
Ba	0.090 ± 0.010	0.099 ± 0.013	0.4769 ±0.0014	0.49 ± 0.03	0.480 ± 0.006
Cr	0.108 ± 0.010	0.12 ± 0.03	0.487 ± 0.004	0.484 ± 0.003	0.486 ± 0.006
Cu	0.38 ± 0.03	0.088 ± 0.018	0.4868 ± 0.0007	0.49 ± 0.02	0.479 ± 0.003
Fe	0.36 ± 0.03	0.16 ± 0.04	0.39 ± 0.12	0.39 ± 0.06	0.39 ± 0.02
Mg	0.43 ± 0.04	0.65 ± 0.03	0.494 ± 0.013	1.21 ± 0.3	0.81 ± 0.02
Mn	0.27 ± 0.02	0.29 ± 0.06	0.33 ± 0.03	0.32 ± 0.04	0.29 ± 0.04
Ni	0.24 ± 0.02	0.27 ± 0.06	0.31 ± 0.03	0.30 ± 0.05	0.27 ± 0.03
Pb	0.34 ± 0.02	0.29 ± 0.07	0.33 ± 0.03	0.33 ± 0.06	0.27 ± 0.05

[*] 95% confidence intervals have been calculated according to $t*s/n^{1/2}$, where t is the student t, s the standard deviation and $n = 5$.

Table 7
Analytical concentration of oil samples found in the literature.

Element	Concentration range found in the present work (mg kg^{-1})	Concentration range found in the literature (mg kg^{-1})	Reference
Al	0.37 – 0.52	0.5	[42]
Cr	0.117 – 0.156	0.116 - 0.368 0.018 – 0.114	[35] [43]
Cu	0.082 – 0.13	< 0.1 0.016 – 0.059 0.04 – 0.13	[34] [44] [33]
Fe	0.139 – 0.17	< 0.5 0.089 – 0.551 0.040 – 0.120	[34] [35] [45]
Mg	0.15 – 0.4	< 0.5 0.056 – 1.032	[46] [47]
Mn	0.26 – 0.385	0.05 – 0.025 < 0.1	[35] [34]
Ni	0.247 – 0.39	0.18 – 0.53 0.0106 – 0.0469	[34] [35]
Pb	0.26 – 0.46	0.0009 – 0.005 0.032 – 0.156	[33] [32]

kidney diseases and increase in the blood pressure, among others. As it may be observed, the concentrations reported in Table 6 were above the limits established by official regulations. However, as Table 5 reveals, the pLOQ was higher than the determined lead concentrations for all the analyzed samples.

As regards chromium, this element was present in all the analyzed samples and, interestingly, its concentration in used cooking oils was similar to or higher than that detected in olive non processed oils. The impact of Cr on health strongly depends on its chemical form. Thus, whereas trivalent Cr is an essential species, hexavalent Cr causes kidney and lung cancers, among other disorders. This element must be present in foods at concentrations below 0.1 mg kg^{-1} [39]. Even though the analyzed samples contained Cr at concentrations slightly above this value, the Cr levels found for olive oils were in agreement with those reported in previous works for this kind of samples (Table 7).

Nickel and manganese are not fully considered in regulations on edible olive oil, but they may have hazardous consequences and affections on organs such as stomach, lungs, kidney, and liver. Both elements were present at similar contents in non-treated and cooked oils, thus suggesting that their origin was rather related with the production process than the cooking one.

Other elements such as Al, Ba or Mg were found at similar concentrations as those included in previously published works (see Table 7).

By comparison of the data for olive oil against those provided for used cooking oils, it was observed that certain elements were present at higher contents in the latter situation. Thus, for instance, Fe concentration is up to around three times higher for used as compared to raw oils. Qualitatively similar results were found for elements such as Al or Ba. Elements such as Mn, Pb, Ni or Cr could be present in the samples because of oil pollution during the fruit processing or caused by exogeneous environmental sources.

Analysis of real samples through ICP-MS/MS

In order to extent the method to the determination of additional trace elements in “clean” samples, an ICP-MS/MS instrument was used. Table 8 provides the multielemental concentration for three additional samples. It was verified that the elemental content was below the procedural limit of detection achieved by the ICP-OES instruments used for the three samples and the elements included in this table. The use of this instrument permitted to have access to information about the content of trace elements because of the lower pLOQs (see Table 5).

The concentrations determined for elements considered in the European regulation for fat were above those reported for the analyzed sample (Table 8). Thus, lead and nickel maximum level in this kind of samples were 0.1 and 0.2 mg kg^{-1}, respectively [39].

Table 8
Concentrations (mg kg^{-1}) and confidence interval (95%, n = 5) for three different samples obtained with the DLLAPE in ICP-MS/MS.

Nuclide	UO1	CO	AG
^{7}Li	0.051 ± 0.006	n.d.	0.047 ± 0.005
^{39}K	0.108 ± 0.020	n.d.	n.d.
^{55}Mn	0.088 ± 0.012	n.d.	0.059 ± 0.012
^{60}Ni	0.072 ± 0.010	n.d.	0.021 ± 0.001
^{107}Ag	0.094 ± 0.016	0.014 ± 0.001	0.059 ± 0.009
^{111}Cd	0.066 ± 0.014	0.067 ± 0.013	0.068 ± 0.012
^{138}Ba	0.035 ± 0.002	0.033 ± 0.002	0.033 ± 0.002
^{208}Pb	0.062 ± 0.008	n.d.	0.064 ± 0.006

Conclusions

The dispersive liquid – liquid aerosol phase extraction, DLLAPE, method is perfectly suitable for the multielemental oils and fat analysis through ICP techniques. Appropriate performances are achieved in both ICP-OES and ICP-MS/MS.

With the DLLAPE method, the sample throughput was close to 25 h^{-1} (two minutes extraction time + 30 s for phases complete separation). This value can be compared against the 4 h^{-1} (five minutes shaking time + 15 min for phases complete separation) achieved in the case of the vortex-based method.

Compared with the dilution and shot analysis method, the DLLAPE provides procedural limits of quantification on the order of up to ten times lower. This is mainly due to the lower dilution factor required when working with the former methodology.

Furthermore, the DLLAPE can be easily automatized by adapting the nebulizer to an ICP autosampler, preparing the diluted samples into polyethylene tubes and programming the autosampler flushing (extraction) time and the samples sequence. With this setup, it was possible to achieve a sample throughput of 30 samples h^{-1}. This was virtually impossible in the case of the vortex-based method.

The use of DES in combination with the DLLAPE is perfectly indicated to the multielemental analysis of oils (both processed and non-processed) and fats. Future work will evolve in two different directions: on the one hand, additional organometallic compounds will be extracted, thus requiring the selection of hydrophobic DES as extracting agent, and, on the other, DES extractions will be applied to the determination of organic compounds present in processed oils such as polyphenols and tocopherols in order to avoid the need of using toxic volatile solvents such as methanol in this kind of determinations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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