Determination of Fe, Cu, and Pb in edible oils using choline chloride: ethylene glycol deep eutectic solvent-based dispersive liquid-liquid microextraction associated with microwave-induced plasma optical emission spectrometry

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ABSTRACT

A new simple, fast and environmentally friendly deep eutectic solvent based dispersive liquid-liquid micro-extraction (DES-based DLLME) methodology assisted by vortex is presented for the separation and preconcentration of three elements (i.e., Fe, Cu and Pb) from edible oil samples (i.e., soybean, sunflower, rapeseed, sesame, and olive oil) prior to the determination by microwave-induced plasma optical emission spectrometry (MIP-OES). The deep eutectic solvent selected as extractant (i.e., choline chloride and ethylene glycol, 1:2) is synthesized and characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and differential scanning calorimetry (DSC), and the extraction conditions are optimized by a two steps experimental design. Under the optimum extraction conditions (i.e., diluted sample weight: 8.6 g; DES volume: 100 μL; extraction time: 1 min; centrifugation time and speed: 3 min and 3000 rpm; and dispersion system: vortex) the analytical method presents excellent linearity (i.e., R^2 values higher than 0.99) in the range 10–500 μg kg^{-1}, repeatability (i.e., CV values lower than 9.2%), and limits of detection (LOD) values of 3, 2 and 0.7 μg kg^{-1} for Pb, Fe and Cu, respectively. None of the analytes displayed amounts over the upper limit permitted by law, and recovery values of all analytes evaluated in the different samples using external standard calibration were close to 100%, which excludes significant matrix effects. Finally, AGREEprep metric has been used to evaluate the method greenness (final score of 0.47) and it has been compared successfully with previous publications for the same type of analytes and matrices.

1. Introduction

The most essential vitamins and unsaturated fatty acids for human health can be found in edible oils [1]. Their consumption has been associated with a variety of health benefits including the lowering of blood cholesterol and the prevention of cardiovascular diseases as they are a source of energy, structural component and contribute in the production of powerful biological regulators [2]. However, the large-scale application of chemical pesticides and fertilizers during the growing season or the contamination during the production and storage process may result in the presence of hazardous substances in the oil [3].

Two of the many elements that can be found in edible oil samples are copper (Cu) and iron (Fe), which are noteworthy for their negative effects on taste and elevated oxidative rate [4]. High levels of these elements in the organism have been linked to the possibility of developing cancer or other pathological effects on the digestive system [2]. Also, the human health and the environment may be threatened by the presence of elements like chromium, cadmium, lead, mercury, zinc, or arsenic due to their high toxicity, persistence and irreversibility. Particularly, Pb consumption has been associated with negative effects on the endocrine and immunological systems, bones, blood flow and neurons in humans [3]. To preserve human health and public trust in the oil food industry,

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the Codex Alimentarius Commission has set maximum permitted levels for most of these elements. Specifically, the maximum concentrations allowed in virgin oil samples are 100, 400 and 5000 µg kg^{-1} for Pb, Cu and Fe, respectively. As for refined oil samples, maximums of 100, 100 and 1500 µg kg^{-1} are established for Pb, Cu and Fe, respectively [5,6].

Atomic spectrometry techniques are generally used for elemental determination in edible oils [7–10]. Nevertheless, sample preparation is necessary due to the complexity of the food matrix sample. The oil sample has a considerable amount of organic matter and low levels of metals, which is one of the main challenges for the determination [11]. The bibliography describes a variety of sample preparation techniques, such as extraction induced by emulsion breaking methods [11,12], dilution with organic solvents [9,13,14] or microwave digestion [15,16] to reduce matrix interferences.

The first study on the use of liquid-liquid microextraction (LLME) for inorganic analyses was published in 2004 [17]. Some of its advantages are low sample and solvent volume requirements, speed, simplicity, high enrichment factor, minimum waste generation and affordability for any laboratory. These characteristics make LLME an environmentally friendly sample preparation method and are in accordance with the majority of principles of the Green Analytical Chemistry [18]. Numerous LLME techniques have been developed and reported for metal separation [19]. Among them, dispersive liquid-liquid microextraction (DLLME), which was first used in 2006 for organic analysis [20], has experienced a significant development in the last years.

Since the first used of DLLME in inorganic analysis in 2007 [21], DLLME has been coupled to different atomic spectrometry techniques such as FAAS [22], ETAAS [23], ICP-OES [24] and ICP-MS [25]. However, less attention has been given to microwave-induced plasma optical emission spectrometry (MIP-OES). This technique was first applied by Mavrodineanu and Hughes in 1963 [26]. However, its development has been slow until the introduction of Agilent commercial equipment in 2011 and its first scientific publication in 2012 [27]. In contrast, few manuscripts proposed the combination of DLLME and MIP-OES, probably because of the negative effects of organic matrices in microwave plasma [28]. In fact, the lower energy of the nitrogen plasma can decrease the sensitivity compared with a typical ICP argon plasma, as a consequence, MIP-OES is more prone to matrix effects than ICP-OES [29, 30].

Despite the several advantages of conventional DLLME, the use of disperser solvent and the consumption of hazardous organic solvents suppose two main limitations. Specifically, the decrease in the partition coefficient of the analytes due to the use of disperser solvents. For this reason, mechanical agitation using ultrasound or vortex-assisted DLLME have been developed [19]. In terms of limiting the use of harmful organic solvents, replacing them with deep eutectic solvents is a considerable alternative due to their low cost, availability and, above all, their ecological nature.

In 2003, Abbott et al. introduced the DESs as more environmentally friendly solvents [31]. Even though electrostatic forces and van der Waals interactions have been described, the majority of DESs are formed by the combination of different hydrogen bond acceptors (HBA) and donors (HBD) [32]. In general, DESs have the benefit of being less toxic, more stable during extraction process and biodegradable in comparison to conventional solvents [33]. Additionally, their preparation are simple and affordable due to inexpensive raw materials. However, some DESs can difficult the analyses due to their high viscosity [34].

In the present work, a DES-based DLLME methodology assisted by vortex is proposed to perform elemental analysis by MIP-OES in edible oil samples for the first time. The replacement of toxic disperser solvents (e.g., chloroform or toluene) by mechanical vortex agitation, the use of environmentally friendly extraction solvents in miniaturized processes, as well as the use of a more economical detection technique than those commonly used, highlight the novelty of the method.

The extractant (i.e., choline chloride:ethylene glycol, 1:2) is synthesized and characterized, and the extraction conditions are optimized

by an experimental design (i.e., two steps multivariate approach). The DES-based DLLME-MIP-OES method is validated and the applicability assessed analyzing five real samples. Finally, a critical comparison is made with previous works developed for the same purpose, paying special attention to their ecological nature through a quantitative assessment using the AGREEprep metric [35].

2. Experimental

2.1. Apparatus and instrumentation

During the experimental process, a mechanical multivortex stirrer (Heidolph Instrumens, Schwabach, Germany) was used as the dispersion system, and centrifuge equipment (Mixtasel BL Selecta, Barcelona, Spain) was used to carry out the separation of phases.

The elements were quantified using an Agilent 4100 microwave plasma atomic emission spectrometer (Agilent Technologies, Melbourne, Australia). The equipment includes a OneNeb® nebulizer (Ingeniatrics Technologies, Seville, Spain) and double pass cyclonic spray chamber (Glass Expansion, Victoria, Australia). Nitrogen and compressed air were supplied via bottled gas at a rate of 25 L min^{-1} to generate plasma (Carburos Metálicos, Barcelona, Spain). The plasma operating conditions used in MIP-OES are shown in Table S1. For the characterization of hydrophilic DES, infrared spectra were measured on a Jasco FT/IR-4100 Fourier Transform Infrared (FT-IR) spectrometer (Jasco International Co. Ltd., Tokyo, Japan). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker AC-300 (300 MHz) or AC-400 (400 MHz) NMR spectrometers (Bruker Corporation, Billerica, MA, USA) in proton coupled mode. Differential Scanning Calorimetry (DSC) analyses were performed on a Mettler Toledo equipment, model TGA/SDTA851e/LF/1600 (Mettler Toledo AG, Greifensee, Switzerland). In DSC, the samples were continuously purged with 50 mL min^{-1} of nitrogen. About 6 mg of each compound was crimped in an aluminum standard melting pot and analyzed under dynamic nitrogen atmosphere by heating (5 or 1 °C min^{-1}) and cooling (5 or 1 °C min^{-1}) cycles between −70 and 120 or 350 °C.

2.2. Reagents, standard solutions and samples

A commercial solution of Conostan at a concentration of 500 g g^{-1} (SCP Science, Baie D'Urfé, Canada) in petroleum ether (QP, Panreac, Barcelona, Spain) was used to prepare the calibration standards and the optimization was performed at a concentration of 500 µg kg^{-1} for all the analytes. The extracting solvent was a hydrophilic DES made from choline chloride and ethylene glycol (ChCl:EG) at a molar ratio of 1:2.

In the present work, five commercial edible oil samples were purchased in the supermarket and were analyzed: virgin soybean oil (Clearspring Ltd., London, UK), virgin sunflower oil (Naturgreen, Spain), extra virgin olive oil (Carbonell, Spain), refine rapeseed oil (Carrefour, France) and refine sesame oil (Youwok, Netherlands).

Choline chloride (purity ≥98%) provided by Alfa-Aesar™ (Kandel, Germany) was used as hydrogen bond acceptor (HBA) component for the DES. Dry ethylene glycol (purity ≥98%) provided by Acros Organics (Morris Plains, NJ, USA) was used as hydrogen bond donor (HBD) component. Reagents were used without any further purification. Choline chloride was recrystallized with absolute ethanol (HPLC grade) provided by Panreac to remove any water content that might have. For NMR experiments a deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent (Eurisotop, Sant-Aubin, France).

2.3. Preparation of the DES

The hydrophilic DES formed by choline chloride and ethylene glycol (1:2) was prepared by simply mixing choline chloride (10 mol) with ethylene glycol (20 mol) at 60 °C under argon atmosphere, stirring the mixture until a clear and homogenous liquid was formed (usually 30

min). DES was stored under argon atmosphere; however, it was used under air conditions. This hydrophilic DES was chosen because it allows the extraction of analytes present in organic samples, it is fast and easy to synthesize and it has a low viscosity (37 cP at 25 °C) [36], which facilitates the analysis.

2.4. Experimental design for optimization of the DLLME conditions

A multivariate optimization of two stages was used to carry out the experimental design using NemrodW statistical software (Nemrod® v.2007/2010, LPRAI, Marseille, France). First, a screening stage using a factorial Placket-Burman design was used to evaluate all the parameters that significantly and non-significantly affect the extraction process and the evaluated responses were the emission intensities obtained from MIP-OES. The parameters were evaluated factorially at two levels, establishing a range of values based on aspects related to the miniaturization of the extraction procedure or experimental and instrumental limitations. For example, a narrow time range was chosen for extraction (1–3 min) and centrifugation (1–3 min) in order to minimize the analysis time; the amount of diluted sample (5–8 g) was limited by the maximum volume of the test tube (10 mL). The centrifugation speed was considered according to the instrumental limitations of the centrifuge, which has a minimum and maximum speed of 1000 and 4000 rpm, respectively. Therefore, intermediate values were chosen (2000–3000 rpm). In case of dispersion system, vortex agitation corresponded to the low level and ultrasonic dispersion was the high level (Table S2). A total of twelve experiments were performed to examine the effects of these six factors (Table S3). The significant factors obtained from the screening stage were diluted sample weight and DES volume which were studied using a central composite design (CCD) to obtain their optimal values. For this design the factor levels are shown in Table S4, and the twelve experiments are presented in Table S5. In order to assure the independence of the outcomes and reduce the impact of uncontrollable factors, the experiments on both designs were carried out in a random order.

2.5. Dispersive liquid-liquid microextraction procedure

A weight of 8.6 g of the 10-fold diluted sample was put into 10 mL glass tubes. The samples were diluted in petroleum ether to reduce the high viscosity of the oil samples and to facilitate the extraction step with vortex agitation. A micropipette was then used to add 100 μL of the DES extractant solvent (ChCl:EG; 1:2). Following the addition of DES, the mixture was shaken for 1 min in a vortex shaker. Then, the cloudy solution obtained was centrifuged at 3000 rpm for 3 min to separate the organic sample and the extractant. After centrifugation, the extractant solvent containing the analytes of interest remained at the bottom of the tube. Then, the supernatant was removed and approximately 80 μL of the extract was collected. Finally, the extract was introduced directly into the MIP-OES instrument according to the experimental setup proposed by Sáez et al. [37] where a pipette tip of 200 μL was inserted in the peristaltic tube of the nebulizer, allowing the introduction of 80 μL of the extract. A schematic illustration of the general optimized DES-based DLLME-MIP-OES process is shown in Fig. 1.
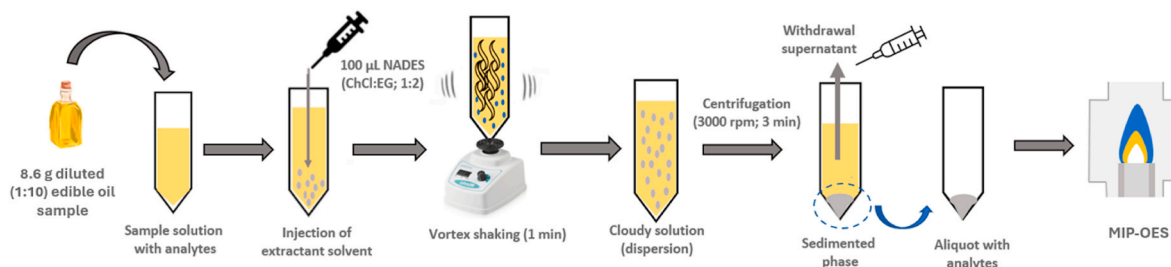
3. Results and discussion

3.1. Characterization of hydrophilic DES

To confirm the structure of DES, FT-IR spectra of pure choline chloride, pure ethylene glycol and DES were studied, and results are illustrated in Fig. S1. In the spectrum of pure choline chloride, absorptions corresponding to the tension and flexion –OH (3220, 1484 cm^{-1}, respectively) and the absorption corresponding to the tension C–O (1068 cm^{-1}) were observed. Additionally, the tension C–N was also detected (952 cm^{-1}). In the spectrum of pure ethylene glycol, the signals corresponding to the tension and flexion –OH as well as the tension C–O were observed (3301, 1403 and 1033 cm^{-1}, respectively). As somehow expected, all these characteristic peaks were also found in DES FT-IR spectrum demonstrating that the DES was comprised of choline chloride and ethylene glycol. Some slight shifts in the tension and flexion –OH and the tension C–O (3293, 1488, 1049 cm^{-1}, respectively) were noticed. These somewhat changes in O–H and C–O peaks might be due to the presence of some hydrogen bond interactions between HBA and HBD components.

Drawing attention to ^{1}H NMR experiments on DES performed in DMSO-d_6, a clear interaction between the hydroxy substituents of both choline chloride and ethylene glycol was observed since a significant shift in the signals was detected in comparison with pure starting materials (Fig. S2, compare **a**, **b** and **c**). A closer view could be seen in Fig. S2d to clarify the changes in shift observed, since all spectra were overlapped. Also, the integration of the signals in Fig. S2c shows that the components of the DES were in 1:2 M ratio. In case of ChCl the integration of the signal is 1.00 and for EG is 4.28. These results might indicate the successful preparation of the hydrophilic DES.

The existence of hydrogen-bond interactions between DES components has been previously detected in different mixtures by using 2DNMR experiments [38]. Thus, some close-proximity relationships through space were observed in a nuclear Overhauser effect spectroscopy (NOESY) experiment (Fig. 2) utilizing DMSO-d_6 as solvent. Some major polyol-polyol interactions were observed, in contraposition with some weaker interactions between the hydroxy groups of both ethylene glycol and choline chloride with the methyl groups from choline chloride and methylene from ethylene glycol, respectively were also noticed [39,40]. Fig. 3 corresponds to a proposed structure of choline chloride: ethylene glycol (1:2).

In relation to the DSC experiments (see Electronic Supporting Information), different samples were mixing and grinding with different proportions of choline chloride and ethylene glycol until a homogeneous mixture was reached. Those samples were analyzed by DSC. The phase diagram obtained after plotting the melting points from the DSC results shows a noticeable change in the shape for a molar ratio 1:2 of choline chloride:ethylene glycol (Fig. S3), although in typical deep eutectic solvent this point is correlated with the eutectic point, in strict sense this mixture is not a typical DES [41]. This phase diagram has an unusual slight depression which makes controversial the determination of the eutectic point, nevertheless this mixture is an eco-friendly liquid with unique and remarkably properties [42–48].
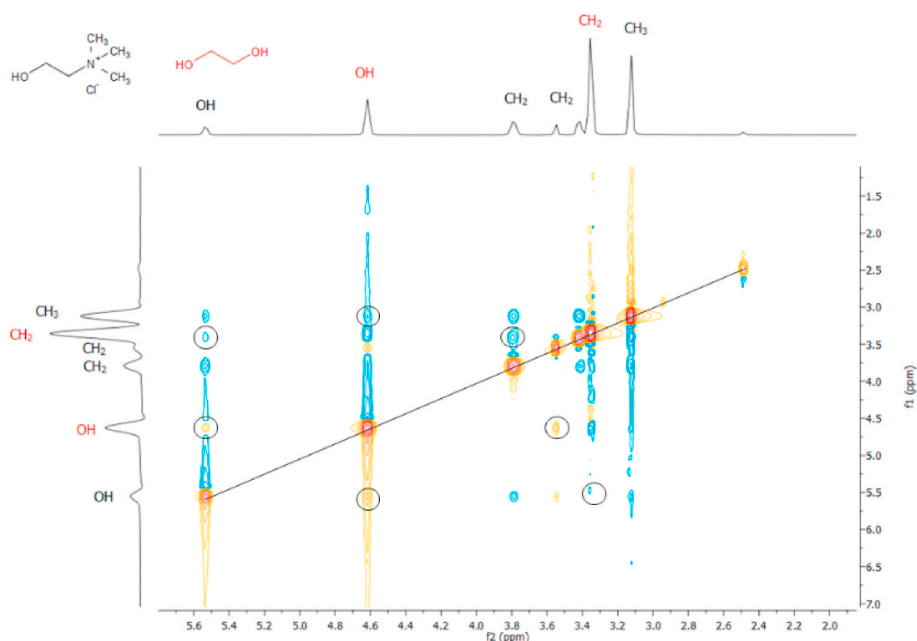

Fig. 1. Scheme of the DES-based DLLME-MIP-OES process assisted by vortex shaking.

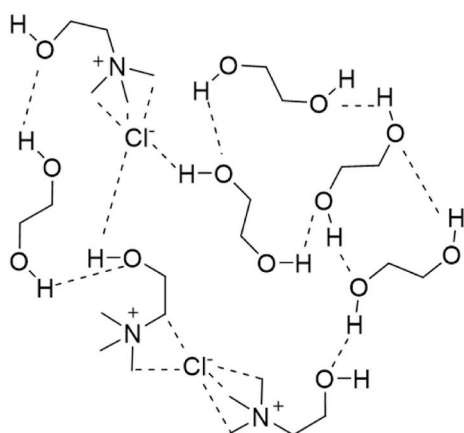**Fig. 2.** NOESY experiments of the mixture choline chloride:ethylene glycol (1:2).

Fig. 3. Possible structure of choline chloride:ethylene glycol (1:2).

3.2. Optimization of DLLME procedure

The vertical dashed lines in Pareto charts (Fig. 4) indicate the point at which the factor has a significant effect with a 95% confidence level. In turn, those parameters with a significant effect on the extraction process are represented by orange bars. The extraction process will be more favorable depending on whether the bars are displaced to the right (i.e., positive effect) or to the left (i.e., negative effect). On the other hand, the blue bars represent parameters with a non-significant effect on the extraction process.

Pareto charts obtained in the screening study of the main factors affecting the DLLME of Cu, Fe and Pb are showed in Fig. 4. Diluted sample weight and DES volume are the factors with a significant effect for each of the analytes investigated (i.e., Fe, Cu and Pb). Specifically, the diluted sample amount has a positive effect on the response. This can be explained due to the fact that a greater amount of sample implies a greater presence of analytes and, consequently, a greater response. On the contrary, the extraction process will be favored at a lower amount of DES volume (i.e., negative effect), since the higher the DES volume, the higher the dilution effect. On the other hand, centrifugation speed and time, the extraction time and dispersion system are not significant

factors with the exception of Fe, where the dispersion system has a significant negative effect. Therefore, it was decided to use vortex-assisted DLLME.

Extraction time has a negative effect on Cu and Pb and positive on Fe. The shortest extraction time (i.e., 1 min) was set in this situation because it reduced the extraction process. Centrifugation time has a positive effect for all the analytes studied. Similarly, centrifugation speed has a positive effect with the exception of Cu. As a result, it was decided to use a 3-min centrifugation time and a centrifugation speed of 3000 rpm. The results obtained after the optimization of significant parameters (diluted sample weight and DES volume) by using the CCD design show that the optimum values were at the extremes of the response surface in Fig. 5. Specifically, in all cases the optimized value of diluted (1:10) sample weight was 8.6 g and the optimized value of DES volume was 100 μL. Summarizing, the optimized DLLME factors are shown in Table S6.

3.3. Analytical figures of merit

All the analytical figures of merit were obtained under optimized extraction conditions (Table 1). In order to calculate limit of detection (LOD) and quantification (LOQ), the recommendations of the IUPAC (International Union of Pure and Applied Chemistry) were followed [49]. The LOD was computed as 3 times the standard deviation of the blank signal divided by the slope of the calibration curve, and the LOQ was calculated as 10/3 of the LOD. In both situations, the standard deviation of the blank signal was calculated from a total of 10 measurements. Linearity was evaluated for all the investigated analytes using standard solutions of 10, 50, 100, 250 and 500 μg kg^{-1}. A linear interval was achieved with coefficient of determination (R^2) for Fe, Cu, and Pb of 0.996, 0.994, and 0.994, respectively.

On the other hand, the repeatability of the analytical method proposed was investigated by performing five extractions of each analyte at 50 μg kg^{-1} and at 250 μg kg^{-1}. The coefficient of variation (CV) was calculated for both concentrations and CV values lower than 9.2 % were obtained for all the elements evaluated.

3.4. Commercial sample analysis

For all studied samples, the recovery values for all analytes under investigation were close to 100% using external standard calibration
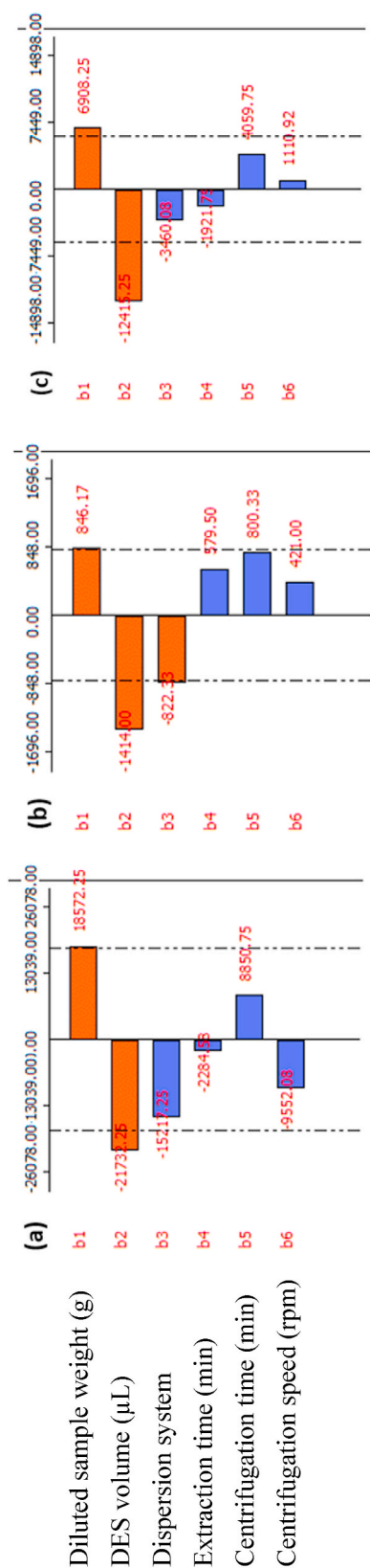
(Table 2). This suggests that there were no significant matrix effects and all the elements had concentrations lower than the legal limit [5], as can be seen in Table S7.

3.5. Evaluation of the procedure with AGREEprep method

The AGREEprep method was used for the evaluation under sustainability criteria of the developed method [35]. The description of each criterion can be found in Table S8. As can be seen in Fig. 6, the criteria that have been favored in the proposed method was criterion 6 corresponding to maximizing sample performance taking into account the number of samples prepared per hour. The criterion was favored because the proposed extraction method uses short times and the use of a multivortex and a centrifuge with a capacity of up to 12 samples simultaneously favors the analysis of a large number of samples in a short time. Criterion 8, which refers to minimizing the energy consumption of the process, was also favored in the metric because the equipment used in the extraction process (i.e., multivortex and centrifuge) requires little amount of energy per sample (67 Wh/sample). Finally, criterion 5 referred to minimizing the amount of sample in the analysis, it was also favored since the sample was diluted 1:10, thus the real amount was 0.86 g of oil sample.

On the other hand, the intermediate points of the evaluation correspond to criteria 9 and 10, which refer to the detection technique used and operator safety, respectively. In terms of simplicity and energy consumption, MIP-OES receives a similar score to AAS in criteria 9 as it is an intermediate level between molecular optical spectroscopy techniques (i.e., fluorimetry, chemiluminescence, among other) and ICP-based methods (i.e., ICP-OES and ICP-MS). This is because the MIP-OES equipment used for elemental determination is considered a greener option than techniques such as ICP-MS or ICP-OES, but not so much as molecular optical spectroscopy techniques (i.e., fluorimetry, chemiluminescence, among other). Regarding criterion 10, the hazardous of the reagents used in the analysis is taken into account, with petroleum ether being the only substance that contains two danger pictograms. With respect to criterion 4, referring to minimizing the amount of waste generated after the extraction process, the waste of 8.6 g was penalized in the metric as well as the lack of automated stages (criterion 7). Criteria 3 referred to the use of sustainable materials was also penalized for the use of petroleum ether.

Finally, the criterion most penalized in the evaluation of the method was criteria 1 related to the *in situ* preparation of the samples because it was carried out *ex situ* in the laboratory; and, criterion 2 corresponding to the use of safe reagents because of the amount of petroleum ether used (7.74 g). Considering the value obtained in each of the commented criteria, the final score of the evaluation was 0.47 on a scale from 0 to 1, considering green method values higher than 0.5. Therefore, it is necessary to take into consideration some aspects to improve the final score. For example, improving the automation of the processes, reducing the amount of waste generated or replacing petroleum ether with other less harmful solvents to achieve a more environmentally friendly method.

3.6. Comparison with previous works

Last decade, several studies on elemental determination in edible oil samples have been reported. The ecological aspects assessed using the calculated AGREEprep score, as well as the main figures of merit of the developed analytical method have been compared with other previous works reported in the bibliography (Table 3). As can be seen, the majority of the reported methods involved relatively high sample preparation time of 20 min or longer [9,11,50–52], although in one of them, the time consumed in sample preparation was lower than the proposed method [53]. However, this method has been validated for only one element (i.e., Cu) with a higher LOD value and more expensive detection equipment [53]. Regarding the study of DES as extractant phase and
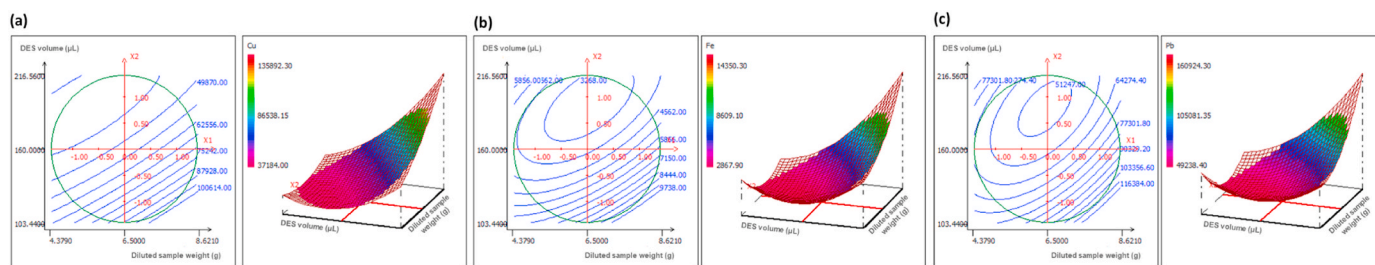

Fig. 4. Pareto charts obtained in the screening study of the Plackett-Burman design of **(a)** Cu, **(b)** Fe and **(c)** Pb.

Fig. 5. Response surfaces of the CCD design of **(a)** Cu, **(b)** Fe and **(c)** Pb.

Table 1
Analytical figures of merit of the method proposed.

	Emission line (nm)		
	Pb (405.781)	Fe (259.940)	Cu (324.754)
Linear range ($\mu g\ kg^{-1}$)	10–500	10–500	10–500
Sensitivity (cps kg μg^{-1})	550 ± 20	17.1 ± 0.7	155 ± 7
R^{2a}	0.994	0.996	0.994
LOD ($\mu g\ kg^{-1}$)	3	2	0.7
LOQ ($\mu g\ kg^{-1}$)	9	6	2
Repeatability (CV %; 50 $\mu g\ kg^{-1}$)	8.8	7.1	7.8
Repeatability (CV %; 250 $\mu g\ kg^{-1}$)	8.7	7.2	9.1

[a] Determination coefficient (five calibration points).

Table 2
Relative recovery values obtained for the spiked samples (50 and 250 $\mu g\ kg^{-1}$) and found concentrations values ($\mu g\ kg^{-1} \pm s^{a}$) in edible oil diluted samples analyzed for Fe, Cu and Pb determination.

Samples	Found concentration ($\mu g\ kg^{-1}$)	Recovery (%) (50 $\mu g\ kg^{-1}$)	Recovery (%) (250 $\mu g\ kg^{-1}$)
Soybean oil			
Fe	142 ± 8	94 ± 7	93 ± 3
Cu	35 ± 4	93 ± 4	107 ± 8
Pb	<LOD[b]	96 ± 8	98 ± 3
Sunflower oil			
Fe	262 ± 5	101 ± 8	98 ± 4
Cu	12 ± 2	95 ± 7	93 ± 3
Pb	<LOD[b]	107 ± 3	91 ± 6
Olive oil			
Fe	231 ± 15	93 ± 6	94 ± 4
Cu	30 ± 6	98 ± 2	107 ± 8
Pb	<LOD[b]	99 ± 2	106 ± 4
Rapeseed oil			
Fe	68 ± 12	95 ± 8	98 ± 5
Cu	<LOD[c]	104 ± 7	100 ± 5
Pb	<LOD[b]	95 ± 7	92 ± 8
Sesame oil			
Fe	32 ± 1	105 ± 7	99 ± 4
Cu	<LOD[c]	102 ± 5	96 ± 16
Pb	<LOD[b]	104 ± 4	95 ± 6

[a] Standard deviation (N = 3).
[b] < LOD indicates a value lower than 3 $\mu g\ kg^{-1}$.
[c] < LOD indicates a value lower than 0.7 $\mu g\ kg^{-1}$.
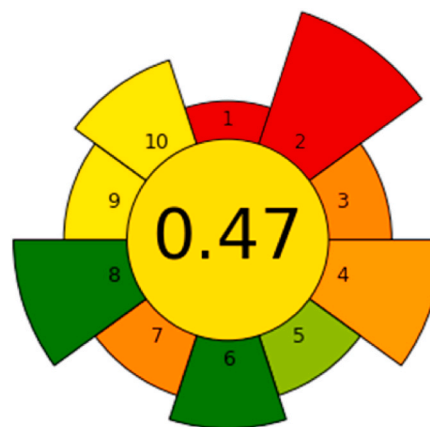

Fig. 6. Ecological assessment of the method proposed by the AGREE-prep method.

method used much smaller amount of sample in comparison with the studies with comparable LOD values. Most probably is that if the amount of sample analyzed in the proposed method would have been higher than 0.86 g, the LOD values would decrease. Besides, the LOD values satisfy the threshold limit established by the Codex Alimentarius Commission.

From ecological point of view, the proposed method provided one of the best scores according to the AGREEprep metric. While some of the methods required large volumes of acids (i.e., hydrochloric acid or nitric acid), amount of sample, and relatively high time consumption for sample preparation, the proposed method involved the replacement of acids and toxic extraction solvents due to the use of eco-friendly solvents such as DES. Additionally, the amount of sample and chemical waste as well as the analysis cost were reduced while a high sample throughput was achieved.
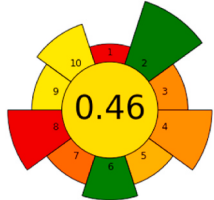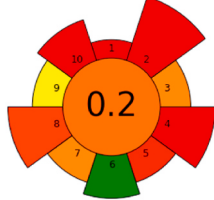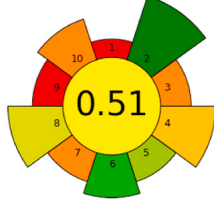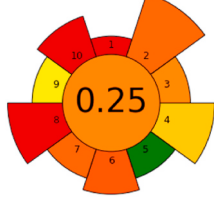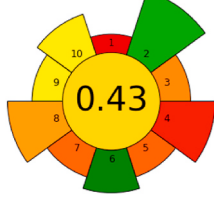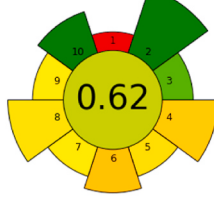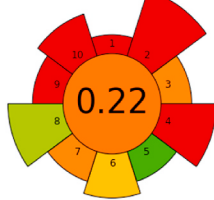
4. Conclusions

A new DES-based DLLME methodology assisted by vortex is presented for the separation and preconcentration of three elements (i.e., Fe, Cu, and Pb) from edible oil samples prior to the determination by MIP-OES. The greenness of this method has been quantitatively evaluated using the AGREEprep metric, and critically compared with previous publications.

To the best of our knowledge, this is the first time that association DES-based DLLME-MIP-OES has been used for metal analysis in oil samples.

The use of small volumes of DES extractant allows the reduction of reagents and residues, and increases the ecological character of the method. In addition, the use of multivortex as a dispersing system means a reduction in reagents by replacing disperser solvents and improves sample throughput while reducing analysis time. Regarding the MIP-OES technique, the analytical figures of merit were adequate for the

detection by stripping voltammetry [54], the LOD values obtained were lower but the analysis time is still longer than the proposed method. In addition, most of the works described in Table 3 used analytical instrument with higher sensitivity, yet higher cost and complexity, in comparison to MIP-OES. For example, ETAAS [50,55,56] and ICP-MS [9, 51,52] provided lower LOD values, however, it can be seen that the LOD value of Cu was slightly higher (i.e., 0.80 $\mu g\ kg^{-1}$) using ETAAS [50] and much higher (i.e., 2 $\mu g\ kg^{-1}$) using ICP-OES [53]. When the proposed method was compared with analytical techniques with the same or lower sensitivity (i.e., FAAS) it can be seen that the LOD values were comparable [11,57] and much better (i.e., 41 $\mu g\ kg^{-1}$ for Cu and 61 $\mu g\ kg^{-1}$ for Fe) [58]. It is worthy to remark that the proposed analytical

Table 3
Comparison of the proposed method with previous works for elemental determination in edible oil samples.
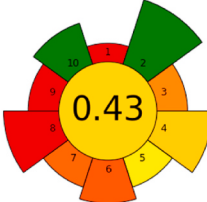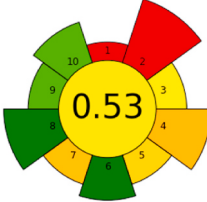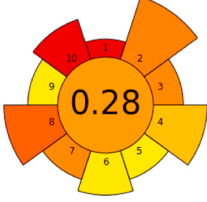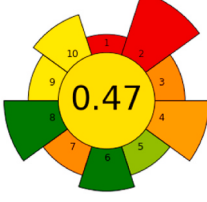
Detection technique	Sample preparation	Sample preparation time (min)	Analytes	LOD (µg kg^{-1})	AGREEprep evaluation	Ref
FAAS	10 g oil sample and 200 µL of water with 3% HNO$_3$; Vortex and ultrasonic bath 60 °C; Centrifugation at 4000 rpm; Dilution to 500 µL with deionized water.	12	Cu Cd Ni Pb Zn	0.7 0.3 0.5 1.5 0.5	0.46	[57]
HR-CS FAAS	50 g oil sample with 10 mL nitric acid; Ultrasonic 400 W, 24 kHz; Centrifugation at 3000 rpm.	6	Cu Fe Ni Zn	41 61 63 12	0.2	[58]
ICP-OES	1 g oil sample and 300 µL of 0.25% (w/v) chitosan in 1% (v/v) acetic acid with 200 µL HCl; Vortex and addition of 4 mL deionized water.	2	Cu	2	0.51	[53]
ETAAS	0.1 g oil sample, 2.5 mL (25% v/v) of TMAH and 1.5 mL 2% EDTA; pH is adjusted to 12 with 0.2 mL of concentrated HNO$_3$; Water bath at 80 °C; Ultrasound waves and centrifugation.	60	Pb Cu Fe Mn Cd Cr Zn	0.11 0.80 0.60 0.07 0.016 0.50 0.31	0.25	[50]
ETAAS	28 g oil sample, 200 µL (4:1) of DES (ChCl-urea) and 2% HNO$_3$; Vortex and water bath at 50 °C; Centrifugation at 5000 rpm.	10	Pb Cd	0.008 0.0002	0.43	[55]
ETAAS	4.0 g oil sample, 100 µL of DES (ChCl:lactic acid-water); magnetic stirrer; Dilution with 400 µL water.	10	Cu	0.1	0.62	[56]
ICP-MS	0.5 g oil sample with 15% v/v TMAH; The mixture is shaken and kept at 90 °C in a water bath; Flasks are diluted up to 50 mL with 1% HNO$_3$.	30	Cu &V Mn & Sr Ge Mo Ni Sb Ti	0.10 0.02 0.25 0.04 0.06 1.60 1.40	0.22	[9]

Table 3 (*continued*)

Detection technique	Sample preparation	Sample preparation time (min)	Analytes	LOD (µg kg^{-1})	AGREEprep evaluation	Ref
ICP-MS	3 g oil sample and 2 mL of 0.01 M EDTA solution adjusted to pH 8; Shaken vigorously and vortex; Sonication and centrifugation at 3000 rpm.	35	Al Ca Cd Cu Mg Mn Ni Ti V Zn	2.47 2.81 0.013 0.037 1.37 0.050 0.049 0.47 0.032 0.087	0.2	[52]
ICP-MS	3 g oil sample and 1 mL of 1% Lipase solution; The mixture is shaken in a vortex; Ultrasonic bath and centrifugation at 3000 rpm.	30	Al Ba Cd Cu Fe Mn Mo Ni Ti V Zn	0.46 0.03 0.007 0.028 0.67 0.038 0.022 0.14 0.17 0.05 0.07	0.43	[51]
Stripping voltammetry	5 g oil sample, 300 µL DES (menthol, formic acid, water) and 100 µL ultrapure water. Shaken manually and centrifugation at 6000×g; 10% HNO$_3$ and ultrapure water for cleaning.	10	Pb Cd	0.01 0.006	0.53	[54]
MIP-OES	3 g oil sample, 1 mL of HNO$_3$ (30%, v/v) and 1 mL of Triton X-100 (30%, w/v) was stirred on a vortex; Thermostatic bath 90 °C.	20	Al Ba Cu Cr P Ni Ti Zn	3.7 0.6 0.6 0.7 0.9 1.0 2.0 0.4	0.28	[11]
MIP-OES	0.86 g oil sample (diluted 1:10 in ether petroleum) and 100 µL DES; Vortex and centrifugation 3000 rpm.	4	Cu Fe Pb	0.7 2 3	0.47	This work

elemental determination in edible oil samples. It should be noted that this detection technique is less expensive than those normally used in the food industry for elemental analysis.

Therefore, the proposed analytical method is fast, simple, economical and presents an acceptable green quantitative metric. However, there are still some limitations and aspects that should be considered to improve the proposed method, such as the substitution of petroleum ether with a solvent of lower toxicity.

Finally, the figures of merit justified the adequacy of the proposed new methodology for the type of matrix and analyte analyzed, showing that the concentrations of the evaluated analytes are lower than the maximum limits allowed by international regulations.

CRediT authorship contribution statement

Cristina Zapater: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation. **Miguel Ángel Aguirre:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Nerea González-Gallardo:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Diego J. Ramón:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Lorena Vidal:** Writing – review & editing, Supervision, Investigation. **Antonio Canals:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2024.125939.

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