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Extraction induced by emulsion breaking ICP-MS for trace multi-element determination in edible vegetable oils

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[Abstract]: In this study a simple, fast and reliable method for the simultaneous determination of Mg, Mn, Fe, Zn, Ag, Ba, Pb and Cr in edible vegetable oils, using extraction induced by emulsion breaking ICP-MS is proposed. In the method, each sample of oil was emulsified with a Triton X-114 solution containing HNO_3 and the emulsion was broken by centrifugation for 12 min at 6800 rcf, then the acid aqueous phase deposited in the bottom of the centrifuge tube was collected for the determination of the metals of interest. The optimization of the method was performed by studying the effect of several parameters that could affect the extraction efficiency such as the concentrations of HNO_3 and the emulsifying agents (Triton X-114 and Triton X-100) in the extractant solution, the centrifugal speed and the extraction time. The limits of detection and quantification for Mg, Mn, Fe, Zn, Ag, Ba, Pb and Cr were in the range of 0.004–0.271 μg L^{-1} and 0.013–0.903 μg L^{-1}, respectively. The proposed method was applied in the metals determination of eighty edible vegetable oil samples produced with different oleaginous. The accuracy of the method was performed by spiking the samples with known amounts of the metals in the form of organometallic standards and the recoveries were in the range of 87–108%.

[Keywords]: Inductively coupled plasma–mass spectrometry (ICP-MS); Extraction induced by emulsion breaking (EIEB); Trace metals; Edible vegetable oils

1   Introduction

Edible oils play a fundamental role in the human nutrition and are largely consumed worldwide.[1] The quality of edible oils with regard to freshness, storability and toxicity can be evaluated by the determination of trace metals. Trace levels of metals like Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the rate of oil oxidation while other elements such as Cr, Cd, and Pb are very important on account of their toxicity and metabolic role.[2] The metals in edible vegetable oils might come from the soil, environment, genotype of the plant, fertilisers and/or metal-containing pesticides, introduced during the production process (by processing actions, such as bleaching, hardening, refining and deodorisation) or by contamination from the metal processing equipment.[3-5]

Atomic spectrometric methods like flame and graphite furnace atomic absorption spectrometry (F-AAS and GF-AAS), as well as inductively coupled plasma optical emission and mass spectrometry (ICP-OES and ICP-MS), can be used for metal determinations in oil samples.[2, 6-8] However, the accurate determination of trace metals in edible oils is an analytical challenge, on account of their low concentration level and the difficulties that arise due to the characteristic of the matrix; therefore, sample preparation is a critical step in the whole analytical procedure.[6,9] It may involve dry ashing, wet digestion, and focused open-vessel microwave dissolution, as well as acid extraction or solid phase extraction.[2, 10-14] However, these procedures are time consuming and present the potential risks of sample contamination and analyte loss. The metals present in some edible oils were determined by atomic absorption spectrometry (AAS),[15,16] inductively coupled plasma atomic emission spectrometry (ICP-AES),[7,17] and inductively coupled plasma mass spectrometry ICP-MS[8,9,18] after microwave digestion. It was required sensitive metal

determination techniques after the sample decomposition process in the mentioned techniques. Dilution with an appropriate solvent (xylene, kerosene, toluene, etc.) as well as emulsification and microemulsification are also alternatives;[19-23] however, they impoverish the overall limit of detection and the maintenance of emulsions stability for an acceptable period of time is frequently problematic. Additionlly, a method for the direct determination of Ni and Cu in oils by graphite furnace AAS using the the solid sampling strategy has been developed in the literature. [10]

Recently, Cassella et al. [24-26] proposed a novel extraction approach, named extraction induced by emulsion breaking (EIEB), for the extraction of metals from diesel oil samples. The approach was based on the formation and breaking of detergent emulsions, prepared by mixing the oil samples with acid aqueous solutions. During emulsion breaking, which can be induced by heating or centrifugation, the analytes were transferred to the aqueous phase that is separated from the oil. The method was successfully applied in the determination of trace metals (Cu, Fe, Ni, Pb, Zn, Al, Mn, Sn and V) from diesel oil by different analytical techniques (FAAS, ETAAS and ICP-MS).

The aim of this study was the development of a new method for the simultaneous determination of Mg, Mn, Fe, Zn, Ag, Ba, Pb and Cr in edible vegetable oils by ICP-MS using the extraction induced by emulsion breaking as a sample preparation strategy. In this study, the emulsions were broken by centrifugation at 6800 rcf and the emulsion breaking time is 12 min which is much lower than that reported by Cassella et al. The proposed method is cited the separation of analytes from a more complex matrix into a simpler one so that the calibration can be performed with aqueous solutions, allows the preconcentration of the metals in an aqueous phase, which is easier to measure than the original sample, avoids the use of large amounts of solvents or acids, and reduces the time required to complete the extraction process.

2 Experimental

2.1 Apparatus

The determination of the selected metals was performed with a Elan DRC-e inductively coupled plasma mass spectrometer (Perkin-Elmer, Concord, Canada), operated under the conditions summarized in Table 1. The determination of Mg, Mn, Fe, Zn, Cr, Ag, Ba and Pb was performed by measuring the isotopes ^{25}Mg, ^{55}Mn, ^{57}Fe, ^{66}Zn, ^{53}Cr, ^{107}Ag, ^{138}Ba and ^{208}Pb respectively. Rhodium was employed as internal standard and it was measured as the ^{103}Rh isotope. A 5804 centrifuge (Eppendorf, Hamburg, Germany) was used for the emulsion breaking, which was carried out by centrifuging the tubes containing the emulsions. A SRT-202 roller mixer (Kylin-Bell, Haimen, China) was used for the agitation of the emulsions. The digestion of the rapeseed oil sample used in the experiments of optimization was carried out with an Multiwave 3000 (Anton Paar, Graz, Austria) microwave oven equipped with PFA vessels.

Table 1 Operating conditions of the Elan DRC-e ICP-MS

RF power	1,100 W
Auxiliary gas flow	1.2 L min^{-1}
Plasma gas flow	15 L min^{-1}
Sampler cone	Nickel
Skimmer cone	Nickel
Scan mode	Peak Hopping
Dwell time	50 ms per a.m.u
Integration time	1000ms
Nebulizer	Cross-flow pneumatic nebulizer
Spray chamber	Scott type
Nebulizer gas flow	0.85 L min^{-1}
Flow rate	400 μL min^{-1}
Sampling depth	5.5 mm

2.2 Reagents, standards and samples

A multi-elemental standard solution of 10 mg L^{-1} containing 29 elements (Al, As, Ba,Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Tl, V, U, Zn) dissolved

in 5% HNO$_3$ (Perkin-Elmer, Shelton, USA) was used as stock solutions for calibration. The

standard solutions with intermediary concentration used in the experiments were prepared by

suitable dilution of the stock solutions with 1% v/v HNO$_3$ solution. The nitric acid employed in the

experiments was of MOS grade (Sinopharm Chemical Reagent, Shanghai, China). Ultrapure water,

from a Milli-Q Element A10 water purification System (Millipore, Bedford, MA, USA), was used

throughout the experiment.

The acid Triton X-114 and Triton X-100 (Acros Organics, New Jersey, USA) solutions

employed for emulsification purposes were prepared by dissolving suitable masses of each

surfactant in exactly 100 mL of HNO$_3$ solution. The desired concentration of the HNO$_3$ solution

was established according to the experiment.

Multi-element Standard Oiled stock solutions of 100 μg g^{-1} were purchased from Conostan

(Houston, TX, USA). Diluted oiled standard solutions were prepared by diluting the oil stock

standard solutions in HPLC-grade hexane (Tjshield, Tianjin, China).

Total 80 samples and ten varieties of edible vegetable oils were collected from supermarkets

in China. They were stored in a low-density polyethylene flask and kept in a light-free place at

laboratory ambient temperature (20±1℃).

2.3   Procedure

The metals were extracted from the oils through the application of the extraction induced by

emulsion breaking, which was based on the formation of stable emulsions between the samples

and an acid solution of Triton X-114. Initially, stable water-in-oil emulsions were achieved by

vigorous mixing of 4ml of oil with 2 mL of the acidic Triton X-114 solution in a capped plastic

tube of 15 mL capacity. Then the emulsions were transferred to a roller mixer where it was

agitated for 20 min in order to improve the extraction of the analytes. Afterwards, the tubes were

transferred to the centrifuge where they were centrifuged at 6800 rcf to promote the emulsion

breaking. The emulsion breaking resulted in two well-separated phases, as shown in Fig. 1: (i) an

upper organic phase, containing the edible oil and the emulsifying agent and (ii) a lower aqueous

phase, containing the metals extracted by the acid and a residual amount of emulsifying agent.

After the emulsion breaking, the separation of the phases was carried out. The total volume of the

aqueous phase was equal to 2 mL and approximately 1.5 mL was collected with the aid of a

micropipette. The metals were measured by ICP-MS using Rh as the internal standard. The

dilution was carried out in order to adjust the concentration of the metals in solution to the linear

portion of the analytical curves and minimize possible interferences due to the injection of

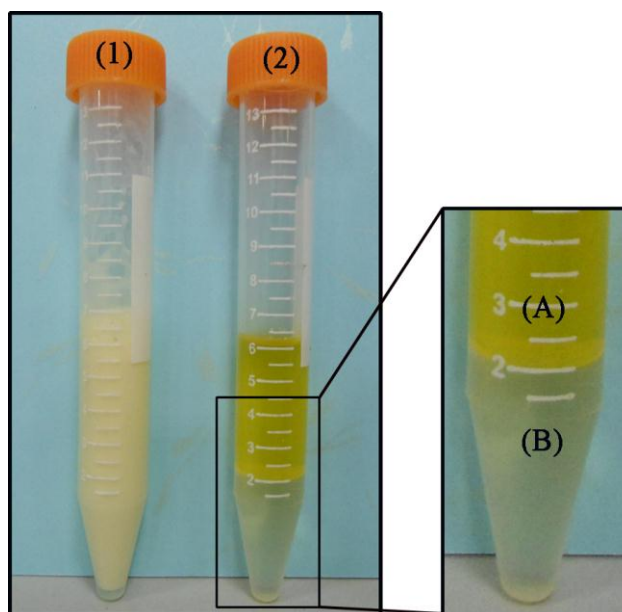complexes matrices into the ICP-MS spectrometer.

Fig. 1 Emulsion (1) before and (2) after breaking by centrifugation at 6800 rcf. (A) Edible oil phase and (B)

aqueous phase. The phase separation process took 12 min.

3   Results and discussion

In this work, the concentration levels of metals in ten varieties of edible vegetable oil samples (Mg,

Mn, Fe, Zn, Ag, Ba, Pb and Cr) were analysed by ICP-MS after the extraction induced by

emulsion breaking procedures. The optimization of the methodology was studied taking into

account the extraction efficiency, evaluated by the magnitude of the analytical signals for each

metal, and the time required to break the emulsions, once the breaking time was limit step of the

time spent to complete the procedure. In the experiments, relative signals were used to evaluate

the results because of the different magnitude of the signals obtained for each metal. Relative

signals can be defined as the ratio between each analytical signal and the highest analytical signal

obtained in the set. In order to achieve these objectives, the influences of different parameters

were investigated.

3.1 Influence of the nitric acid concentration

The first parameter studied in the optimization of the proposed procedure was the influence of the

concentration of HNO_3 in the extractant solution. It is good to remember that the H^+ ion is

responsible for the extraction of the metals in oils, where they can be present in the free form, in

the organic molecules or as part of organic complexes. In order to evaluate the effect of this

variable, the concentration of HNO_3 in the extractant solution was varied in the range of 0–40%

v/v. Emulsions prepared with both Triton X-114 and Triton X-100 (5% m/v) were evaluated and

the extraction was performed with 4 mL of the oil and 2 mL of the aqueous solution. Once the

emulsions were formed, they were agitated for 20 min on the roller mixer to extract the analytes,

centrifuged at 6800 rcf until the emulsion breaking. Then, the aqueous phase was collected and

each metal was measured by ICP-MS in the conditions presented in Table 1.

As it can be seen in Fig. 2, the concentration of HNO_3 did not significantly influence the

extraction efficiency for Mg, Mn, Fe, Zn, Ba and Pb. But for Ag and Cr, it presented noticeable

effect on their extraction. In this case, the signals clearly increased with the increase of the

concentration of HNO_3. For all metals, the extraction increased up to a HNO_3 concentration of

20% v/v and, after this point, the extraction efficiency remained almost constant. This fact could

indicate that Ag and Cr were bonded to the organic molecules present in the oil through stronger

interactions than the other elements under study. Additionally, except for Ag, the use of a solution

without HNO_3 could extract part of the analytes, indicating that a fraction of the metals are in the

free form or weakly bonded to the organic molecules of the oil. Herein, the HNO_3 concentration of

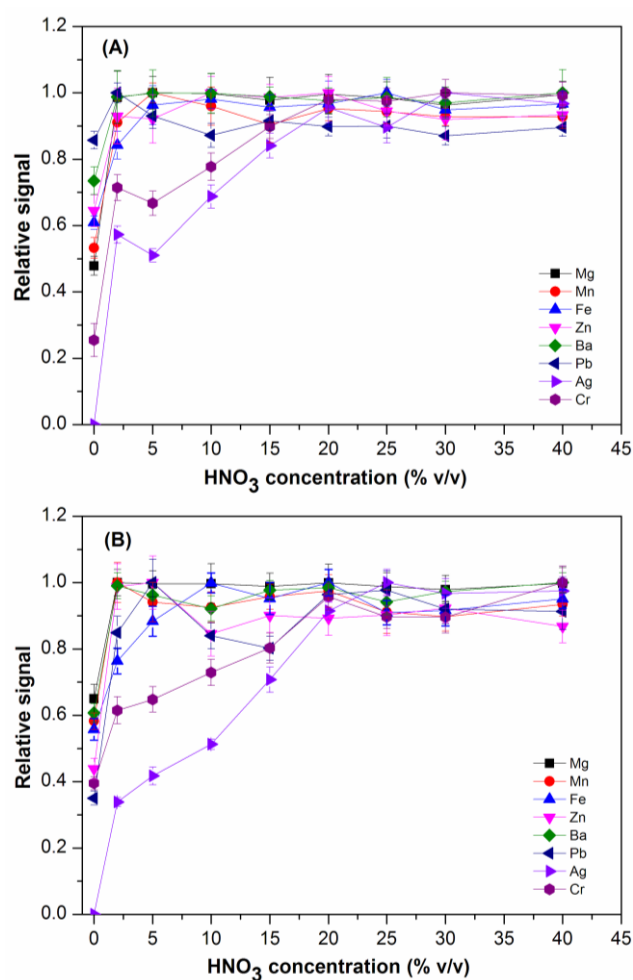20% v/v was chosen for the method to ensure maximum extraction of the metals.

Fig. 2 Effect of the HNO_3 concentration on the extraction of metals by the proposed procedure. (A) Triton X-114

and (B) Triton X-100. Emulsifying agents concentration were 5% m/v.

3.2   Influence of the concentration and structure of the emulsifying agent

The use of the emulsifying agent is of fundamental importance in the proposed procedure, since it plays a major role in the emulsification process. The emulsifying agent makes possible the high dispersion of the acid solution in the oil, increasing the contact between the oil and the extractant solution, and enhances the extraction efficiency. The experiment was carried out by changing the concentration of the emulsifying agent (Triton X-114 or Triton X-100) in the range of 1–20% m/v. The concentration of HNO_3 was maintained at 20% v/v and the emulsion breaking was carried out by centrifugation at 6800 rcf.

As it can be seen in Fig. 3, no remarkable variation in the magnitude of the signals for Mg, Fe, Zn, Ba, Ag and Pb was verified employing different concentrations of Triton X-114 or Triton X-100 for emulsification. But for Mn and Cr, the extraction efficiency clearly increased with the increase of the concentration of the emulsifying agents, when maximum extraction was achieved with the Triton X-114 or Triton X-100 concentration of 12% m/v or higher. It indicated that an efficient extraction of the metals can be reached independently of the types of emulsifying agents. These results also showed that the increase of the concentration of the emulsifying agent leaded to the formation of more stable emulsions, with smaller water droplets, which caused more intense contact between the aqueous (extractant) and organic phases (sample). As result, the extraction efficiency was enhanced. However, it is important to remark that the formation of more stable emulsions also increased the time needed to their breaking. So, it was decided to employ a emulsifier concentration of 12% w/v in all further experiments.
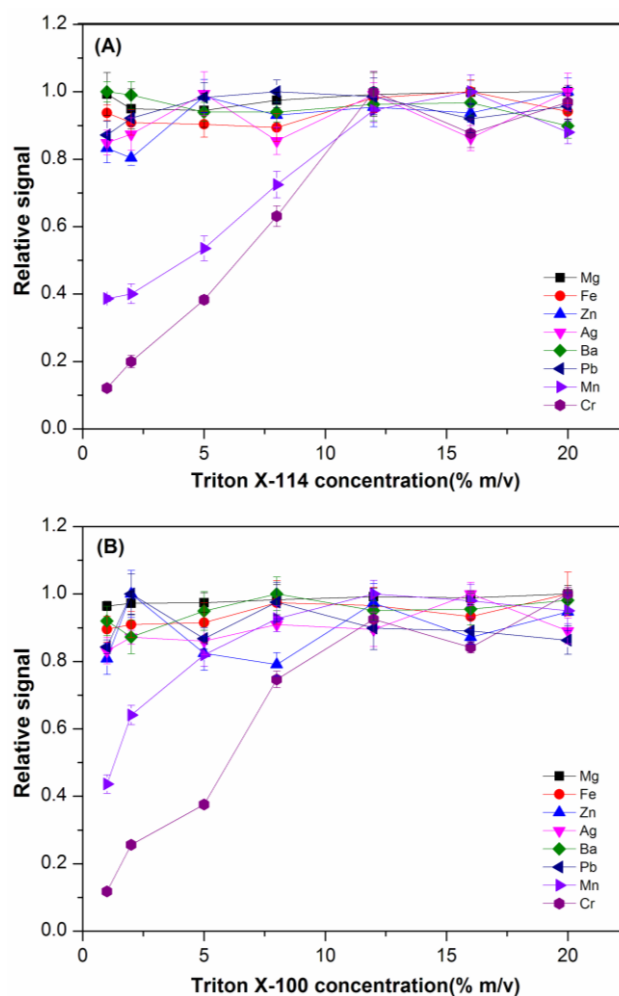
Fig. 3 Influence of the concentration of the emulsifying agent on the extraction of metals by the proposed method.

(A) Triton X-114 (B) Triton X-100. HNO$_3$ concentration was 20% v/v.

3.3   Evaluation of the extraction time

The extraction time was considered as the time elapsed between the formation of the emulsions

and their breaking. It is important to highlight that the emulsions were kept under continuous

agitation on a roller mixer before breaking. The experiment was carried out by preparing

emulsions with the same oil using the conditions already optimized. It can be seen in Fig. 4, the

extraction time was changed in the range of 0–60 min and only had significant influence on the

extraction of Mn, Ag and Pb. For these metals, the extraction efficiency increased up with the

increase of the extraction time in the range of 0–15 min. For other elements, no variation in the

analytical signals was observed. It indicated that Mn, Ag and Pb are more slowly to cleave to

produce hydrophilic species when compared to the other metals. In order to ensure the complete

extraction of all analytes under study, an extraction time of 20 min was chosen for the method.
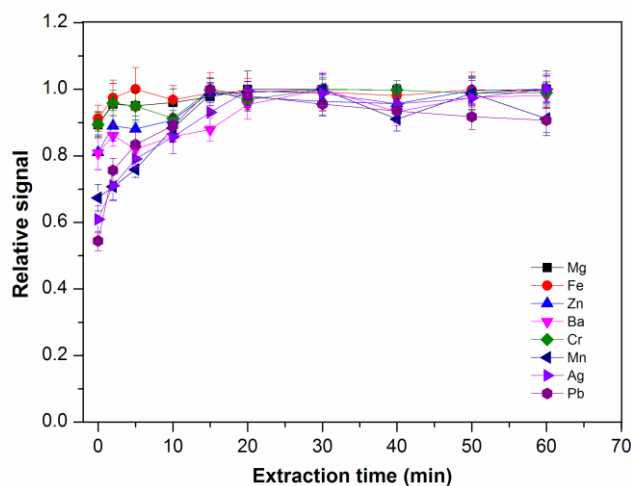
Fig. 4 Effect of the extraction time on the extraction of metals by the proposed procedure. $HNO_3 = 20\%$ v/v, Triton

X-114 = 12% m/v.

3.4 Influence of speed on the emulsion breaking by centrifugation

The influence of the centrifugal speed applied to the emulsion breaking on the extraction

efficiency was tested in the range of 1700-12850 rcf using both Triton X-114 and Triton X-100 as

emulsifying agents. The concentration of the emulsifying agents in the experiments was 12% m/v.

No variation of the analytical signals was noted for all the analytes, evidencing that the extraction

efficiency did not depend on the centrifugal speed employed for the emulsion breaking. On the

other hand, the time of the emulsion breaking was strongly decreased with the increase of

centrifugal speed for both emulsifying agents (Fig. 5). Also, the emulsions formed with Triton

X-114 were broken in a reduced time than Triton X-100, indicating that the emulsions formed

with Triton X-114 are less stable and more suitable for the procedure. Additionally, at 6800 rcf,

only 12 min were needed to promote the emulsion breaking, and the time of the emulsion breaking

was almost the same when the centrifugal speed was 6800 rcf or higher. So, the centrifugal speed

of 6800 rcf was selected and Triton X-114 (12% m/v) was chosen as emulsifying agent for the

method.
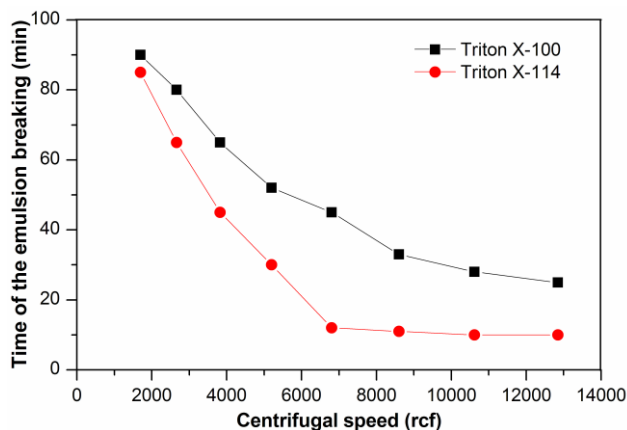
Fig. 5 Effect of the centrifugal speed on the time of emulsion breaking. $HNO_3 = 20\%$ v/v, Triton (X-114 or X-100)

= 12% m/v.

3.5 Analytical features of the developed methodology

In order to derive the limits of detection and quantification of the methodology for Mg, Mn, Fe, Zn,

Ag, Ba, Pb and Cr, analytical curves prepared in 1% v/v HNO_3 medium were constructed for each

analyte employing online internal standard method with $10\,\mu g\,L^{-1}$ Rh as an internal standard. The

limits of detection (3s criterion) and quantification (10s criterion) were estimated from eleven

measurements of blank solutions containing only 1% v/v HNO_3. The limits of detection and

quantification are summarized in Table 2 along with the relative standard deviation observed for

ten measurements of the analytes at the first point of the internal standardization curve (1 $\mu g\,L^{-1}$).

Table 2 Limits of detection (3s criterion) and quantification (10s criterion), RSD and correlation coefficient for the

determination of the eight metals in edible oils by the developed procedure

Element	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD (%) (at 1 μg L^{-1})	Correlation coefficient (r^2)
Mg	0.093	0.311	0.59	0.9994
Mn	0.052	0.173	1.28	0.9999
Fe	0.271	0.903	2.65	0.9991
Zn	0.177	0.591	0.87	0.9993
Ag	0.007	0.024	3.40	0.9999
Ba	0.009	0.031	2.78	0.9999
Pb	0.004	0.013	1.98	0.9999
Cr	0.033	0.111	0.96	0.9999

3.6   Application of the developed methodology

After the optimization of the experimental parameters for the EIEB procedure, the developed methodology was applied in the determination of trace metals in ten varieties of edible vegetable oils, which were purchased in the supermarkets of China. The results are given in Table 3. The metal concentrations in edible vegetable oils were found between as 15.58–6636.25, 0.99–825.83, 18.85–1221.47, 26.52–141.46, 0.67–7.88, 1.03–115.95, 0.69–16.34 and 10.64–31.93 μg L^{-1} for magnesium, manganese, iron, zinc, silver, barium, lead and chromium, respectively. The lowest and highest metal concentrations were observed in silver and magnesium in all samples. It is easily to find that the metal concentrations differed between oil types and element types.

The presence of analysed metals was observed in all the ten typical oils, which can be due to the factors such as species, soil used for the cultivation, irrigation water, variety, stage of maturity, and treatment processes or packaging procedures. From these experiments, it can be concluded that the content of trace metals is directly related to their provenance and the production, which has been an important issues.

Once there are no certified reference materials of edible oils for metals, the efficiency of the extraction procedure and the evaluation of the accuracy of the proposed procedure was assessed by performing the recovery test, which is the strategy widely employed for this kind of sample.[19] In this case, the samples were spiked with the elements of interest in the form of organometallic

compounds (Conostan standards). The recoveries verified in this experiment are shown in Table 4.

For all elements under study, the recoveries were suitable for quantitative purposes, being situated

between 87 and 108%.

Additionally, the concentration of analytes in the rapseed oil sample determined by the

proposed method were compared with those by microwave digestion. The results obtained in this

experiment are shown in Table 5. There was no statistical difference between the results when the

Student-t test (95% confidence level) was applied, which also proved the accuracy of the proposed

method for metals determination in edible vegetable oils.

Table 3 The concentration levels of metals in edible vegetable oil samples. Results are expressed in μg L^{-1} as mean

$\pm$ standard deviation (n = 3)

Type of oil	Element							
	Mg	Mn	Fe	Zn	Ag	Ba	Pb	Cr
Rapeseed	1908.28	75.28	887.75	69.73	5.61	12.79	10.58	31.93
	$\pm$15.18	$\pm$3.79	$\pm$9.25	$\pm$1.85	$\pm$0.79	$\pm$0.28	$\pm$0.25	$\pm$1.99
Edible blend	202.31	7.59	78.24	104.39	1.79	9.78	5.09	17.28
	$\pm$2.99	$\pm$0.17	$\pm$1.58	$\pm$2.99	$\pm$0.13	$\pm$0.56	$\pm$0.18	$\pm$1.05
Soybean	18.07	14.76	18.85	48.19	1.11	1.03	5.78	18.03
	$\pm$0.58	$\pm$0.79	$\pm$1.44	$\pm$1.33	$\pm$0.08	$\pm$0.05	$\pm$0.28	$\pm$2.67
Sunflower	15.58	7.28	59.52	26.52	0.67	5.76	2.67	15.85
	$\pm$1.18	$\pm$0.32	$\pm$2.78	$\pm$0.11	$\pm$0.05	$\pm$0.66	$\pm$0.09	$\pm$1.22
Corn	25.38	24.19	72.64	65.64	3.80	2.56	1.56	10.64
	$\pm$1.01	$\pm$0.55	$\pm$3.68	$\pm$2.99	$\pm$0.56	$\pm$0.11	$\pm$0.21	$\pm$0.91
Olive	67.21	15.56	189.48	68.42	2.99	2.34	8.98	17.84
	$\pm$3.57	$\pm$1.11	$\pm$2.13	$\pm$1.11	$\pm$0.38	$\pm$0.18	$\pm$0.89	$\pm$2.43
Peanut	6336.25	243.16	1221.47	141.46	2.67	115.95	3.59	19.08
	$\pm$101.67	$\pm$11.01	$\pm$20.18	$\pm$7.22	$\pm$0.38	$\pm$3.51	$\pm$0.51	$\pm$1.18
Rice bran	19.49	0.99	83.19	54.40	3.01	3.89	0.69	17.20
	$\pm$1.88	$\pm$0.07	$\pm$2.99	$\pm$3.44	$\pm$1.67	$\pm$0.88	$\pm$0.12	$\pm$0.91
Camellia	2240.05	825.83	327.84	63.48	7.88	58.51	10.25	15.93
	$\pm$19.87	$\pm$21.14	$\pm$10.01	$\pm$5.18	$\pm$1.08	$\pm$2.99	$\pm$1.54	$\pm$1.03
Canola	862.46	369.31	176.99	37.23	6.23	34.50	16.34	17.43
	$\pm$15.18	$\pm$12.19	$\pm$4.57	$\pm$3.88	$\pm$0.24	$\pm$1.34	$\pm$1.08	$\pm$2.11

Table 4 Results obtained in the recovery test applied to the oil samples for Mg, Mn, Fe, Zn Ag, Ba, Pb and Cr.

Recovery values are expressed as mean $\pm$ Standard deviation (n= 3)

Element	Added ($\mu g\ L^{-1}$)	Recovery (%)									
		Rapeseed	Blend	Soybean	Sunflower	Corn	Olive	Peanut	Rice bran	Camellia	Canola
Mg	10	99 $\pm$1	101 $\pm$2	102 $\pm$1	101 $\pm$5	96 $\pm$5	104 $\pm$4	100 $\pm$5	97 $\pm$1	99 $\pm$4	99 $\pm$3
	50	107 $\pm$5	87 $\pm$1	96 $\pm$2	99 $\pm$3	99 $\pm$3	102 $\pm$2	100 $\pm$1	103 $\pm$6	107 $\pm$8	99 $\pm$1
	100	99 $\pm$3	102 $\pm$2	108 $\pm$4	93 $\pm$1	88 $\pm$2	90$\pm$3	106 $\pm$3	99 $\pm$5	105 $\pm$5	100 $\pm$4
Mn	10	89 $\pm$2	100 $\pm$1	96 $\pm$3	99 $\pm$1	102 $\pm$2	88 $\pm$2	89 $\pm$2	89 $\pm$2	98 $\pm$2	90 $\pm$4
	50	99 $\pm$1	89 $\pm$1	108 $\pm$2	87 $\pm$1	106 $\pm$1	100 $\pm$1	108 $\pm$7	88 $\pm$1	103 $\pm$3	90 $\pm$2
	100	102 $\pm$4	95 $\pm$1	104 $\pm$3	103 $\pm$3	99 $\pm$5	100 $\pm$5	105 $\pm$7	88$\pm$1	87 $\pm$1	90 $\pm$2
Fe	10	105 $\pm$5	87 $\pm$2	100 $\pm$3	89 $\pm$2	107 $\pm$2	100 $\pm$1	101 $\pm$5	88$\pm$1	98 $\pm$2	98 $\pm$1
	50	105 $\pm$3	107 $\pm$3	100 $\pm$2	99 $\pm$4	105 $\pm$6	100 $\pm$5	107 $\pm$4	102 $\pm$1	96 $\pm$1	95 $\pm$2
	100	97 $\pm$1	98 $\pm$5	100 $\pm$5	107 $\pm$5	88 $\pm$2	105 $\pm$2	99 $\pm$3	105 $\pm$4	101 $\pm$3	95 $\pm$1
Zn	10	108 $\pm$4	101 $\pm$1	88 $\pm$2	105 $\pm$2	89 $\pm$1	108 $\pm$5	93 $\pm$6	93 $\pm$1	106 $\pm$2	96 $\pm$1
	50	99 $\pm$1	101 $\pm$2	100 $\pm$1	105 $\pm$2	99 $\pm$1	107 $\pm$2	100 $\pm$3	92 $\pm$3	105 $\pm$1	106 $\pm$3
	100	89 $\pm$1	92 $\pm$1	103 $\pm$6	105 $\pm$5	99 $\pm$5	104 $\pm$1	92 $\pm$1	87 $\pm$1	99 $\pm$5	100 $\pm$6
Ag	10	98 $\pm$2	99 $\pm$2	106 $\pm$4	99 $\pm$2	95 $\pm$2	105 $\pm$4	94 $\pm$1	102 $\pm$1	98 $\pm$2	100 $\pm$1
	50	100 $\pm$1	89 $\pm$2	108 $\pm$5	104 $\pm$3	97 $\pm$2	105 $\pm$1	106 $\pm$3	100 $\pm$3	99 $\pm$4	106$\pm$4
	100	106 $\pm$4	100 $\pm$1	99 $\pm$1	102 $\pm$1	102 $\pm$4	95 $\pm$2	107 $\pm$3	89 $\pm$1	100 $\pm$2	108 $\pm$4
Ba	10	88 $\pm$1	102 $\pm$4	91 $\pm$1	88$\pm$2	100 $\pm$1	105$\pm$1	101 $\pm$2	101 $\pm$3	100 $\pm$4	88 $\pm$1
	50	99 $\pm$1	102 $\pm$4	103 $\pm$1	89 $\pm$1	100 $\pm$2	104 $\pm$3	95 $\pm$1	101 $\pm$3	99 $\pm$1	90 $\pm$1
	100	89$\pm$2	100 $\pm$4	100 $\pm$2	97 $\pm$3	87$\pm$1	104 $\pm$4	96 $\pm$1	97 $\pm$4	92 $\pm$2	98 $\pm$1
Pb	10	102 $\pm$2	89 $\pm$2	98 $\pm$2	95 $\pm$1	106 $\pm$3	96 $\pm$2	100 $\pm$3	90 $\pm$2	102 $\pm$3	99 $\pm$1
	50	99 $\pm$2	97 $\pm$3	104 $\pm$1	101 $\pm$3	102 $\pm$4	98 $\pm$1	100 $\pm$1	95 $\pm$2	103 $\pm$4	98 $\pm$1
	100	89 $\pm$1	97 $\pm$1	97 $\pm$2	107 $\pm$1	96 $\pm$2	99 $\pm$1	105 $\pm$4	98 $\pm$3	107 $\pm$4	108 $\pm$2
Cr	10	100 $\pm$1	100 $\pm$2	99 $\pm$2	108 $\pm$7	103 $\pm$3	98 $\pm$2	107 $\pm$4	96 $\pm$2	101 $\pm$3	97 $\pm$1
	50	97 $\pm$2	87 $\pm$1	100 $\pm$4	99 $\pm$3	103 $\pm$2	107 $\pm$4	103 $\pm$1	88 $\pm$1	102 $\pm$4	100 $\pm$2
	100	103 $\pm$4	89 $\pm$1	105 $\pm$3	97 $\pm$1	101 $\pm$1	106 $\pm$2	96 $\pm$1	105 $\pm$4	105 $\pm$4	95 $\pm$1

Table 5 Comparison between the concentration levels of metals in the rapeseed oil sample by the EIEB and microwave digestion method. Recovery values are expressed as mean $\pm$ Standard deviation (n= 3)

	Element							
Method	Mg	Mn	Fe	Zn	Ag	Ba	Pb	Cr
EIEB	1908.28	75.28	887.75	69.73	5.61	12.79	10.58	31.93
	$\pm$15.18	$\pm$3.79	$\pm$9.25	$\pm$1.85	$\pm$0.79	$\pm$0.28	$\pm$0.25	$\pm$1.99
Microwave	1925.09	78.35	890.99	67.68	5.68	12.61	11.02	33.03
digestion	$\pm$13.79	$\pm$2.88	$\pm$10.45	$\pm$3.22	$\pm$0.88	$\pm$0.36	$\pm$0.22	$\pm$1.76

4   Conclusions

The results obtained in this work proved that the extraction induced by emulsion breaking procedure was very adequate for the total extraction of Mg, Mn, Fe, Zn, Ag, Ba, Pb and Cr in edible vegetable oil, which made possible their quantification in the samples by ICP-MS using internal calibration with aqueous standard solutions. This procedure avoids the laborious and time-consuming digestion of the samples. At optimized conditions, the emulsions were prepared by vigorous mixing of 4mL of edible oil with 2mL of a solution containing 12% w/v Triton X-114 and 20% v/v HNO_3, and then an agitation time of 20 min was used. The emulsions could be broken in approximately 12min when centrifuged at 6800 rcf, which can be considered a short time for the preparation of edible oil samples. The developed method was applied in the determination of the elements of interest in ten varieties of edible vegetable oils of different origin. The results observed in the analysis of the spiked samples clearly showed that the method could be used very accurately in the routine analysis of metals in edible oils by ICP-MS. The proposed method is simple, fast and provides good limits of detection and quantification, which showed that it is an excellent alternative to other sample preparation methods such as total digestion of the samples, sample dilution with an appropriate solvent or the direct injection of the oil as emulsion or microemulsion.

References

1 H. D. Belitz, W. Grosch, P. Schieberle, *Food Chemistry*, 4th edition, SpringerVerlag, Berlin, Germany, 2009.

2 A. N. Anthemidis, V. Arvanitidis, J. A. Stratis, *Analytica Chimica Acta*, 2005, **537**, 271-278.

3 I. Karadjova, G. Zachariadis, G. Boskou, J. Stratis, *J. Anal. Atom. Spectrom*, 1998, **13**, 201-204.

4 M. Zeiner, I. Steffan, I. J. Cindric, *Microchem. J*, 2005, **81**, 171-176.

5 M. K. Jamali, T. G. Kazi, M. B. Arain, H. I. Afridi, N. Jalbani, R. A. Sarfraz, J. A. Baig, *J. Hazard. Mater*, 2008, **158**, 644-651.

6 E. K. Baran, S. B. Yasar, *Eur. J. Lipid Sci. Technol*, 2012, **114**, 1320–1326.

7 F. K. Zhu, W. X. Fan, X. J. Wang, L. Qu, S. W. Yao, *Food. Chem. Toxicol*, 2011, **49**, 3081-3085.

8 A. Szydłowska-Czerniak, K. Trokowski, G. Karlovits, E. Szłyk, *J. Agr. Food. Chem*, 2013, **61**, 2276–2283.

9 E. J. Llorent-Martínez, P. Ortega-Barrales, M. L. F. Córdova, A. Domínguez-Vidal, A. Ruiz-Medina, *Food. Chem*, 2011, **127**, 1257-1262.

10 M. D. Garrido, I. Frias, C. Diaz, A. Hardisson, *Food. Chem*, 1994, **50**, 237-243.

11 V. Carbonel, A. R. Mauri, A. Salvador, M. de la Guardia, *J. Anal. Atom. Spectrom*, 1991, **6**, 581-584.

12 M. N. Matos Reyes, R. C. Campos, *Talanta*, 2006, **70**, 929-932.

13 F. Anwar, T. G. Kazi, R. Saleem, M. I. Bhanger, *Grasas y Aceites*, 2004, **55**, 160-168.

14 B. Bati, H. Cesur, *Anal. Sci*, 2002, **18**, 1273-1274.

15 R. Ansari, T. G. Kazi, M. K. Jamali, M. B. Arain, M. D. Wagan, N. Jalbani, H. I. Afridi, A. Q. Shah, *Food. Chem*, 2009, **115**, 318-323.

16 D. Mendil, O. D. Uluözlü, M. Tüzen, M. Soylak, *J. Hazard. Mater*, 2009, **165**, 724-728.

17 I. J. Cindric, M. Zeiner, I. Steffan, *Microchem. J*, 2007, **85**, 136-139.

18 E. J. Llorent-Martínez, P. Ortega-Barrales, M. L. F. Córdova, A. Ruiz-Medina, *Food Control*, 2011, **22**, 221-225.

19 F. G. Lepri, E. S. Chaves, M. A. Vieira, A. S. Ribeiro, A. J. Curtius, L. C. C De Oliveira, R. C. De Campos, *Appl Spectrosc Rev*, 2011, **46**, 175-206.

20 C. M. Canário, D. M. Katskov, *J. Anal. At. Spectrom*, 2005, **20**, 1386-1388.

21 R. Marfil, C. Cabrera-Vique, R. Giménez, P. R. Bouzas, O. Martinez, J. A. Sánchez, *J. Agr. Food Chem*, 2008, **56**, 7279-7284.

22 S. J. Huang, S. J. Jiang, *J. Anal. At. Spectrom*, 2001, **16**, 664-668.

23 Y. T. Chang, S. J. Jiang, *J. Anal. At. Spectrom*, 2008, **23**, 140-144.

24 R. J. Cassella, D. M. Brum, C. E. R. Paulaa, C. F. Lima, *J Anal At Spectrom*, 2010, **25**, 1704-1711.

25 R. J. Cassella, D. M. Brum, C. F. Lima, L. F. S. Caldasa, C. E. R. Paulaa, *Anal Chim Acta*, 2011, **690**, 79-85.

26 R. J. Cassella, D. M. Brum, N. F. Robaina, A. A. Rochaa, C. F. Lima, *J Anal At Spectrom*, 2012, **27**, 364-370.