Extraction induced by emulsion breaking as a tool for simultaneous multi-element determination in used lubricating oils by ICP-MS

Yang-Ming He, [a] Fang-Fang Zhao, [a] Ying Zhou, [*ab] Farooq Ahmad[a] and Zhao-Xing Ling[a]

[a] College of Chemical Engineering, Zhejiang University of Technology

18 Chaowang Road, Hangzhou 310032, Zhejiang Province, China

[b] Research Center of Analysis and Measurement, Zhejiang University of Technology

18 Chaowang Road, Hangzhou 310032, Zhejiang Province, China

[*]Corresponding author:

Research Center of Analysis and Measurement, Zhejiang University of Technology,

18 Chaowang Road, Hangzhou 310032, Zhejiang Province, China

Tel: +86 571 88320568; Fax: +86 571 88320961

E-mail: yingzhou@zjut.edu.cn

[Abstract]: This paper reports, for the first time, rapid simultaneous multi-element determination of Mg, Cr, Ni, Cu and Pb in used lubricating oils after their extraction/preconcentration from samples using the novel extraction induced by emulsion breaking. The quantification of the metals of interest in the extracts was performed by ICP-MS using rhodium as internal standard. Firstly, in order to make it possible to prepare the emulsion, 4 mL of each oil sample was mixed with 1mL of toluene. Then the diluted oil sample was emulsified with 1mL of Triton X-114 acid solution. Once the extraction of the metals was completed, the emulsion was broken by centrifugation for 10min at 6000rpm. After that, the lower aqueous phase, containing the analytes that were extracted from oil, was collected for the determination by ICP-MS. Several parameters affecting the extraction efficiency of the procedure were investigated including the nature and concentration of the solvent used for sample dilution, the type and concentration of the surfactant, the concentration of HNO_3, and the other operational conditions (extraction time, collection time and centrifugal speed). The limits of detection for Mg, Cr, Ni, Cu and Pb were 0.126, 0.058, 0.028, 0.078 and 0.009μg L^{-1}, respectively. The accuracy of the method was checked by application of a recovery test, by an analysis of standard reference materials (SRM 1084a and 1085b) and by comparison with the microwave digestion method.

[Keywords]: Used lubricating oils; Extraction induced by emulsion breaking; Metals; ICP-MS

1 Introduction

Lubricating oil is one of the most important liquids that are used in almost all vehicles and machines. Lubricating oil plays a dual role of heat transfer and friction reduction which reduces the heat generated in internal combustion engines.[1] The accurate and fast determination of metals in lubricating oils can be used for quality control of oils, engine diagnosis, preventive maintenance and oil wastes assessment.[2] Trace level of metals like Mg, Cr, Ni, Cu and Pb are known to monitor the extent of wearing in engines as metallic particles and organometallic species can be produced during normal operation.[3] Besides, Mg, Cr and Ni are also incorporated into lubricating oils as additives to improve their performance.[4]

Sensitive techniques are required for analysis of used lubricating oils since the capability of monitoring small concentration changes in the key elements is needed.[5] Apart from the existence of a few electroanalytical,[6-8] laser-induced breakdown spectroscopy,[9, 10] and XRF[11] methods for the determination of metals in lubricating oils, the majority of analytical methods reported in the literature were based on atomic spectrometric techniques such as FAAS, ET-AAS, DC or ICP-OES, ICP-MS and AFS.[5] Among these, ICP-MS has been recognized as one of the most powerful and widely applied instrumental techniques in analytical chemistry due to the combination of high sensitivity and fast multi-element capabilities.[12] However, the accurate determination of metals in used lubricating oils by plasma-based techniques like ICP-MS is still an analytical challenge, especially because of the nature of the samples, which present very high carbon content, intrinsic heterogeneity and unfavorable physical characteristics such as high viscosity and turbidity. Therefore, designing optimal lubricating oil pretreatment is critical for reliable metal determination in such a matrix.

The traditional way to introduce oil samples into ICP is directly diluting with an appropriate organic solvent.[13-16] This procedure does not minimize the problems associated with the high organic load, and necessarily requires the use of expensive and unstable organometallic standards for calibration. Besides, the manipulation of toxic organic solvents makes the procedure very harmful for the analysts. Alternatively, acid digestions with classical heating, ultrasonic irradiation or microwaves have been proposed, [17-19] allowing the measurement of metallic ions without serious interferences due to the total (or almost total) elimination of the organic carbon. However, these procedures are laborintensive, thus implicating a low sample throughput. Also, the excessive dilution is imposed to the samples, which impairs the limit of quantification and brings possible contamination. Emulsification of the sample with detergents and water leading to oil-in-water emulsion is another alternative.[4, 5, 17, 20] This approach does not require the destruction of the organic matter or the use of large amounts of organic solvents, and presents relatively high sample throughput. Using emulsion, the main problem is its instability, which causes phase separation in a short period of time. Meanwhile, emulsion formation results in sample dilution and degradation of detection limit. Additionally, a method to determine metals in lubricating oils using pressurized solvent extraction (PLE) with a semi-automatic extractor ASE 200 by ICP-MS has been developed in the literature.[21]

Only several papers described the direct determination of metals in lubricating oils. Bings[22] developed a method for the direct determination of Na, Mg, Al, Ti, Cr, Fe, Ni, Co, Cu, Ag and Pb in used lubricating oils by combining direct laser ablation (LA) of the samples with inductively coupled plasma time-of-flight mass spectrometry (ICP-TOFMS). Yu et al.[10] proposed a method based on laser-induced breakdown spectroscopy (LIBS) technique to directly determine metals in lubricating oils. However, these methods were prohibitive for several analytical laboratories because the high-cost instrumentations needed to be used.

Recently, Cassella et al.[23-25] reported a new procedure, based on the extraction induced by emulsion breaking (EIEB), to extract analytes from oil samples into an aqueous solution. In this case, the emulsions were prepared by mixing the oil samples with acidic surfactant solutions, and broken with heating or centrifugation. But, a cleaner aqueous phase was obtained by centrifugation than heating. After the emulsion breaking, the metals were efficiently transferred from oil to the aqueous phase. The method was successfully applied in the extraction of various metals from diesel oil, edible oil, biodiesel and lubricating oil.[23-31] In these works, the determination of the metals was performed by different analytical techniques (FAAS, ETAAS and ICP-MS), which proved the versatility of the methodology.

The main goal of this study was to propose a novel method for the simultaneous determination of Mg, Cr, Ni, Cu and Pb in used lubricating oils by ICP-MS after a simple extraction/preconcentration procedure based on EIEB. In this work, all the samples were diluted with an organic solvent before the formation of emulsions and the amount of nitric acid and surfactant was reduced, when compared to our previous work on edible vegetable oils. [31] In addition, the emulsions were broken by centrifugation at 6000rpm for 10min which was shorter than that reported by Caldas et al.[27] As a result, the total pretreatment time was reduced, which had vital significance especially if a great number of samples are to be measured.

2 Experimental

2.1 Apparatus

The determination of the analytes was performed using a Perkin-Elmer (Concord, Canada) inductively coupled plasma mass spectrometer, model Elan DRC-e, operated under the conditions listed in Table 1. The determination of Mg, Cr, Ni, Cu and Pb was performed by measuring the isotopes ^{25}Mg, ^{53}Cr, ^{60}Ni, ^{63}Cu and ^{208}Pb respectively, while rhodium (^{103}Rh) was employed as internal standard. The emulsion breaking was induced by centrifugation using an Eppendorf (Hamburg, Germany) 5804 centrifuge. The evaluation of the extraction time was performed by shaking (80 rpm) the emulsions with a roller mixer, model SRT-202, supplied by Kylin-Bell (Haimen, China). The total digestion of used lubricating oil samples was performed with an Anton Paar (Graz, Austria) microwave oven, model Multiwave 3000, equipped with PFA vessels.

Table 1 Operating conditions used in the ICP-MS measurement of Mg, Cr, Ni, Cu and Pb

Parameter	Value
RF power	1300 W
Auxiliary gas flow	1.20 L min^{-1}
Plasma gas flow	15.0 L min^{-1}
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	0.89 L min^{-1}
Flow rate	400 µL min^{-1}
Sampling depth	5.5 mm

2.2 Reagents, standards and samples

Ultrapure water employed for the preparation of all aqueous solutions was obtained in a Milli-Q Element A10 water purification System (Millipore, Bedford, MA, USA). All solvents employed in the test of the influence of the solvent (ethyl benzene, toluene and hexane) were HPLC-grade (Tjshield, Tianjin, China).

A multi-elemental aqueous stock 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 was supplied by Perkin-Elmer (Shelton, USA). Aqueous stock solution of rhodium (10 mg L^{-1}) was also supplied by Perkin-Elmer (Shelton, USA).The aqueous standard solutions used in the experiments were prepared by dilution of the stock solutions with 1% v/v HNO_3. The nitric acid was of MOS grade (Sinopharm Chemical Reagent, Shanghai, China).

Certified reference materials, SRM 1084a and 1085b (Wear-Metals in Lubricating Oil) were from the National Institute of Standards Technology (NIST, Gaithersburg, MD, USA). Oil-based stock solutions of magnesium, chromium, nickel, copper and lead of 1000 μg g^{-1} were supplied by Conostan (Houston, TX, USA). The oil standard solutions used to spike the samples in the recovery test were prepared by suitable dilution of the stock solutions with HPLC-grade hexane.

The acid solutions of Triton X-114 and Triton X-100 (Acros Organics, New Jersey, USA), used for emulsification of lubricating oils, were prepared by dissolving suitable masses of each surfactant in exactly 100 mL of HNO_3 solution. The concentrations of Triton X-114, Triton X-100 and HNO_3 were established according to the value desired for each experiment.

Total ten used lubricating oil samples were collected from gas stations located in the city of Hangzhou, China, and no information regarding the type of oils or their time of use could be obtained. They were stored in a low-density polyethylene flask and kept in a light-free place at ambient temperature.

2.3 Extraction/preconcentration procedure

The extraction of metals from used lubricating oils was performed by using EIEB procedure. The EIEB procedure was involved in three main steps:

(1) Dilution: 4 mL of each oil sample (approximately 3.45 g) was mixed with 1mL of toluene, in order to decrease the viscosity and allow a convenient mixing with the emulsifying

aqueous solution.

(2) Emulsification: 1 mL of solution containing the acidic Triton X-114 was added to the capped plastic tube of 15 mL capacity, which contained 5 mL of diluted oil sample, and then was mixed vigorously in order to obtain stable water-in-oil emulsion. Afterwards, the emulsion was transferred to a roller mixer, agitated for 25 min in order to improve the extraction of the analytes.

(3) Emulsion breaking: The tube was transferred to the centrifuge, centrifuged at 6000 rpm to reach the phase separation, and also the emulsion breaking time was recorded during this step. At the end of the emulsion breaking, two well-separated phases were observed, as shown in Fig. 1: (A) an upper phase containing the diluted oil and the surfactant and (B) a lower phase, containing the aqueous acid solution with the extracted metals. Then, the lower aqueous phase was collected (approximately 0.8 mL) with the aid of a micropipette and used to measure the metals of interest by ICP-MS. The calibration strategy was based on the internal standardization approach, using Rh as the internal standard to minimize possible interferences due to the injection of complexes matrices (residual concentrations of the surfactant). When necessary, a defined volume of the aqueous phase was taken and diluted with ultrapure water in order to adjust the concentration of the metals to the linear portion of the analytical curves. The blank was prepared in the same way of the sample, but without adding lubricating oil.

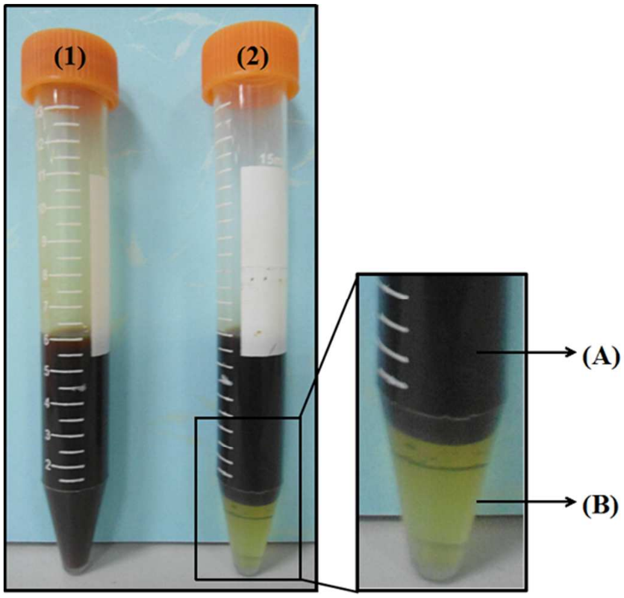

Fig. 1 Emulsion (1) before and (2) after breaking by centrifugation at 6000rpm. (A) Used lubricating oil phase and (B) aqueous phase. The phase separation process took 10 min.

2.4 Microwave digestion of the samples

The microwave digestion of the oil samples was performed by acid dissolution in a closed-vessel microwave oven. For this purpose, approximately 0.250 g of oil was digested with 5 mL of concentrated HNO_3. The microwave heating program consisted of five steps: 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 10 min at 600 W and 10 min at 800 W. The final volume was completed to 25 mL with ultrapure water. The metals were also measured by ICP-MS using Rh as the internal standard.

3 Results and discussion

The optimization of the proposed methodology was studied by investigating the effect of some parameters on the extraction efficiency and the time spent to complete the procedure: (A) type and concentration of the solvent used to dilute the oils, (B) the concentrations of Triton X-114 and Triton X-100 used for emulsification (C) the concentration of HNO_3 used for extraction and (D) the operational extraction conditions. 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 are defined as the ratio between each analytical signal and the highest analytical signal obtained in the set.

3.1 Effect of the type and concentration of the solvent

The first parameter studied in the optimization of the proposed procedure was the influence of the type and concentration of the solvent. The formation of a convenient emulsion has fundamental importance for the success of the procedure, because a proper dispersion of water droplets through the oil samples enhances the extraction efficiency due to the increase of the interfacial area between oils and extractant aqueous solutions. However, the mixture of the samples with the acid solutions of Triton X-114 or X-100 was impaired by the characteristic of high viscosity of used lubricating oils, which made it practically impossible to prepare the emulsions. In order to overcome this drawback, an organic solvent was introduced to reduce the viscosity of the oil and to facilitate the interaction between oil and the non-ionic surfactant, resulting in good formation of emulsion. Three solvents were carried out where used lubricating oils were highly soluble: toluene, ethylbenzene and hexane. The volumetric proportion of solvent was kept constant at 20% v/v and the extraction efficiency was evaluated. And no significant difference of the signals was noted for all analytes by using any of the three solvents (Fig. 2). Nevertheless, when the sample was diluted with toluene, the separation of an aqueous phase with lowest turbidity was observed. It indicated that the transference of organic material to this phase was minimized with toluene. So, toluene was chosen as solvent for the method.

Meanwhile, the effect of the concentration of toluene was performed in the range of 10-50%

v/v. There was a significant decrease among the signals obtained with the increase proportion of toluene, which could be explained by the increased dilution factor. However, when the proportion of toluene was between 35 and 50% v/v, a practical problem appeared that the emulsion breaking was very difficult. In this case, residual amounts of emulsified oil remained in the interface between the two phases and it was extremely inconvenient to collect the lower aqueous phase. In order to avoid excessive dilution of the samples and make the collection of the aqueous phase easier, a proportion of 20% v/v was chosen for the method.

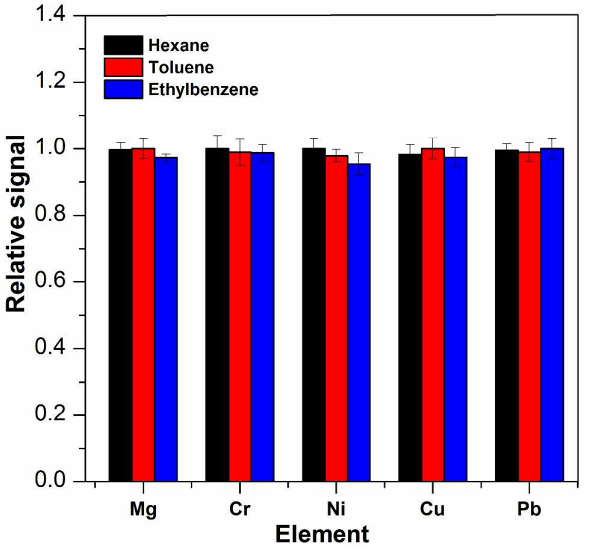

Fig. 2 Effect of the solvent type to decrease the viscosity of used lubricating oil on the extraction of metals by the proposed procedure. The solvents concentrations were 20% v/v.

3.2 Effect of the surfactant type and concentration

Surfactants are able to improve the characteristics of many chemical reactions and the performance of certain analytical methods. The surfactant (Triton X-114 or X-100) plays an important role in this proposed method, since it decreases the surface tension between aqueous and oil phases, lowering the energy required for emulsification. The experiment was carried out by changing the concentration of Triton X-114 or X-100 in the range of 1–8% m/v. The concentration of HNO_3 was fixed at 15% v/v, the sample was diluted with toluene (20% toluene + 80% sample) before emulsification and the emulsion breaking was performed by centrifugation at 6000 rpm. Fig. 3 shows the results obtained in the experiment.

In the range of 1–3% m/v, the increase of the concentration of the surfactants enhanced the extraction efficiency which was denoted by the increase of the analytical signals for all analytes. But there is no remarkable variation in the magnitude of the signals in the range of 3–8% m/v. And an efficient extraction of the metals can be reached independently of the type of surfactants, since the curves with similar profiles were verified when Triton X-114 and X-100 were employed for the emulsification. The effect of the surfactant concentration was also examined in terms of the time required for the emulsion breaking. It is important to remark that the use of higher concentrations of surfactants resulted in the formation of more stable emulsions, which took longer time to be broken. And the emulsions prepared from Triton X-114 were broken at a reduced time than Triton X-100, which indicated that Triton X-114 was more suitable for the EIEB procedure. Therefore, Triton X-114 concentration of 3% m/v was selected for further experiments to achieve the highest extraction efficiency and form emulsions easy to break.

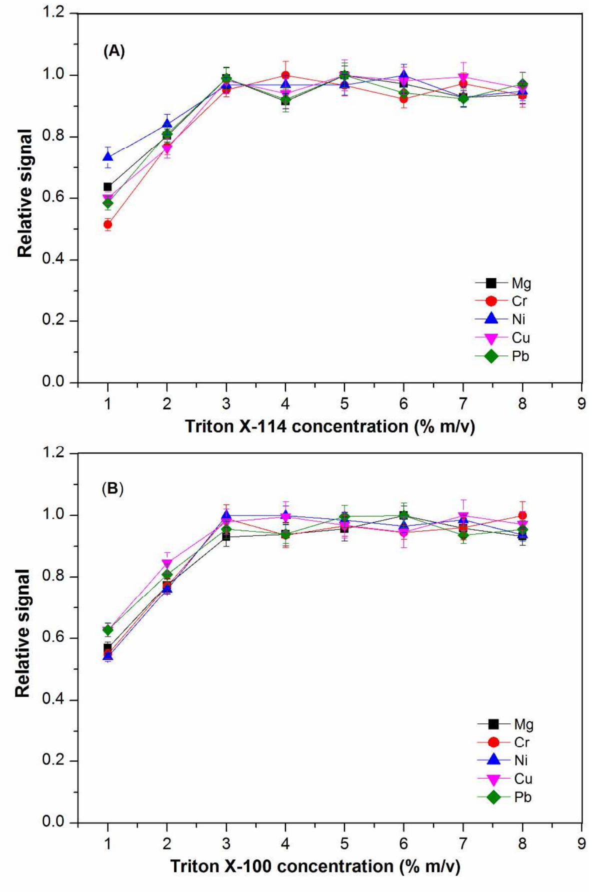

Fig. 3 Effect of the concentration of the surfactants on the extraction of metals by the proposed method. (A) Triton X-114 (B) Triton X-100. Toluene concentration was 20% v/v, HNO_3 concentration was 15% v/v.

3.3 Effect of the nitric acid concentration

Nitric acid is responsible for the extraction of metals in used lubricating oils, where they can be present in free form, in metallic particles, in oxide species or as part of organic structures. When the acid is used, the organic matrix is not destroyed; only element extraction is carried-out.[32] In order to investigate the effect of this variable, the concentration of HNO_3 in the extract solution was changed in the range of 1-30% v/v, always maintaining the Triton X-114 concentration at 3% w/v, and the emulsion breaking was carried out by centrifugation at 6000 rpm. Fig. 4 showed the variation of the analytical signals with the variation of the concentration of HNO_3.

The analysis of the results showed that the concentration of HNO_3 presented noticeable effect on the extraction of Cr, Ni and Cu. For Mg and Pb, the extraction efficiency was practically unaltered along the whole range evaluated, while for Cr, Ni and Cu, there was a clear increase of the extraction efficiency with the increase of the HNO_3 concentration until 15% v/v. For concentrations higher than 15% v/v, the signals remained almost constant. This fact could indicate that the particles of Cr, Ni and Cu were more difficult to dissolve than the particles of Mg and Pb. Herein, the HNO_3 concentration of 15% v/v was chosen for the method to ensure maximum extraction of all analytes only at one condition.

The emulsions breaking time was also influenced by the concentration of HNO_3. But they were always very low, varying from 7 to 13 min in the range of 1-30% v/v. In the experiment using 15% v/v of HNO_3, the time needed to break the emulsions was 10min, which was considered satisfactory because it did not affect the total time taken to complete the procedure.

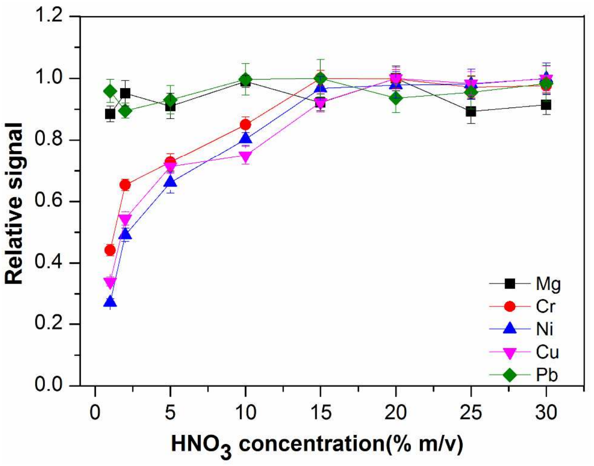

Fig. 4 Effect of the HNO_3 concentration on the extraction of metals by the EIEB procedure. Toluene concentration was 20% v/v and Triton X-114 concentration was 3% m/v.

3.4 Effect of the operational extraction conditions

In this study, some practical aspects, related to the operational conditions, were also evaluated. In this context, three parameters were tested: (i) extraction time; (ii) collection time and (iii) centrifugal speed.

The extraction time is considered as the time elapsed between the formation and breaking of the emulsions. In this experiment, emulsions were prepared and agitated on a roller mixer for increasing time in the range of 0–60 min to evaluate the importance of the contact time between the same lubricating oil and extractant solution. As it can be seen in Fig. 5, no influence of this parameter was observed on the signals of Mg and Pb. But for Cr, Ni and Cu, the increase of the extraction time increased the extraction efficiency, which was denoted by the increase of the analytical signals, and the maximum extraction could only be achieved when the emulsions were agitated for at least 20 min. These results could further indicate that the transference of Cr, Ni and Cu to the acidic aqueous phase was more difficult than Mg and Pb in used lubricating oil. In order to ensure the maximum extraction of all analytes, an extraction time of 25 min was established for the method.

The collection time is the time passed from the end of the emulsion breaking until the collection of the aqueous phase. The importance of collection time grows if a greater number of emulsions are broken simultaneously. In order to test this effect, the collection time was varied from 2 (the minimum time for the separation of the phases with the micropipette) to 100 min. The variation of the signals was negligible, evidencing that all analytes remained in the solution even if the separated oil and aqueous phase were maintained in contact as long as 100 min.

In order to evaluate the effect of the centrifugal speed on the extraction efficiency, this variable was varied in the range of 2000-10000 rpm and no remarkable differences among the analytical signals was verified. This fact evidences that the extraction efficiency did not depend on the centrifugal speed employed for the emulsion breaking. However, the centrifugal speed presented noticeable effect on the emulsion breaking time, which was strongly decreased with the increase of centrifugal speed in the range of 2000-6000 rpm. At centrifugal speed higher than 6000 rpm, the time of the emulsion breaking (10 min) remained almost constant. Therefore, a centrifugation speed of 6000 rpm and a centrifugation time of 10 min were selected for the method.

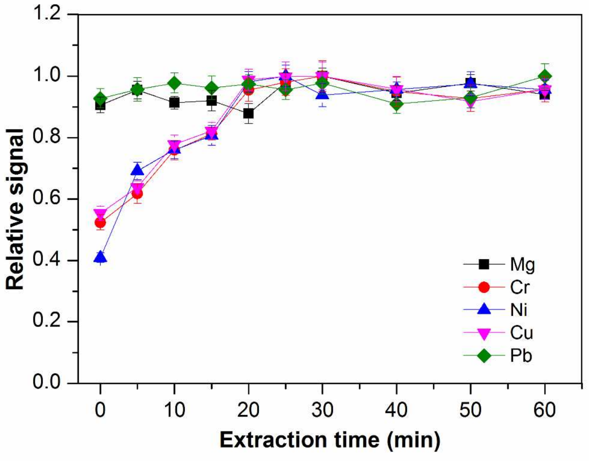

Fig. 5 Effect of the extraction time on the extraction of metals by the proposed procedure. Toluene = 20% v/v, Triton X-114 = 3% m/v, HNO_3 = 15% v/v.

3.5 Analytical features of the proposed methodology

The limits of detection and quantification for Mg, Cr, Ni, Cu and Pb determination in used lubricating oils were derived from the calibration curves based on online internal standard method with 20µg L^{-1} Rh as an internal standard, which were constructed with aqueous standard solutions prepared in 1% v/v HNO_3 medium. The instrumental limits of detection (3s criterion) and quantification (10s criterion) were estimated from eleven measurements of 1% v/v HNO_3 solution. The limits of detection and quantification of the methodology were estimated from the analysis of the blank solution obtained in the EIEB procedure. The repeatability (within-run) of the methodology was estimated in the determination of analytes in the sample ULO_1. Reproducibility (between-run) was tested by analyzing independent aliquots of same sample ULO_1 in three consecutive days. These data are presented in Table 2.

Table 2 Analytical features of the proposed methodology

Parameters	Metals				
	Mg	Cr	Ni	Cu	Pb
Instrumental LOD (µg L^{-1})	0.089	0.032	0.012	0.057	0.005
Instrumental LOQ (µg L^{-1})	0.297	0.107	0.041	0.190	0.017
Methodological LOD (µg L^{-1})	0.126	0.058	0.028	0.078	0.009
Methodological LOQ (µg L^{-1})	0.420	0.194	0.093	0.262	0.031
Repeatability (%) (n=3, sample ULO_1)	2.99	4.01	1.87	2.98	2.55
Reproducibility (%) (n=3, sample ULO_1)	5.03	6.23	6.76	5.44	4.95

3.6 Validation and application of the proposed methodology

Three different strategies were carried out to assess the efficiency and accuracy of the method. In the first case, the accuracy of the EIEB and microwave digestion procedure was calculated from six aliquots of the certified lubricating oil SRM 1084a and 1084b, each measured three times. Table 3 presents satisfactory recoveries for the EIEB (90–108%) and microwave digestion (93–106%) procedure. Secondly, the results obtained by the developed method were compared with those obtained when the samples were analyzed using microwave digestion. As it can be seen in Table 4, there was no statistical difference between the results of them when the Student-t test (95% confidence level) was applied. Lastly, the recovery test was performed by the analysis of real samples spiked with known amounts of analytes in the form of organometallic standards (Conostan standards). The results are given in Table 5a and b, recovery percentages ranging from 86% to 110% were observed in the determination of Mg, Cr, Ni, Cu and Pb, showing that these metals were quantitatively extracted by EIEB procedure and confirming that no matrix interferences were present in the measurement of metals by ICP-MS.

The developed methodology was applied in the determination of Mg, Cr, Ni, Cu and Pb in ten samples of used lubricating oils (Table 4). The magnesium values were lower than those reported by Paradelo et al.,[21] but higher than the literature values by Zmozinski et al.[17] The chromium and nickel contents were in agreement with those reported in the literatures.[13,16,20,23] The copper levels were higher than those found by Yawar,[16] but lower than those reported by Paradelo et al. and Caldas et al.[21,27] Our lead levels were lower than those found in the literatures,[13,21,22] indicating less wearing in engines.

Table 3 Concentrations of Mg, Cr, Ni, Cu and Pb in lubricating oils SRM 1084a and SRM 1085b

		SRM 1084a			SRM 1085b		
Methods	Analytes	Certified value (μg g^{-1})	Obtained value (μg g^{-1})	Recovery (%)	Certified value (μg g^{-1})	Obtained value (μg g^{-1})	Recovery (%)
EIEB	Mg	99.5 ± 1.7	107.3 ± 3.2	108	297.3 ± 4.1	282.8 ± 8.2	95
	Cr	98.3 ± 0.8	88.9 ± 1.8	90	302.9 ± 3.9	316.9 ± 4.6	105
	Ni	99.7 ± 1.6	102.5 ± 2.7	103	295.9 ± 7.4	315.6 ± 6.9	107
	Cu	100.0 ± 1.9	92.2 ± 3.1	92	295.6 ± 8.5	306.2 ± 8.2	104
	Pb	101.1 ± 1.3	99.3 ± 1.9	98	297.7 ± 6.8	292.5 ± 7.5	98
Microwave digestion	Mg	99.5 ± 1.7	98.8 ± 2.5	99	297.3 ± 4.1	314.1 ± 9.4	106
	Cr	98.3 ± 0.8	104.0 ± 4.5	106	302.9 ± 3.9	282.9 ± 5.7	93
	Ni	99.7 ± 1.6	95.9 ± 2.3	96	295.9 ± 7.4	304.7 ± 12.1	103
	Cu	100.0 ± 1.9	101.8 ± 3.6	102	295.6 ± 8.5	310.3 ± 10.3	105
	Pb	101.1 ± 1.3	99.4 ± 0.9	98	297.7 ± 6.8	280.3 ± 9.9	94

Table 4 Results obtained for the determination of Mg, Cr, Ni, Cu and Pb in used lubricating oils by the EIEB and microwave digestion extraction methods. Results are expressed in mg L^{-1} as mean ± standard deviation (n = 3)

Elements	Methods	Samples									
		ULO_1	ULO_2	ULO_3	ULO_4	ULO_5	ULO_6	ULO_7	ULO_8	ULO_9	ULO_{10}
Mg	EIEB	16.8 ± 0.9	9.82 ± 0.11	6.79 ± 0.54	13.5 ± 1.6	5.33 ± 0.48	9.43 ± 0.75	2.95 ± 0.09	6.78 ± 0.44	15.2 ± 1.2	4.77 ± 0.29
	Microwave digestion	16.9 ± 1.2	8.91 ± 0.22	7.70 ± 0.67	13.9 ± 2.2	4.39 ± 0.25	10.2 ± 0.5	2.69 ± 0.12	7.09 ± 0.48	17.7 ± 1.0	5.05 ± 0.22
Cr	EIEB	1.64 ± 0.16	1.28 ± 0.19	0.44 ± 0.05	1.65 ± 0.21	0.95 ± 0.03	1.79 ± 0.07	1.53 ± 0.06	2.08 ± 0.11	2.04 ± 0.09	0.68 ± 0.03
	Microwave digestion	1.46 ± 0.14	1.54 ± 0.25	0.49 ± 0.03	1.56 ± 0.23	1.21 ± 0.12	1.53 ± 0.12	1.66 ± 0.14	2.41 ± 0.28	2.19 ± 0.13	0.76 ± 0.07
Ni	EIEB	0.38 ± 0.02	0.22 ± 0.01	1.23 ± 0.07	0.68 ± 0.06	1.15 ± 0.13	0.81 ± 0.07	0.99 ± 0.05	1.78 ± 0.19	1.52 ± 0.27	0.87 ± 0.04
	Microwave digestion	0.31 ± 0.03	0.28 ± 0.03	1.16 ± 0.06	0.69 ± 0.05	1.40 ± 0.07	0.59 ± 0.15	1.11 ± 0.13	1.94 ± 0.17	1.46 ± 0.26	0.79 ± 0.05
Cu	EIEB	1.85 ± 0.11	2.47 ± 0.09	1.47 ± 0.18	3.08 ± 0.23	4.05 ± 0.38	1.81 ± 0.13	1.96 ± 0.05	1.37 ± 0.09	3.44 ± 0.29	2.58 ± 0.14
	Microwave digestion	1.93 ± 0.08	2.29 ± 0.15	1.61 ± 0.12	3.38 ± 0.14	3.85 ± 0.18	1.88 ± 0.21	2.13 ± 0.06	1.29 ± 0.05	3.61 ± 0.17	2.37 ± 0.14
Pb	EIEB	0.95 ± 0.04	0.47 ± 0.01	1.45 ± 0.11	0.58 ± 0.06	1.05 ± 0.08	1.01 ± 0.03	1.95 ± 0.14	1.33 ± 0.05	0.91 ± 0.04	0.76 ± 0.05
	Microwave digestion	0.93 ± 0.05	0.56 ± 0.06	1.61 ± 0.12	0.57 ± 0.04	0.99 ± 0.07	1.15 ± 0.12	2.13 ± 0.18	1.29 ± 0.09	0.90 ± 0.10	0.88 ± 0.04

Table 5a Recoveries of the EIEB procedure obtained for the determination of Mg, Cr, Ni in real used lubricating oil samples by ICP-MS (n= 3)

	Mg			Cr			Ni		
Samples	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
ULO$_1$	0	16.8 ± 0.9	–	0	1.64 ± 0.16	–	0	0.38 ± 0.02	–
	8	25.6 ± 0.6	110 ± 7	1	2.61 ± 0.12	97 ± 2	0.5	0.81 ± 0.02	86 ± 1
	16	32.7 ± 0.8	99 ± 5	2	3.77 ± 0.08	107 ± 4	1	1.27 ± 0.04	89 ± 1
ULO$_2$	0	9.82 ± 0.11	–	0	1.28 ± 0.19	–	0	0.22 ± 0.01	–
	4	14.2 ± 0.5	109 ± 4	1	2.38 ± 0.13	110 ± 3	0.5	0.69 ± 0.02	93 ± 3
	8	17.4 ± 0.3	95 ± 3	2	3.23 ± 0.24	98 ± 2	1	1.21 ± 0.01	99 ± 1
ULO$_3$	0	6.79 ± 0.54	–	0	0.44 ± 0.05	–	0	1.23 ± 0.07	–
	4	10.3 ± 0.6	87 ± 1	0.5	0.93 ± 0.02	97 ± 3	0.5	1.77 ± 0.06	107 ± 5
	8	14.7 ± 0.7	99 ± 2	1	1.44 ± 0.05	100 ± 1	1	2.23 ± 0.09	100 ± 3
ULO$_4$	0	13.5 ± 1.6	–	0	1.65 ± 0.21	–	0	0.68 ± 0.06	–
	8	21.3 ± 1.4	97 ± 3	1	2.74 ± 0.13	109 ± 3	0.5	1.15 ± 0.01	94 ± 1
	16	30.2 ± 0.3	105 ± 4	2	3.77 ± 0.10	106 ± 5	1	1.66 ± 0.05	98 ± 2
ULO$_5$	0	5.33 ± 0.48	–	0	0.95 ± 0.03	–	0	1.15 ± 0.13	–
	4	9.38 ± 0.21	101 ±5	1	1.86 ± 0.03	91 ±3	0.5	1.67 ± 0.05	101 ± 3
	8	12.3 ± 0.4	87 ±4	2	3.05 ± 0.08	105 ±4	1	2.02 ± 0.12	87 ± 2
ULO$_6$	0	9.43 ± 0.75	–	0	1.79 ± 0.07	–	0	0.81 ± 0.07	–
	4	13.8 ± 0.8	110 ± 2	1	2.81 ± 0.04	102 ± 3	0.5	1.29 ± 0.04	96 ±3
	8	17.8 ± 0.9	104 ± 5	2	3.59 ± 0.08	90 ± 1	1	1.86 ± 0.06	105 ±2
ULO$_7$	0	2.95 ± 0.09	–	0	1.53 ± 0.06	–	0	0.99 ± 0.05	–
	2	4.97 ± 0.04	101 ± 2	1	2.39 ± 0.03	86 ±3	0.5	1.53 ± 0.03	108 ± 4
	4	6.63 ± 0.11	92 ± 1	2	3.67 ± 0.13	107 ± 7	1	1.98 ± 0.10	99 ± 1
ULO$_8$	0	6.78 ± 0.44	–	0	2.08 ± 0.11	–	0	1.78 ± 0.19	–
	4	11.1 ± 0.2	108 ± 5	2	3.82 ± 0.10	87 ± 5	1	2.73 ± 0.13	95 ± 3
	8	15.6 ± 0.8	110± 1	4	6.27 ± 0.18	105 ± 2	2	3.54 ± 0.16	88 ± 3
ULO$_9$	0	15.2 ± 1.2	–	0	2.04 ± 0.09	–	0	1.52 ± 0.27	–
	8	23.9 ± 1.5	108 ± 7	2	3.76 ± 0.06	86 ± 3	1	2.58 ± 0.13	106 ± 3
	16	32.0 ± 1.3	105 ± 2	4	5.93 ± 0.16	97 ± 4	2	3.66 ± 0.12	107 ± 5
ULO$_{10}$	0	4.77 ± 0.29	–	0	0.68 ± 0.03	–	0	0.87 ± 0.04	–
	4	8.22 ± 0.32	86 ± 3	0.5	1.23 ± 0.04	110 ± 5	0.5	1.36 ± 0.02	98 ± 4
	8	11.9 ± 0.2	89 ± 2	1	1.70 ± 0.07	102 ± 3	1	1.86 ± 0.09	99 ± 3

Table 5b Recoveries of the EIEB procedure obtained for the determination of Cu, Pb in real used lubricating oil samples by ICP-MS (n= 3)

	Cu			Pb		
Samples	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
ULO$_1$	0	1.85 ± 0.11	–	0	0.95 ± 0.04	–
	1	2.93 ± 0.05	108 ± 5	0.5	1.43 ± 0.03	95 ± 2
	2	3.76 ± 0.13	96 ± 1	1	1.83 ± 0.01	88 ± 3
ULO$_2$	0	2.47 ± 0.09	–	0	0.47 ± 0.01	–
	1	3.49 ± 0.04	102 ± 4	0.5	0.96 ± 0.02	98 ±3
	2	4.53 ± 0.11	103 ± 5	1	1.38 ± 0.02	91 ±2
ULO$_3$	0	1.47 ± 0.18	–	0	1.45 ± 0.11	–
	1	2.37 ± 0.14	90 ± 4	0.5	1.88 ± 0.06	86 ± 2
	2	3.58 ± 0.07	106 ± 3	1	2.48 ± 0.16	103 ± 6
ULO$_4$	0	3.08 ± 0.23	–	0	0.58 ± 0.06	–
	2	4.82 ± 0.14	87 ± 2	0.5	1.10 ± 0.12	103 ± 4
	4	6.61 ± 0.24	88 ± 1	1	1.60 ± 0.05	102 ± 5
ULO$_5$	0	4.05 ± 0.38	–	0	1.05 ± 0.08	–
	2	6.06 ± 0.34	101 ± 2	0.5	1.49 ± 0.02	89 ± 3
	4	8.18 ± 0.42	103 ±3	1	1.99 ± 0.11	94 ± 1
ULO$_6$	0	1.81 ± 0.13	–	0	1.01 ± 0.03	–
	1	2.68 ± 0.15	87 ±5	0.5	1.53 ± 0.03	104 ± 6
	2	3.77 ± 0.13	98 ±1	1	2.01 ± 0.01	100 ± 1
ULO$_7$	0	1.96 ± 0.05	–	0	1.95 ± 0.14	–
	1	2.98 ± 0.04	102 ± 4	1	2.94 ± 0.05	99 ± 5
	2	3.88 ± 0.07	96 ± 2	2	3.72 ± 0.15	89 ± 1
ULO$_8$	0	1.37 ± 0.09	–	0	1.33 ± 0.05	–
	1	2.37 ± 0.02	100 ± 2	1	2.22 ± 0.03	89 ± 3
	2	3.26 ± 0.13	95 ± 1	2	3.41 ± 0.08	104 ±4
ULO$_9$	0	3.44 ± 0.29	–	0	0.91 ± 0.04	–
	2	5.42 ± 0.22	99 ± 6	0.5	1.37 ± 0.01	92 ± 2
	4	7.15 ± 0.11	93 ± 3	1	1.99 ± 0.08	108 ± 8
ULO$_{10}$	0	2.58 ± 0.14	–	0	0.76 ± 0.05	–
	2	4.68 ± 0.26	105 ± 3	0.5	1.22 ± 0.06	92 ±3
	4	6.27 ± 0.17	92 ± 2	1	1.63 ± 0.04	87 ± 3

4 Conclusions

In this work, the extraction induced by emulsion breaking procedure coupled to ICP-MS was proposed for the determination of Mg, Cr, Ni, Cu and Pb in used lubricating oils. The results obtained were in excellent agreement with the certified values of standard reference materials (SRM 1084a and 1085b), proving the accuracy of the developed procedure. Several advantages over existing methods were observed by the application of the proposed method: (A) the transference of the analytes to the water extract eliminated spectral interferences due to carbon compounds and avoided injector clogging which could result in sensitivity loss and precision degradation; (B) inorganic standards could be used for calibration because the determination was always performed in simple aqueous phase instead of complex organic matrix; (C) a preconcentration factor of four was achieved, once all metals present in 4 mL of oil sample were transferred to 1 mL of acidic extractant solution, which improved the limits of detection and quantification; and (D) the whole procedure only employed 15% v/v HNO_3 solution for the extraction, avoiding the use of large amounts of concentrated acid.

One of the main points of the proposed method was the use of toluene for the dilution of used lubricating oils, which decreased the viscosity of the samples and permitted their emulsification. In this case, a volumetric percentage of 20% of toluene was enough to give stable emulsions.

The developed methodology was successfully applied in the analysis of real samples of used lubricating oil. The obtained results were in agreement with those obtained by the microwave digestion method. Meanwhile, recovery percentages in the range of 86–110% were observed when the metals of interest were added to the samples as organometallic standards.

Acknowledgements

The authors are very grateful to the Project of Science and Technology Department of Zhejiang Province (2012C37058) and the Key Innovation Team of Science and Technology in Zhejiang Province (2010R50018) for financial support.

References

1 R. R. Mohammed, I. A. R. Ibrahim, A. H. Taha and G. McKay, *Chem. Eng. J.*, 2013, **220**, 343–351.

2 M. Pouzar, T. Cernohorsky and A. Krejcova, *Talanta.*, 2001, 54, 829–835.

3 R. Q. Aucélio, A. J. Curtius and B. Welz, *J. Anal. At. Spectrom.*, 2000, **15**, 1389–1393.

4 J. L. Burguera, R. Antón de Salager, M. Burguera, J. L. Salager, C. Rondon, P. Carrero, M. Gallignani, M. R. Brunetto and M. Briceño, *J. Anal. At. Spectrom*., 2000, **15**, 549–555.

5 R. Q. Aucélio, R. M. Souza, R. C. Campos, N. Miekeley and C. L. P. Silveira, *Spectrochim. Acta Part B*., 2007, **62**, 952–961.

6 R. A. A. Munoz and L. Angnes, *Microchem. J*., 2004, **77**, 157–162.

7 R. A. A. Munoz, C. S. Silva, P. V. Oliveira and L. Angnes, *Microkhim. Acta*., 2005, **149**, 199–205.

8 R. A. A. Munoz, P. V. Oliveira and L. Angnes, *Talanta*., 2006, **68**, 850–856.

9 P. Yaroshchyk, R. J. S. Morrison, D. Body and B. L. Chadwick, *Spectrochim. Acta, Part B*., 2005, **60**, 986–992.

10 L. J. Zheng, F. Cao, J. S. Xiu, X. S. Bai, V. Motto-Ros, N. Gilon, H. P. Zeng and J. Yu, *Spectrochim. Acta, Part B*., 2014, **99**, 1–8.

11 Z. Yang, X. D. Hou and B. T. Jones, *Talanta*., 2003, **59**, 673–680.

12 R. S. Amais, C. D. B. Amaral, L. L. Fialho, D. Schiavo and J. A. Nobrega, *Anal. Methods*., 2014, **6**, 4516–4520.

13 J. Mora, J. L. Todoli, F. J. Sempere, A. Canals and V. Hernandis, *Analyst*., 2000, **125**, 2344–2349.

14 T. Kuokkanen, P. Peramaki, I. Valimaki and H. Ronnkomaki, *Intern. J. Anal. Chem*., 2001, **81**, 89–99.

15 G. Pignalosa and M. Knochen, *Atom spectrosc*., 2001, **22,** 250–257.

16 W. Yawar, *J. Anal. Chem*., 2010, **65**, 489–491.

17 A. V. Zmozinski, A. de Jesus, M. G. R. Vale and M. M. Silva, *Talanta*., 2010, **83**, 637–643.

18 L. F. S. Caldas, C. E. R. de Paula, D. M. Brum and R. J. Cassella, *Fuel*., 2013, **105**, 503–511.

19 V. R. A. Filho and J. A. G. Neto, *Anal. Sci*., 2009, **25**, 95–100.

20 S. Carballo, J. Terán, R. M. Soto, A. Carlosena, J. M. Andrade and D. Prada, *Microchem. J*., 2013, **108**, 74–80.

21 S. C. Paradelo, R. M. S. Ferreiro, A. C. Zubieta, J. T. Baamonde, J. M. A. Garda and D. P. Rodrıguez, *J. Anal. At. Spectrom*., 2012, **27**, 1694–1700.

22 N. H. Bings, *J. Anal. At. Spectrom*., 2002, **17,** 759–767.

23 R. J. Cassella, D. M. Brum, C. E. R. de Paula and C. F. Lima, *J. Anal. At. Spectrom*., 2010, **25**, 1704–1711.

24 R. J. Cassella, D. M. Brum, C. F. Lima, L. F. S. Caldas and C. E. R. de Paula, *Anal. Chim. Acta*., 2011, **690**,79–85.

25 R. J. Cassella, D. M. Brum, N. F. Robaina, A. A. Rocha and C. F. Lima, *J. Anal. At. Spectrom*., 2012, **27**, 364–370.

26 N. F. Robaina, D. M. Brum and R. J. Cassella, *Talanta*., 2012, **99**, 104–112.

27 L. F. S. Caldas, D. M. Brum, C. E. R. de Paula and R. J. Cassella, *Talanta*., 2013, **110**, 21–27.

28 F. M. Pereira, R. C. Zimpeck, D. M. Brum and R. J. Cassella, *Talanta*., 2013, **117**, 32–38.

29 F. M. Pereira, D. M. Brum, F. G. Lepri and R. J. Cassella, *Microchem. J*., 2014, **117**, 172-177.

30 D. Bakircioglu, N. Topraksever and Y. B. Kurtulus, *Food. Chem*., 2014, **151**, 219–224.

31 Y. M. He, J. J. Chen, Y. Zhou, X. J. Wang and X. Y. Liu, *Anal. Methods*., 2014, **6**, 5105–5111.

32 J. L. Burguera and M. Burguera, *Talanta*., 2012, **96**, 11–20.

Table of contents entry

A novel method was developed for metals determination in lubricating oils by ICP-MS based on extraction induced by emulsion breaking.