



Application of the extraction induced by emulsion breaking for the determination of Cu, Fe and Mn in used lubricating oils by flame atomic absorption spectrometry

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ABSTRACT

A novel approach is proposed for the sample preparation of used lubricating oils to determine Cu, Fe and Mn by FAAS. The method is based on the extraction induced by emulsion breaking, in which the elements of interest are transferred to an aqueous phase before the measurement by FAAS. In the method, each sample of used lubricating oil was diluted with toluene (20% v/v) and the resulting solution was emulsified with a Triton X-114 solution containing HNO_3 . Further, the water-in-oil emulsion was broken by centrifugation for 30 min at 3500 rpm, originating a system with two well-separated phases: (i) the upper phase, containing the used lubricating oil diluted in toluene and (ii) the lower aqueous phase, containing the analytes that were extracted from oil. The lower phase was collected, diluted with water and the analytes were determined by FAAS. The optimization of the methodology was performed by studying the influence of different parameters that could affect the extraction efficiency such as the nature and concentration of the solvent used for sample dilution, the concentrations of HNO_3 and Triton X-114 in the solution employed for emulsification and the operational conditions for extraction (extraction, centrifugation and sampling times). The limits of quantification for Cu, Fe and Mn were 2.9, 77 and 8.2 ng g^{-1} , respectively. The accuracy of the method was evaluated by comparison with the reference method based on the total digestion of the samples in a closed-vessel microwave oven. There were no statistical differences between the results obtained with the proposed method and the reference one, except for Fe in the cases where its concentration was higher than $80 \text{ } \mu\text{g g}^{-1}$.

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1. Introduction

The use of lubricating oils is very important in various sectors of the modern society, since they are largely employed in the lubrication of engines of cars, buses and other vehicles, machines and in the industrial context [1]. In order to prevent engine failure, the lubricating oil must be changed in a given interval of time that depends on the condition of the oil. A good way to evaluate the condition of lubricating oils is the determination of the concentration of metals, which helps one to identify the excessive wear of the engine [2]. Another aspect to be considered is related to environmental issues. Used lubricating oils are classified as hazardous wastes and their characterization is of fundamental importance to guide the treatment before discarding and the final destination of the residues [3].

The determination of metals in used lubricating oils is 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. Because of these characteristics, in general, the determination of metals in used lubricating oils requires a previous treatment of the samples in order to convert them in a form suitable for the introduction into the analytical instruments. In this field, the most common pretreatment employed in the analysis of used lubricating oils is based on the mineralization of the samples [4–6]. The total digestion of the samples presents some advantages such as the total (or almost total) elimination of the organic carbon, which allows the measurement of metallic ions without serious interferences using atomic spectrometric [4–5] or electrochemical techniques [6].

In the last few years, some efforts have been devoted to the development of alternative methods for the treatment of used lubricating oils for metals determination. The introduction of samples in the form of an emulsion or microemulsion is considered a good option [7–9]. In these cases, minimum sample handling is required, which decreases the time required to complete the analytical process. However, these methods are only applied when atomic spectrometric techniques are used to

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measure the analytes. Another possibility is the introduction of samples after their dilution with organic solvents. The solvent is employed to decrease the viscosity of the samples and makes possible their insertion into the instruments. The main drawback of this kind of procedure is the degradation of the limits of detection and quantification, since the dilution factor is, in general, high [10–11]. Besides, the manipulation of toxic organic solvents makes the procedure very harmful for the analysts.

Some few papers describe the direct determination of metals in used lubricating oils. Ko and Kim [12] proposed a method based on the adsorption of metals on the surface of a Si wafer modified with a chelating agent. The analytes were measured using X-ray photoelectron spectroscopy (XPS), directly on the surface, after washing of the loaded wafers with hexane. Bings [13] developed a method for the direct determination of metals in used lubricating oils by laser ablation coupled to inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS). Very low detection limits were achieved by using this approach ($0.5\text{--}63\text{ ng g}^{-1}$), but the use of high-cost instrumentation makes this method prohibitive for several analytical laboratories.

Recently, Cassella et al. [14–16] and Robaina et al. [17] proposed a new methodology, named extraction induced by emulsion breaking, for the extraction of metals from oil samples and their quantification by atomic spectrometric techniques. The methodology 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 concentration of various metals in different types of oils.

The aim of this work was to apply the extraction induced by emulsion breaking for the determination of Cu, Fe and Mn in used lubricating oils employing flame atomic absorption spectrometry. The proposed method is simple, fast and allows the preconcentration of the metals in an aqueous phase, which is easier to measure than the original sample.

2. Experimental

2.1. Apparatus

The determination of the metals of interest (Cu, Fe and Mn) in the extracts obtained from the extraction induced by emulsion breaking was performed with an AA240FS flame atomic absorption spectrometer from Varian (Mulgrave, Australia). A lean blue flame (air 13.5 L min^{-1} ; acetylene 2 L min^{-1}) was used for the atomization of the three elements. The determination of Fe in the solutions obtained from the total digestion of the samples was also performed by flame atomic absorption spectrometry.

The determination of Cu and Mn in the solutions obtained from the total digestion of the samples was performed with a graphite furnace atomic absorption spectrometer, model AA240Z, equipped with a Varian GTA 120 atomizer unit and a Varian PSD 120 auto sampler. In this case, graphite tubes with integrated L'vov platform made of pyrolytic graphite (Varian part no. 63-100026-00) were used. The correction of the background was performed with a Zeeman-effect based corrector, operating with a constant magnetic field of 0.8 T. Argon with 99.99% (Linde Gases, Macaé, Brazil) of purity was employed as protective gas for the graphite tubes.

The operational conditions employed in the measurement of the three metals under study are shown in Table 1. It is important to remark that such conditions were utilized in both flame and graphite furnace atomic absorption measurements.

Table 1

Operational conditions used in the atomic absorption (FAAS and GFAAS) measurement of Cu, Fe and Mn.

Parameter	Analyte		
	Cu	Fe	Mn
Wavelength (nm)	324.8	248.3	279.5
Spectral resolution (nm)	0.5	0.5	0.5
Lamp current (mA)	4.0	4.0	5.0

The emulsion breaking was induced by centrifugation using a centrifuge from Sislabs (São Paulo, Brazil), model Twister, which was operated at a maximum rotation speed of 3500 rpm and 60 min.

The evaluation of the extraction time was performed by shaking (90 rpm) the emulsions with a roller mixer, model MR-II, supplied by Biomixer (São Paulo, Brazil).

The total digestion of the used lubricating oil samples was performed with a Berghof microwave oven (Eningen, Germany), model Speedwave Four, equipped with 60 mL PFA vessels.

2.2. Reagents and solutions

The aqueous solutions employed in the present work were prepared with purified water obtained in a Direct-Q 3 System supplied by Millipore (Milford, MA, USA).

All solvents employed in the test of the influence of the solvent (ethyl benzene, toluene and hexane) were supplied by Tedia (Fairfield, OH, USA).

Aqueous stock solutions of copper, iron and manganese with a concentration of $1000\text{ }\mu\text{g mL}^{-1}$ were furnished by SPEX (Metuchen, NJ, USA). The analytical solutions employed in the construction of the analytical curves were prepared by convenient dilution of the stock solutions with purified water.

The solutions utilized in the emulsification were prepared with Triton X-114 (Acros Organics, St. Louis, USA) and trace metal grade HNO_3 (Tedia, Fairfield, OH, USA). The solutions were prepared by dissolving suitable masses (according to the experiment) of the surfactant in exactly 100 mL of HNO_3 solution. The concentration of the HNO_3 in the solution was also established according to the experiment.

One same sample (S_1) of used lubricating oil was employed in the experiments of optimization. This sample was collected in a gas station located in the city of Niterói, Rio de Janeiro, Brazil, and no information regarding the type of oil or its time of use could be obtained. All other samples analyzed by the proposed methodology ($S_2\text{--}S_{12}$) were also collected in gas stations of the city of Niterói. The oils were stored in low-density polyethylene bottles maintained in a light-free place at ambient temperature.

2.3. General procedure of extraction induced by emulsion breaking

The metals were extracted from lubricating 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, 6.4 mL of the oil samples (approximately 5.50 g) were mixed with 1.6 mL of toluene, in order to decrease the viscosity and allow a convenient mixing with the emulsifying aqueous solution. It is important to remark that the used lubricating oils were homogenized by agitation before collecting the aliquots. Then, stable water-in-oil emulsions were obtained by vigorous mixing of the diluted lubricating oils with 2 mL of the acidic Triton X-114 solution, in a capped polyethylene flask of 15 mL. The tubes containing the emulsions were then agitated for 30 min on a roller mixer in

order to improve the extraction of the metals. Afterwards, the tubes were transferred to the centrifuge where they were centrifuged for 30 min at 3500 rpm to promote the emulsion breaking. The emulsion breaking resulted in two well-separated phases: (1) an upper phase containing the diluted oil and (2) a lower phase, with a strong yellow color, containing the aqueous acid solution with the extracted metals. Then, the lower aqueous phase was collected and used to measure the metals of interest. When necessary, a defined volume of the aqueous phase was taken and diluted with purified water in order to adjust the concentration of the metals in solution to the linear portion of the analytical curves.

2.4. Total digestion of the samples and measurement of the metals by ETAAS

The total digestion of the samples of used lubricating oils was carried out by acid dissolution in a closed-vessel microwave-oven. For this task, approximately 0.250 g of each sample was mixed, directly in the PFA flasks of the microwave oven, with 5 mL of concentrated HNO_3 (trace metal grade). Then, the flasks were sealed, transferred to the cavity of the microwave oven and irradiated using a standard program of heating suggested by the manufacturer for the mineralization of oils. Afterwards, the flasks were cooled to ambient temperature and opened. Then, the whole content was transferred to 15 mL volumetric flasks and the volume was completed to the mark with purified water. The obtained solutions were directly introduced (20 μL) into the GFAAS or diluted with purified water, when necessary. The measurement of the analytes was carried out using the temperature program shown in Table 2, using the external calibration approach. No chemical modifier was employed.

3. Results and discussion

The optimization of the methodology proposed in this work was carried out by investigating the effect of some variables on the extraction efficiency: (i) type and concentration of the solvent employed to dilute the samples, (ii) the concentrations of Triton X-114 and HNO_3 in the solution used for emulsification and (iii) extraction conditions. In all experiments, normalized signals were used to evaluate the results. They were employed because of the different magnitude of the signals obtained for each metal. Normalized signals can be defined as the ratio between each absorbance signal and the highest absorbance signal obtained in the set.

Table 2

Temperature program used in the determination of Cu and Mn in the solutions obtained from the total digestion of the samples by graphite furnace atomic absorption spectrometry.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate (mL min^{-1})
Drying	85	5	0	300
	95	40	0	
	120	10	10	
Pyrolysis	800 (Cu) 700 (Mn)	5	3	300
Atomization	2300 (Cu) 2400 (Mn)	1	2	0
Cleaning	2500 (Cu) 2600 (Mn)	2	0	300

3.1. Evaluation of the type and concentration of solvent employed to dilute the samples

One of the main problems observed in the manipulation of the used lubricating oils was their high viscosity. This characteristic of the oils made practically impossible to prepare the emulsions, since the mixture of the samples with the aqueous extractant solutions was impaired. In order to overcome this drawback, the lubricating oils were diluted with an organic solvent to decrease the viscosity. This experiment was performed with three solvents in which the 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. There was no significant difference among the signals obtained when the sample was diluted with any of the three solvents (Fig. 1). However, the use of toluene resulted in the separation of an aqueous phase with lowest turbidity, which could indicate that the transference of organic material to this phase was minimized with this solvent. Therefore, it was employed for dilution of the samples.

Also, the effect of the proportion of solvent was evaluated. In this case, only toluene was tested and the proportion was varied in the range of 10–50% v/v of solvent. As expected, the analytical signal increased with the decrease of the proportion of solvent because the dilution factor increased with the increase of the amount of solvent employed. However, some practical problems appeared with the increase of the solvent proportion. When a proportion of 50% v/v was employed, the emulsion breaking was very difficult. The emulsion was so stable that residual amounts of emulsified oil remained in the interface between the two phases (Fig. 2), which made difficult the collection of the aqueous phase. This problem disappeared when the proportion of solvent decreased to values between 10 and 30% v/v. So, a proportion of 20% v/v was chosen for the method in order to avoid excessive dilution of the samples and make the collection of the aqueous phase easier.

3.2. Influence of the concentration of Triton X-114 (emulsifier agent)

The use of an emulsifier agent is of fundamental importance in the proposed procedure, since it plays a major role in the emulsification process. The emulsifier agent makes possible the dispersion of the small water droplets of the extractant solution in

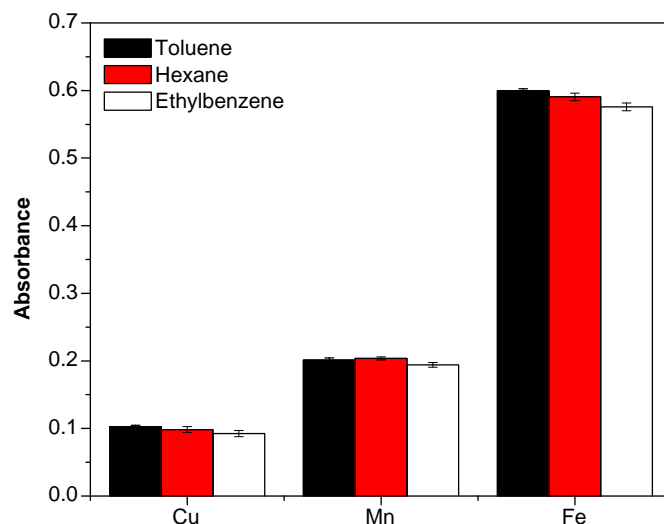


Fig. 1. Effect of the solvent employed to decrease the viscosity of the used lubricating oil on the extraction of Cu, Fe and Mn. Proportion of solvent=20% v/v. Error bars represent the standard deviation of three independent measurements.

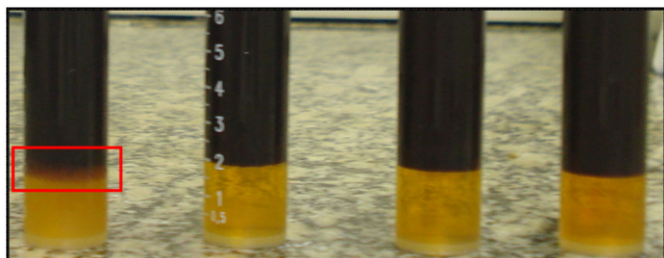


Fig. 2. Influence of the proportion of solvent (toluene) used in the dilution of the used lubricating oil. From left to right: 50, 30, 20 and 10% v/v. The detail highlights the emulsion that was not broken even after centrifugation when the proportion of toluene was 50% v/v.

the oil, increasing the surface of contact between the phases. The high dispersion of the acid solution in the oil enhances the extraction, which occurs at the interface between the oil and acid aqueous phases. In order to evaluate the effect of the concentration of Triton X-114 (emulsifier agent) in the extractant solution on the extraction efficiency, it was varied in the range of 3–20% m/v. The concentration of HNO_3 was maintained at 2.8 mol L^{-1} and the sample was diluted with toluene (20% toluene + 80% sample) before emulsification.

The most evident effect of Triton-X114 concentration on the extraction process was the variation of the volume of aqueous phase recovered after the emulsion breaking. The volume of aqueous phase separated after the emulsion breaking decreased with the increase of the surfactant concentration (Fig. 3). Probably, the increase of the concentration of Triton X-114 leads to the formation of more stable emulsions, which were more difficult to break in the centrifugation conditions employed in the experiment. So, in order to evaluate the effect of the concentration of Triton X-114 on the extraction efficiency, the analytical signals were corrected by multiplying by a factor that takes into account the volume of aqueous phase recovered in each experiment.

There was no significant variation in the extraction efficiency with the variation of the Triton X-114 concentration, although the mean signals obtained with the concentrations of 3 and 5% m/v were slightly higher. The profiles were very similar for the three species under study, showing that the extraction process was independent of the nature of the analyte. So, the concentration of 3% m/v of Triton X-114 was selected to achieve the highest extraction efficiency and form emulsions easy to break.

3.3. Influence of the HNO_3 concentration

Another parameter that plays important role in the extraction induced by emulsion breaking is the concentration of HNO_3 in the extractant solution. It is good to remember that the H^+ ion is responsible for the extraction, displacing the metallic cations from the organic structures where they are in the oils. Additionally, the acid can dissolve small metallic particles that could be present in the used lubricating oil as a result of the wear of the metallic parts of the engines. In order to evaluate the effect of this variable, the concentration of HNO_3 in the extractant solution was varied in the range of $0.28\text{--}4.2 \text{ mol L}^{-1}$. As it can be seen in Fig. 4, the concentration of HNO_3 presented noticeable effect on the extraction of Cu and Fe from the used lubricating oil. For Mn, the extraction efficiency was practically unaltered along the whole range evaluated, while for Cu and Fe there was a clear increase of the extraction efficiency with the increase of the HNO_3 concentration. For both metals, the extraction (or dissolution) increased up to a HNO_3 concentration of 2.8 mol L^{-1} and, after this point, the extraction efficiency remained almost constant. This behavior could be related to the fact that the particles of Cu and Fe are

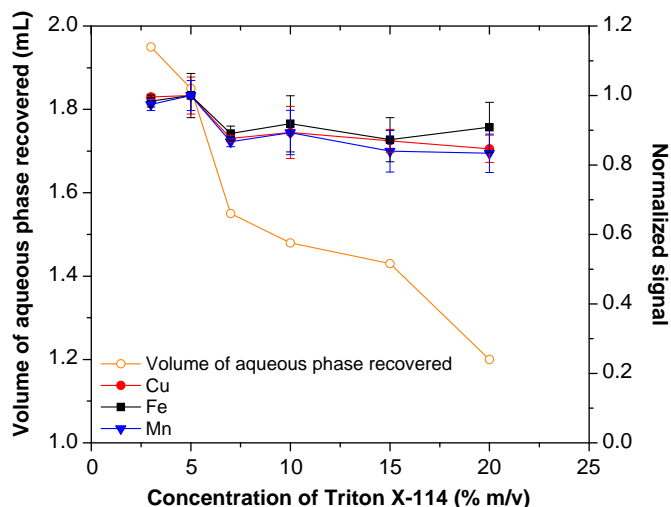


Fig. 3. Effect of the concentration of Triton X-114 on the extraction of Cu, Fe and Mn and on the volume of aqueous phase recovered after application of the proposed procedure. Error bars represent the standard deviation of three independent measurements.

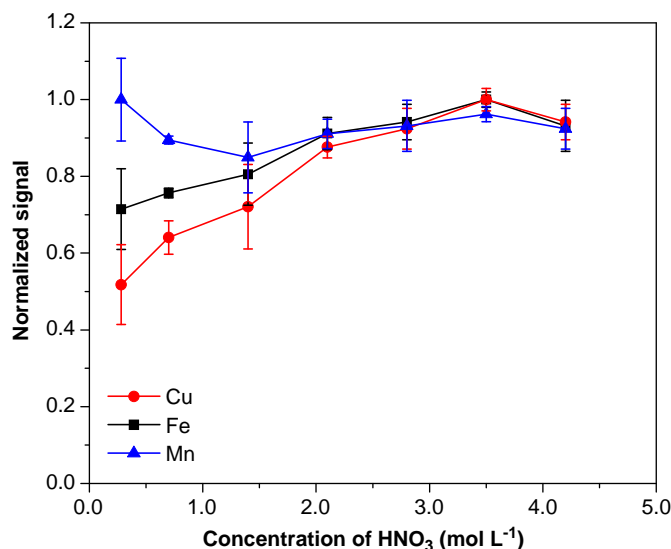


Fig. 4. Effect of the HNO_3 concentration on the extraction of Cu, Fe and Mn from used lubricating oil by the extraction induced by emulsion breaking. Error bars represent the standard deviation of three independent measurements.

more difficult to dissolve than the particles of Mn, which only occurred for HNO_3 concentration of 2.8 mol L^{-1} or higher. So, in order to ensure maximum extraction of the metals from the samples, the HNO_3 concentration of 2.8 mol L^{-1} was chosen for the method.

3.4. Evaluation of the operational extraction conditions

Some practical aspects, related to the operational conditions, were also considered in this work. In this context, three parameters were tested: (i) the extraction time; (ii) the sampling time and (iii) the centrifugation time.

The extraction time refers to 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 before breaking by centrifugation. The experiment was carried out by preparing emulsions with the same lubricating oil using the conditions already optimized. Then, they were shaken during

times that varied in the range of 0–60 min. After the elapsing time required in the experiment, each emulsion was centrifuged at 3500 rpm for 60 min. The aqueous phase was collected and the metals were measured. The results obtained in this experiment showed that the extraction time did not have remarkable influence on the magnitude of the analytical signals for the three analytes under study (Fig. 5), evidencing that they were easily extracted from the samples just after the formation of the emulsions. However, the precision of the measurements was improved with the increase of the extraction time, probably because the agitation helped the homogenization of the emulsions. So, as the precision of the measurements was better in the range of 30–60 min, the extraction time of 30 min was chosen for the method.

The sampling time is the time passed from the end of the emulsion breaking until the collection of the aqueous phase. In this interval, the extracted metals could be adsorbed on the interfacial film, especially if the time is high. In order to evaluate the effect of this variable, the sampling time was varied from 0 (collection just after centrifugation) to 60 min. It is important to remark that the emulsions were kept on the bench, at laboratory ambient temperature (23 °C), until collection of the aqueous phase. No remarkable differences among the analytical signals for the three analytes were verified in the whole range employed in the study. This fact indicated that all analytes remained in the

solution even if the separated oil and aqueous phase were maintained in contact for times as long as 60 min.

One of the main concerns in this study was related to the establishment of the centrifugation conditions, which was responsible for the emulsion breaking. In the previous experiments, the centrifugation of the emulsions was always carried out by 60 min at 3500 rpm (maximum allowed), which was considered excessive for this type of procedure. So, in order to evaluate the influence of the centrifugation time on the phase separation, the emulsion breaking was performed in different centrifugation times, always keeping the rotation at 3500 rpm. The centrifugation time was changed in the range of 5–60 min and a convenient separation of the phases was observed with a minimum time of 30 min. For times lower than 15 min, the emulsions were not completely broken, since residual amounts of the emulsions remained in the interface between the oil and water. Also, in these cases, the volume of aqueous phase recovered was always lower than 1.5 mL, evidencing that a noticeable part of the aqueous phase remained emulsified with the used lubricating oil.

Additionally, the effect of the centrifugation time was also tested in relation to the analytical signal for Cu, Fe and Mn. There was no variation of the analytical signal in the range of 30–60 min. Therefore, a centrifugation time of 30 min was selected for the method in order to make it faster.

4. Analytical features of the developed methodology

The calculation of the limits of detection and quantification of the proposed methodology for the determination of Cu, Fe and Mn was performed using analytical curves constructed with standard solutions prepared in water, which was exactly the medium used in the preparation of the standard solutions for the external calibration procedure used in the quantification of the metals in the aqueous extracts. It is important to remark that, for all samples, the extracts must be diluted 40-fold, at least, before the measurement of the metals by FAAS, in order to adjust the signals to the linear portion of the analytical curves. The instrumental limits of detection (3s criterion) and quantification (10s criterion) were estimated from 10 measurements of blank solutions. Also, it was possible to derive the methodological limits of detection and quantification as well as the intermediate precision of the procedure (Table 3) from five repetitive determinations of the metals in the sample S₉.

5. Application of the developed methodology

The evaluation of the accuracy of the developed method was assessed by comparison with a well-established reference method.

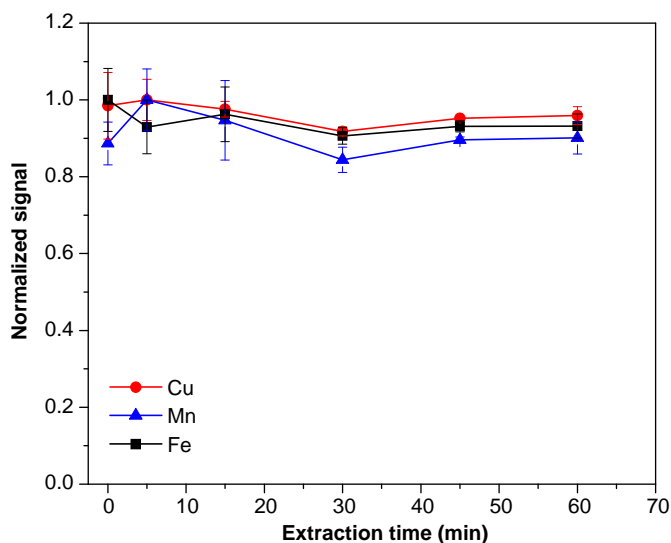


Fig. 5. Influence of the extraction time on the extraction of Cu, Fe and Mn by the proposed procedure. Error bars represent the standard deviation of three independent measurements.

Table 3

Analytical features of the proposed methodology for the analysis of used lubricating oils.

Parameter	Analyte		
	Cu	Fe	Mn
Typical analytical curve	$A = 0.1450[\text{Cu}] + 0.0009$	$A = 0.0749[\text{Fe}] + 0.0022$	$A = 0.2361[\text{Mn}] + 0.0041$
r^2	0.9968	0.9907	0.9997
Instrumental LOD ($\mu\text{g L}^{-1}$)	2.4	63	6.8
Methodological LOD ^a (ng g^{-1})	19	70	8.2
Instrumental LOQ ($\mu\text{g L}^{-1}$)	7.9	211	22.5
Methodological LOQ ^a (ng g^{-1})	63	233	27
Intermediate precision (%) ^b	6.4	3.9	7.4

^a The methodological LOD and LOQ were calculated taking into account the variability of the whole analytical process and the preconcentration factor of the procedure.

^b The intermediate precision was calculated by analyzing one sample (S₉) in five straight days using the developed methodology.

Table 4
Results obtained in the determination of Cu, Mn and Fe in the samples of used lubricating oils by the proposed method. Values are expressed as mean \pm standard deviation ($n=3$).

Sample	Cu ($\mu\text{g g}^{-1}$) (proposed method)	Cu ($\mu\text{g g}^{-1}$) (reference method) ^c	Mn ($\mu\text{g g}^{-1}$) (proposed method)	Mn ($\mu\text{g g}^{-1}$) (reference method) ^c	Fe ($\mu\text{g g}^{-1}$) (proposed method)	Fe ($\mu\text{g g}^{-1}$) (reference method) ^c
S ₁	2.73 \pm 0.19	3.13 \pm 0.13	4.34 \pm 0.26	2.85 \pm 0.22	47.2 \pm 3.2	82.4 \pm 11.3
S ₂	3.41 \pm 0.04	3.22 \pm 0.22	1.59 \pm 0.08	1.27 \pm 0.13	44.7 \pm 1.9	54.8 \pm 9.6
S ₃	4.82 \pm 0.24	4.21 \pm 0.45	0.22 \pm 0.04	0.52 \pm 0.04	4.31 \pm 0.32	4.35 \pm 0.90
S ₄	14.8 \pm 2.2	14.1 \pm 0.2	0.89 \pm 0.06	1.01 \pm 0.12	58.0 \pm 3.2	57.5 \pm 2.3
S ₅	8.40 \pm 1.64	8.56 \pm 0.76	0.92 \pm 0.02	1.05 \pm 0.10	67.0 \pm 7.8	88.0 \pm 6.0
S ₆	6.13 \pm 0.09	6.63 \pm 0.62	0.84 \pm 0.04	0.86 \pm 0.09	40.0 \pm 1.6	44.7 \pm 2.2
S ₇	5.37 \pm 0.70	5.85 \pm 0.13	1.04 \pm 0.11	1.11 \pm 0.04	37.8 \pm 0.3	44.1 \pm 0.6
S ₈	8.65 \pm 0.15	9.67 \pm 1.01	3.78 \pm 0.46	3.73 \pm 0.061	78.8 \pm 1.1	120 \pm 9
S ₉	3.91 \pm 0.04	3.93 \pm 0.38	1.49 \pm 0.23	1.37 \pm 0.16	24.1 \pm 0.5	24.0 \pm 1.9
S ₁₀	2.95 \pm 0.14	3.14 \pm 0.24	0.93 \pm 0.03	0.89 \pm 0.03	46.4 \pm 0.7	52.4 \pm 5.0
S ₁₁	5.68 \pm 0.05	5.70 \pm 0.53	0.46 \pm 0.01	0.51 \pm 0.07	35.0 \pm 0.1	36.7 \pm 3.6
S ₁₂	5.70 \pm 0.37	5.89 \pm 0.50	1.74 \pm 0.07	1.45 \pm 0.06	42.5 \pm 0.7	42.0 \pm 2.1
t_{value}^a	$t_{\text{critical}}=2.20$ (DF=11)		$t_{\text{critical}}=2.20$ (DF=11)		$t_{\text{critical}}=2.20$ (DF=11)	
t_{value}^b	$t_{\text{calculated}}=0.785$		$t_{\text{calculated}}=1.01$		$t_{\text{calculated}}=2.66$	
					$t_{\text{critical}}=2.306$ (DF=8)	
					$t_{\text{calculated}}=1.907$	

^a t_{values} considering all samples.

^b t_{values} not considering the samples S₁, S₅ and S₈, which contain more than 80 $\mu\text{g g}^{-1}$ of iron (only applied for iron).

^c Reference method was adapted from Ref. [23] and based on total dissolution of the samples. Detailed procedure can be found in the experimental section.

In this case, 12 samples of used lubricating oil were analyzed by the proposed methodology and after total digestion of the samples, which is the strategy regularly employed in the determination of metals in oil samples [18–22], including used lubricating oils [4–6]. Although the high dilution factor imposed to the samples in the total digestion procedure, the metals of interest could be determined because of their high concentration in the samples. Copper and manganese were determined by GFAAS and iron was determined by FAAS.

The results obtained in the analysis of the samples by applying the extraction induced by emulsion breaking and the total digestion methods [23] are shown in Table 4. The values were compared using a paired Student-*t* test, which showed that there was no statistical difference between the concentrations of Cu and Mn determined after application of the proposed method and the total digestion. This result evidenced that the metals were quantitatively transferred from the samples to the aqueous phase by using the extraction strategy optimized in this work. On the other hand, the application of the same statistical test for Fe indicated that there was difference between the values obtained by the two methods. However, analyzing the results for Fe in detail it was possible to realize that these differences occurred due to the discrepant values observed in the analysis of the samples that contained concentrations of Fe higher than 80 $\mu\text{g g}^{-1}$. When the samples S₁, S₅ and S₈ (samples with more than 80 $\mu\text{g g}^{-1}$ of Fe, according to the results verified after application of the reference method) were taken out of the set, the application of the paired Student-*t* test revealed that there was no difference statistical between the results obtained with the application of the two methods. For these samples, the concentration of Fe determined after their treatment by the extraction induced by emulsion breaking was always lower than the concentration determined after the total digestion of the samples, which indicated that the maximum amount of Fe that can be extracted, in the optimized conditions, can be around 80 $\mu\text{g g}^{-1}$.

6. Conclusions

The results obtained in this work proved that the extraction induced by emulsion breaking can be considered an excellent alternative to the total digestion for the determination of Cu, Mn and Fe in used lubricating oils. This strategy leads to the pre-concentration of the metals in the extracts, which allowed their

quantification by flame atomic absorption spectrometry. Another advantage was the use of aqueous standard solutions for methodological calibration, which made the procedure very simple. Also, only diluted solutions of HNO₃ were employed for the extraction, instead of the concentrated acids regularly used in the total dissolution procedures.

One of the main points of the proposed method was the dilution of the used lubricating oils with a convenient solvent in order to decrease the viscosity of the samples and permit their emulsification. Toluene was chosen for this purpose and a volumetric percentage of 20% v/v of solvent was enough to give stable emulsions.

The results obtained in the determination of Cu and Mn in the 12 samples analyzed by the proposed method were in agreement with those obtained after their total digestion. On the other hand, the determination of Fe was dependent on the concentration of the analyte in the samples. In the samples containing high concentration of Fe (typically higher than 80 $\mu\text{g g}^{-1}$), the extraction induced by emulsion breaking was not efficient for the quantitative removal of the analyte for the aqueous phase, which limited the application of the method for determination of this metal.

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