

Analytical Methods

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3 **Determination of iron, chromium and copper in used lubricating**
4 **oils by electrothermal atomic absorption spectrometry using**
5 **microemulsion as sample preparation**
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Abstract

The analysis of metals in used lubricating oils is widely reviewed and published in the literature, especially because provide valuable information about the lubricated system. The determination of metal such as Fe, Cr and Cu may indicate the presence of contaminants in the oil or wear of parts of motors. In this work, a method for determination of Fe, Cr and Cu by atomic absorption spectrometry with electrothermal atomization (ET AAS) using microemulsion as sample preparation has been developed. A pseudo-ternary phase diagram was built in order to investigate the region where a homogeneous and stable system (microemulsion) could be achieved. The optimized condition for the microemulsion formation was: 2.0% (w/w) of lubricating oil, 31% (w/w) of aviation kerosene, 5% (w/w) of nitric acid 14 mol L⁻¹, 5% (w/w) of Triton X-100 and 57% (w/w) of *n*-propanol. The developed method was simple and fast, involving few steps and avoiding the use of carcinogenic solvents. Moreover, the increased stability of the microemulsion and of the analytes in microemulsified medium and the use of aqueous standards for calibration was achieved. The values of the detection limits for Fe, Cr and Cu were 1.9 mg kg⁻¹, 0.04 mg kg⁻¹ and 0.2 mg kg⁻¹, respectively. Good accuracy was attained since the results obtained were not significant different within 95% level of confidence (Student's t-test) from those of acid-digestion method and the certified value of NIST certified reference material wear-metals in lubricating oil (SRM 1084a). Therefore, the method developed in this work becomes an efficient alternative for the determination of Fe, Cr and Cu in used lubricating oil.

Keywords: Iron, Chromium, Copper, used lubricating oil, microemulsion, ET AAS

1. Introduction

The determination of metals in used lubricating oils is a usual practice in the maintenance of engines, which is being implemented as part of the predictive or

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3 proactive maintenance program.¹ In predictive maintenance, the
4 physicochemical properties of the oil are studied to determine the appropriate
5 time to be replaced.^{2,3} In the case of proactive maintenance, the engine wear is
6 monitored by the presence of metals in the used oil. When the concentration of
7 one or more metals suddenly increases, it is possible that some component is
8 experiencing some excessive wear.¹ In most cases, the presence of specific
9 metals could indicate the origin and the extension of damages in the
10 mechanical system.^{1,2}

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The complexity of the lubricant oil matrix and its viscosity increases the difficulty of analysis. Another analytical challenge is the presence of solid particles, because they may interfere with the accuracy of the analysis, if not eliminated or dissolved.^{3,4}

In the determination of metals in used lubricating oils, sensitive techniques, capable of monitoring small changes in concentration of the metallic elements, are necessary.² According to reviews published in this field,^{4,5} most studies are based on analytical spectrometry techniques. Inductively coupled plasma optical emission spectrometry (ICP OES) is the most widely used technique^{2,6,7,8,9} due to its multi-element capability and low detection limits. Inductively coupled plasma mass spectrometry (ICP-MS) also provides multi-element analysis, though has higher sensitivity in comparison with ICP OES and the possibility of isotopic analysis.¹⁰ However, both techniques present problems as plasma instability in the presence of organic solvents and high cost of implementation and maintenance.⁴ Despite of having less sensitivity compared to other techniques and mono-elemental characteristic, the flame atomic absorption spectrometry (F AAS) remains an important technique for the determination of metals in lubricating oils, due to the low cost and robustness regarding the use of most organic solvents.⁴ It should be pointed out that in techniques using sample introduction by nebulization such as F AAS, ICP OES, ICP-MS, transport Interference may occur for oily samples due to changes in viscosity and the presence of solid particles, thus causing errors in the analytical results.¹¹ The electrothermal atomic absorption spectrometry (ET AAS) technique is an excellent alternative for the determination of metals in used lubricating oils since the introduction of the sample is not affected by the

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3 physical characteristics and the heating program frequently allows complete
4 elimination of matrix.^{2,6,8} Other techniques that have also been used for this
5 application include Anodic Stripping Voltammetry,¹² Stripping
6 Chronopotentiometry,¹³ High-Resolution Continuum Source Flame Atomic
7 Absorption Spectrometry (HR-CS F AAS),^{14,15} X-ray Fluorescence
8 Spectrometry,¹⁶ LASER-Induced Breakdown Spectroscopy (LIBS),^{17,18}
9 Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry
10 (ETV ICP-MS)¹⁹.

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17 Concerning the sample pre-treatment, the analytical procedures used are
18 acid-digestion (open system or microwave assisted digestion), dilution in
19 organic solvent, emulsion and microemulsion (or three component solution).⁴
20 The lubricating oil dissolved in organic solvents such as xylene,⁹ kerosene,²⁰
21 isobutyl methyl ketone (IBMK)^{21,22} have been used due to its convenience and
22 speed. However the organic standards used in this type of analysis are
23 relatively expensive and less stable than inorganic standards. Moreover,
24 problems concerning the stability of the analytes arise due to the change in
25 concentration caused by evaporation of the solvent and/or deposition of the
26 analyte in the walls of storage vials.^{4,10,23} Aucélio *et al.*⁴ also pointed out
27 problems due to the presence of metal particles in used lubricant oil, arising
28 from physical wear, which are not dissolved by organic solvents and may
29 interfere with the accuracy and precision of the analysis. On the other hand, the
30 acid-digestion of the oil sample ensures that the organic matrix is mineralized
31 and the dissolution of the metal particles, allowing calibration with aqueous
32 standards. Problems may arise due to trace contamination from used digestion
33 vessels and from the larger amount of mineralizing acids used. Probably for this
34 reason, and the reduced sample throughput, this procedure is still seldom
35 practiced for lubricating oils.^{8,24,25}

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51 Alternatively, the use of emulsions/microemulsions water-in-oil (w/o) or
52 oil-in-water (o/w) has been shown to be a strong trend to replace dilution
53 methods.^{4,10,22,26} The emulsification consists in a homogeneous dispersion and
54 stabilization of the oil micro-droplets in the aqueous phase, which brings the
55 viscosity close to that of an aqueous solution, reduces the organic load of the
56 system, and allows the use of acids that promote the dissolution of the metal
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3 particles, transforming the analyte species in a uniform form and avoid losses
4 by adsorption, improving the analytical performance measures.^{3,4} Nevertheless,
5 they are instable, resulting in a phase separation in a short period of time.
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7 Besides all advantages cited for emulsion, the microemulsions are
8 thermodynamically stable.²⁷ Macroscopically the microemulsions are
9 homogeneous, isotropic and transparent. Due to the high viscosity and the
10 presence of particles, the achieving of the microemulsion for used lubricating
11 oils is more difficult. Although there are few studies^{3, 28, 29, 30, 31, 32} involving the
12 use of microemulsions (or three component solution) for the determination of
13 metals in used lubricating oils, the method of preparation generally involves
14 several steps,¹⁰ making the process relatively slow, and the presence of a
15 higher quantity of toxic and carcinogenic reagents, such as xylene, toluene and
16 IBMK and most of the times the stability of the microemulsion is relatively short
17 (3-4 hours). The papers dealing with microemulsion for determination of trace
18 elements in lubricating oil published in the last 15 years are summarized in
19 Table 1. Considering the advantages of microemulsion methods of sample
20 preparation and its reduced number of applications for lubricating oils, besides
21 the fact that important elements, such as Fe were not investigated yet, it is
22 worthwhile to propose a new method based on this technique for determination
23 of wear metals in used lubricating oils.
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39 The goal of this work was the development of a simple, fast, and accurate
40 analytical method, which can be applied routinely on the determination Fe, Cr
41 and Cu in used lubricating oil by ET AAS. Emphasis was given on a faster
42 method and higher stability of the microemulsion. A composition as well as the
43 stability of the analytes in the microemulsion was also investigated. To evaluate
44 the accuracy of the developed method the results were compared with a
45 method of acid digestion and certified reference material (NIST SRM 1084a)
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Table 1-Trace elements determination in lubricating oils using microemulsion (or three component solution) as sample preparation

Element(s) / sample	Analytical technique	Sample processing (mixing type)	Preparation time	Stability of the microemulsion	LD	RSD (%)	Ref.
Al / new and used lubricating oil	SI-ET AAS	Sample* + surfactants mixture + sec-butanol (Flow direction changes and US radiation)	~4min (on-line)*	1 month	2.3 $\mu\text{g L}^{-1}$	1.5	3
Cr / new and used lubricating oil	FI-ET AAS	Sample* + hexane + NaCl + SDS + sec-butanol (US radiation)	Not informed (on-line)*	1 month	4 $\mu\text{g L}^{-1}$	0.6 \pm 0.8	28
Sb, Sn / used lubricating oil	ET AAS	Samples + HNO ₃ + US bath+ xylene + Triton X-100 + water	25 min	100 min	(85; 190) ng g^{-1}	-	29
V, Ni, Cu, Cr, Pb, Mo, Ag / used lubricating oil	ET AAS	Sample + IBMK + HNO ₃ + HCl + <i>n</i> -propanol	5 min	>35 min	(0.45; 0.60; 0.27; 0.15; 0.54; 0.70; 0.14) $\mu\text{g g}^{-1}$	3-13	31
Ag / used lubricating oil	ET AAS	lubricating oil + HNO ₃ + US bath + xylene + Triton X-100 + water	20 min	30 min	23 ng g^{-1}	5	32
Ca, Mg, Zn / new lubricating oil	F AAS	Sample + AVK + <i>n</i> -propanol + water	~ 5 min	>10 months	(1.3; 0.05; 0.41) $\mu\text{g g}^{-1}$	0.9 - 4.3	33
Fe, Cr, Cu / used lubricating oil	ET AAS	Sample + AVK + HNO ₃ + US bath + Triton X-100 + <i>n</i> -propanol	~ 15 min	> 48 hours**	(1.9; 0.04; 0.2) $\mu\text{g g}^{-1}$	3-5	This Work

SI: sequential injection; FI: flow injection; SDS: sodium lauryl sulfate; US: ultrasonic; AVK: aviation kerosene

*The used lubricating oil samples were filtered before analysis (time required: ~5min)

** After 48 hours, the formation of small particles takes place, even though no phase separation was observed for at least six months

2. Experimental

2.1 Instrumentation

All measurements were carried out using a Model AAS 5 EA atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with deuterium background correction, equipped with a transversely heated graphite tube atomizer. NARVA hollow cathode lamps for Fe, Cr and Cu (GLE, Berlin, Germany) were used as the radiation sources with 5.0 mA current, 3.5 mA and 3.0 mA, respectively. The analytical line of 302.8 nm was used for Fe determination with a spectral bandwidth of 0.2 nm, and the main analytical lines at 357.9 nm and 324.8 nm with a spectral bandwidth of 0.2 nm and 0.8 nm were used for Cr for Cu, respectively.

All experiments were carried out using pyrolytically coated graphite tubes (Analytik Jena, Part No. 407-A85.025). A MPE 5 furnace autosampler (Analytik Jena AG) was used for introducing the microemulsion and the digested samples. Argon with purity of 99.9% (White Martins, São Paulo, Brazil) was used as the purge gas with a flow rate of 2.0 L min⁻¹ during all stages, except during atomization, when the gas flow was stopped for determination of Cr and Cu. For the determination of Fe, the argon flow rate of 1.0 L min⁻¹ was maintained during atomization in order to reduce the sensitivity. Integrated absorbance (peak area) was used exclusively for signal evaluation and quantification. The optimized graphite furnace temperature program for the three analytes is given in Table 2.

A Europe balance (Gilbertine Italy) was used for weighing the samples. For the preparation of the microemulsion an ultrasound-USC 2850 bath (Thorton, São Paulo, Brazil) operating at a frequency of 37 kHz was used. An open system (digester block model 324 A 242, Quimis, Brazil), operated at a frequency of 60 Hz with a potency of 2000 W, was used for sample digestion.

Table 2 – Graphite furnace temperature program for determination of Fe, Cr and Cu in used lubricating oils samples using microemulsion and digestion techniques

Step	Temperature / °C	Ramp / °C s ⁻¹	Hold time / s
Drying 1	90	10	20
Drying 2	120	25	35
Pyrolysis	1300 ^a	300	25
Atomization	2300 ^a /2500 ^b /2100 ^c	1500	6
Cleaning	2500	0	6

Purge gas (argon) flow rate: 2 L min⁻¹ in all steps, except in atomization, when the gas flow was interrupted for Cu and Cr, and reduced to 1 L min⁻¹ for Fe.

^a Fe, ^b Cr e ^c Cu * Chemical modifier was not used

2.2 Reagents and samples

All reagents were of analytical grade, except the aviation kerosene. Distilled-deionized water with a specific resistivity of 18 MΩ cm at 25 °C from a Milli-Q water purification system (Millipore, Bedford, MA, USA), coupled to a water distiller (Fisatom, São Paulo, Brazil), was used for the preparation of standards, modifier solutions and acid-digestion. All containers and glassware were soaked in 1.4 mol L⁻¹ nitric acid for at least 24 hours and rinsed three times with distilled-deionized water before use. The nitric acid (Merck, Darmstadt, Germany) used for the preparation of microemulsions, standards, modifier solutions and acid-digestion was further purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany). The following reagents were used for the microemulsion preparation: purified nitric acid (Merck, Darmstadt Germany), n-propanol (Merck, Darmstadt Germany), commercial aviation kerosene (Refinaria Alberto Pasqualini-REFAP, Canoas, Brazil) and Triton X-100 (Union Carbide, USA). Mineral oil base (High Purity Standards, USA) was used to simulate the oleic phase of the calibration standards. Purified nitric acid, 30% H₂O₂ sulfuric acid, and 30% hydrogen peroxide, (all from Merck, Darmstadt, Germany) were used for sample acid-digestion. Aqueous

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3 stock solutions of 1000 mg L⁻¹ of Fe, Cr and Cu were acquired from Specsol (São
4 Paulo, Brazil). The working standards were prepared from serial dilutions of the stock
5 solutions with 0.014 mol L⁻¹ nitric acid, giving the concentration in the range of 50-400
6 µg L⁻¹ for Fe, 5-40 µg L⁻¹ for Cr and 10-50 µg L⁻¹ for Cu. The chemical modifier
7 investigated was a mixture of 0.05% Pd (Pd(NO₃)₂ - Merck, Germany) + 0.03% Mg
8 (Mg(NO₃)₂ - Merck, Germany) + 0.05% Triton X-100 (Union Carbide, USA), all
9 concentrations given in % m/v.
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12 For the evaluation of the accuracy of the proposed method, the certified
13 reference material SRM 1084a (wear-metals in lubricating oil, 100 mg g⁻¹) from the
14 National Institute of Standards & Technology (NIST Gaithersburg, MD, USA), was
15 used. Four different samples of used lubricating oil from some gas stations in the
16 cities of Porto Alegre and Pelotas (RS-Brazil) were analyzed: M-01 (used oil of truck
17 engines), M-02 (used oil of motorcycle engines), M-03 (used oil of car engines) and
18 M-04 (used oil of bus engines).
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30 **2.3 Preparation of the microemulsion**

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33 For the preparation of the microemulsion, the used lubricating oil sample was
34 first mixed with aviation kerosene in order to reduce its viscosity, then with Triton X-
35 100, and concentrated HNO₃. The mixture was then placed in an ultrasound bath for
36 10 min and finally the final volume of the microemulsion was completed with propanol
37 and the system was shaken manually for a few seconds. Various proportions of used
38 lubricating oil, aviation kerosene, Triton X-100, concentrated HNO₃ and *n*-propanol
39 were mixed, until the formation of a transparent and stable solution. Through
40 the different proportions of mixed reagents, a pseudo-ternary phase diagram was
41 constructed, which will be shown afterwards (Fig.1). This procedure was performed
42 at 25 °C, maintained by refrigeration system of the laboratory. The composition
43 adopted in the preparation of the microemulsion for further analysis was 0.15 g
44 sample, 2.5 g of aviation kerosene, 0.4 g of Triton X-100, 0.3 g of concentrated HNO₃
45 and the volume completed to 10 mL with *n*-propanol. All samples were prepared in
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2.4. Acid-digestion procedure

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5 For the acid-digestion method, which was the same used by Zmozinski *et al.*³³,
6 three samples (M-01, M-02 and M-04) were selected. All steps were carried out in a
7 digestion block at reflux using "cold finger." A mass of 0.25 g of sample were
8 weighed, in triplicate, directly into a 50 mL glass tubes and then 5 mL of concentrated
9 H₂SO₄ were added. These tubes were taken to the digestion block and heated
10 gradually up to 160 °C. This temperature was maintained for 2 hours and after this
11 period the tubes were allowed to cool to room temperature. After cooling 8.0 mL of
12 concentrated HNO₃ were added drop wise to avoid foaming. Afterwards, the glass
13 tubes were gradually heated up to a temperature of 170 °C then kept for 2 hours.
14 Finally, 2.0 mL of hydrogen peroxide (30% v/v) was added and of the tubes were
15 heated up to 100 ° C for a further 15 minutes to complete the digestion. The products
16 of the acid decomposition were transferred to volumetric flasks, and volume was
17 completed to 25 mL with ultra pure water. The total digestion time was 8 hours. All
18 samples were digested in triplicate. For determination of Cu, Fe and Cr in the
19 digested samples the same standards used for the analysis of microemulsions were
20 used, as described above.
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37 **3. Results and discussion**

38 **3.1 Formation of the microemulsion**

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43 In this work a few tests with used lubricating oil samples have been
44 accomplished, in order to obtain the formation of a homogeneous and transparent
45 (microemulsion) system to be used as sample preparation method for determination
46 of Cu, Cr and Fe. Different types of solvents have been investigated as ethanol, iso-
47 pentanol, *n*-butanol and xylene. The surfactants sodium dodecyl sulfate and Triton X-
48 100 were also tested in the range of 0.1 to 1.0 g. Mixtures of water (maximum of 10%
49 w/w), surfactants and solvents resulted in an emulsion easily destabilized, i.e., phase
50 separation occurring in a short period of time. The microemulsion used in this work
51 was based on the work of Zmozinski *et al.*³³, with some modifications, as shown in
52 Table 1, that included the use of an ultrasound bath for 10 min after the addition of
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3 the concentrated nitric acid (helps in the stabilization of the analyte and in the
4 dissolution of the small wear metal particles present in the sample) and Triton-X100
5 (lowers the interfacial tension between the aqueous and organic phase allowing for
6 the interaction of the immiscible substances).²⁷ The formation of an homogeneous
7 system was achieved using a small amount of aviation kerosene (to reduce the
8 viscosity of lubricant oil), Triton X-100, nitric acid and *n*-propanol (co-surfactant). In
9 order to investigate the possibility of using commercial aviation kerosene, possible
10 contamination of the elements studied in this work were measured. The results
11 showed that there was no contamination attesting that this inexpensive chemical
12 could be used in the sample preparation.
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21 In order to obtain the region where a homogeneous and stable system could
22 be achieved a pseudo-ternary phase diagram (Fig. 1) was built as described
23 hereafter. To construct the pseudo-ternary diagram the sample of used lubricating oil
24 M-03 was used. First the following solutions of fixed ratio 1:17 (in mass) of lubricant
25 oil/aviation kerosene (OK) and 1:11 (in mass) Triton X-100/*n*-propanol (TP) were
26 prepared. Different ratios for OK were tested, from 1:1 to 1:18 (in mass). The
27 minimum ratio that allowed the formation of microemulsion was 1:17. These mixtures
28 will be treated as if it were a unique component in the diagram. The third component
29 of the system is concentrated nitric acid. Thus the pseudo-ternary diagram has three
30 components in its vertices: OK, TP and HNO₃. In the second step, the points inside
31 the triangle were plotted, as follows: fixing the quantity of one component and varying
32 the others (the variations were 5% for each). The procedure ended when the entire
33 interior of the diagram were plotted. Each point represents a mixture and therefore
34 must have its physical characteristic (transparent or emulsified mixture) identified
35 visually for further delineation of the different regions. The Fig. 1 shows two distinct
36 regions: region II, where a homogeneous and transparent solution is found,
37 (microemulsion) and region I where mixtures form an emulsion. The composition of
38 the microemulsion adopted in this work was: 0.15 g of used lubricating oil, 2.5 g of
39 aviation kerosene, 0.4 g of Triton X-100, 4.0 g of HNO₃ 14 mol L⁻¹ and 4.5 g of *n*-
40 propanol. For this study the sample was subjected to an ultrasonic bath for 10
41 minutes to insure homogeneity of the system and to reduce particulate prior to the
42 addition of *n*-propanol. It is important to emphasize that this composition is not in the
43 border of the microemulsion phase, showed in Fig. 1. This condition was selected
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3 because, even with a small variation in the composition of the system, e.g. using
4 samples with different characteristics and origins (particulate volume, origin and type
5 of engine), the formation of the microemulsion were not affected. The microemulsion
6 developed in this work is of the type w/o, where the aqueous phase is dispersed in a
7 continuous oil phase.⁴
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11 The stability of the microemulsions varied depending on sample characteristic,
12 such as the amount of kilometers the oil was used and the type of engine and
13 vehicles. Different types of lubricating oils were analyzed in this work, and for some
14 of them the microemulsion was stable for a period of 120 hours. In this work the
15 investigations were not very systematic or comprehensive in order to establish a
16 behavior of the microemulsion according to the characteristic of sample, but for all
17 samples investigated, the stability was observed for at least 48 hours. After this
18 period, the formation of small particles takes place, even though no phase separation
19 was observed for at least six months. The time required for preparation of the
20 microemulsion, including all steps, was about 15 min. The method was simple and
21 fast, involving few steps and avoiding the use of carcinogenic solvents widely
22 mentioned such as xylene, toluene, hexane and isobutyl methyl ketone. In Table 1 a
23 comparison between the proposed method and the others found in the literature is
24 presented. It should be pointed out that the stability of the microemulsion reported by
25 Zmozinski *et al.*³³ is much higher than the others because it is the only paper dealing
26 only with new lubricating oils, that is much simpler sample. On the other hand, the
27 method reported by Burguera *et al.*^{3,28} is very fast, but require a sequential or flow
28 injection system coupled to ET AAS to obtain the microemulsion.
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45 46 **3.2 ET AAS conditions**

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48 A microemulsions prepared with used lubricant oil samples (M-02 for Fe and
49 Cr and M-01 for Cu) with the composition optimized before was used to establish the
50 furnace parameters, i.e., the optimum pyrolysis and atomization temperatures.
51 Different samples were used because the sample M-02 presented a high Cu content.
52 An aqueous standard of each analyte was also used for this purpose. A volume of 10
53 μL of microemulsified sample or aqueous standard was used which was introduced
54 into the graphite tube with autosampler.
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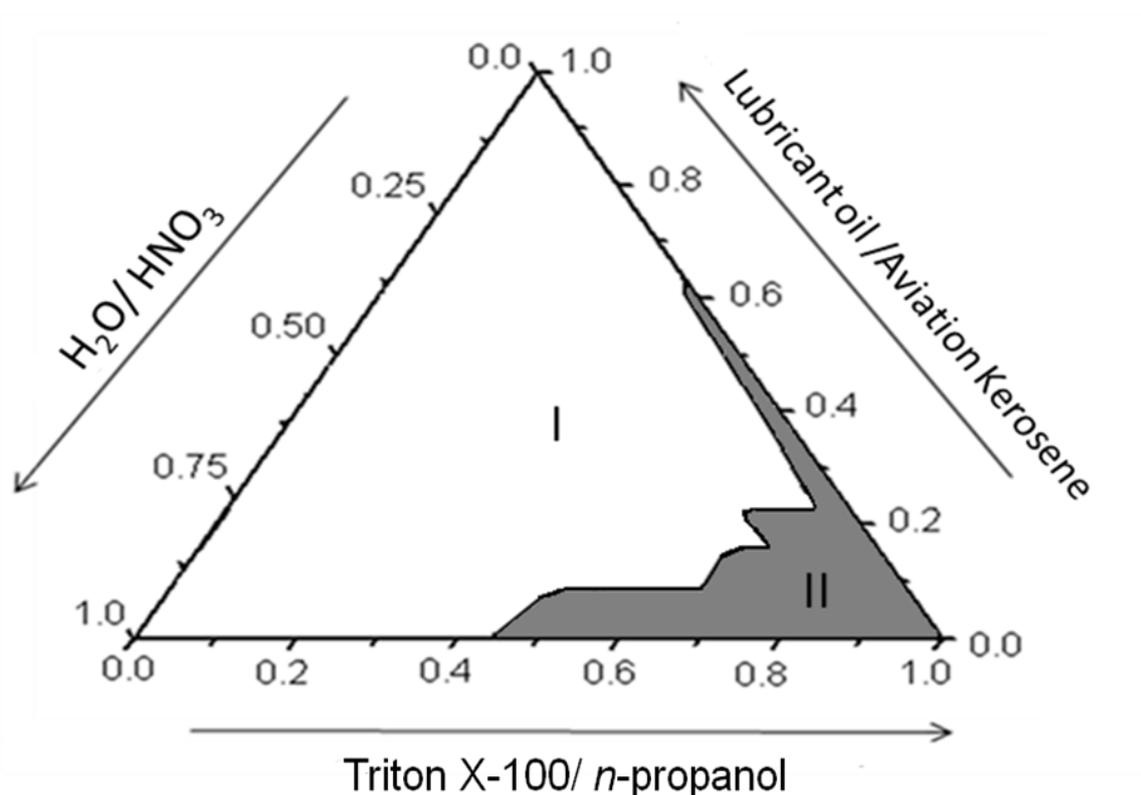


Figure 1. Pseudoternary phase diagram of HNO₃ 14 mol L⁻¹, Triton X-100/n-propanol (1:11 w/w) and lubricant oil/aviation kerosene (1:17 w/w) mixtures at 25 °C. Region I: emulsion; Region II: microemulsion.

The temperature program is described in Table 2. Two drying temperatures were utilized in order to provide a homogeneous heating, thereby preventing splattering of the samples in the microemulsion. Due to the high concentration of Fe in the samples, even using the less sensitive analytical line of 302.06 nm, it was also necessary to use argon gas flow during the atomization step aiming to “dilute” the atomic cloud, thus reducing sensitivity. In all cases it was found that the optimal temperature for pyrolysis is 1300 ° C, as can be seen in Fig. 2, which is used in all future investigations.

It has been reported that some elements with thermally stable behavior, such as Ni and V, could form volatile compounds in crude oil and derivatives^{34,35} In this way, Pd/Mg was investigated as chemical modifiers because it has been used successfully for a large number of elements³⁶ and for Ni and V in crude oil.^{35,37,38}

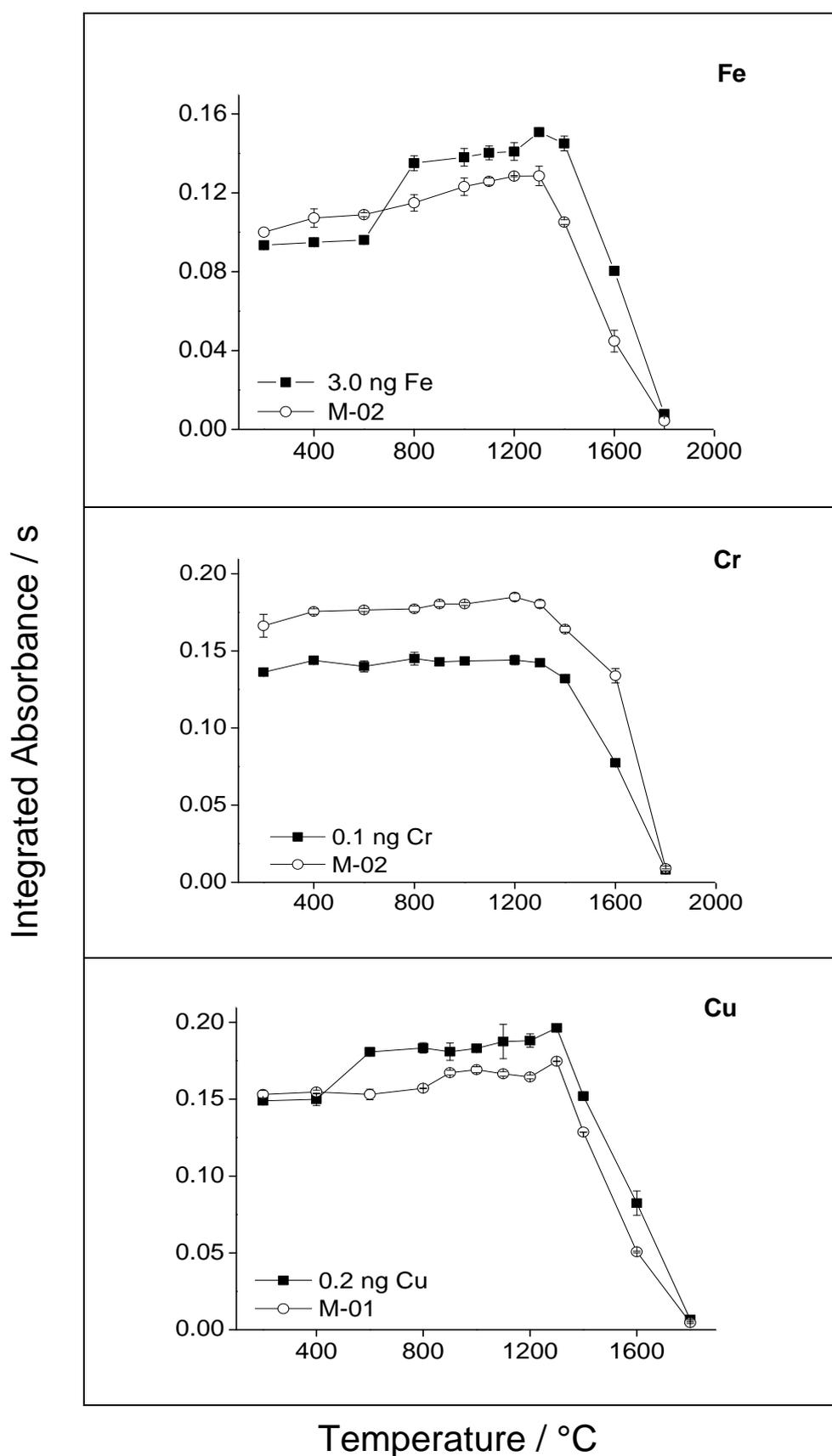


Figure 2. Pyrolysis curves for Fe, Cr and Cu. (-■-) aqueous standards and (-O-) used lubricant oil sample microemulsions. Atomization temperatures = 2300 °C, 2500 °C and 2100 °C for Fe, Cr and Cu, respectively.

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4 However in this work no changes in the sensitivity or pyrolysis temperature
5 was observed for the three elements studied, indicating that the use chemical modifier
6 for determination of Cr, Cu and Fe in microemulsified lubricating oils is not necessary.
7 This statement was also confirmed with the analyses of the certified reference material,
8 which will be shown afterwards.
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13 Absorbance profiles and the background signal were also considered when
14 choosing the proper furnace conditions for Fe, Cr and Cu atomization; some typical
15 atomization and background signals are shown in Fig. 3. As can be seen, there is a
16 good similarity between the profiles from aqueous standard and microemulsified
17 samples, mainly for Cr and Cu. This figure also shows the background signal was
18 completely eliminated with the high pyrolysis temperature used. The atomization
19 temperatures were selected based on the sensitivity and the analytical signal profile,
20 which is in agreement with literature data for a transversely heated atomizer.³⁶ The
21 complete furnace temperature program is shown in Table 2.
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32 **3.3. Stability studies**

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35 In routine procedures, it is essential that samples and calibration standards
36 remain stable for at least a few hours so that the analysis can be performed
37 accurately. Therefore, stability assays of analytes in the microemulsified used
38 lubricating oils were performed. For comparison purpose a microemulsion prepared
39 with aqueous standards was also analysed in this study. It was prepared in the same
40 way as the sample, replacing the sample by 0.15 g of mineral oil to simulate the
41 lubricating oil. Samples and standards were monitored for a period of five days as
42 shown in Fig. 4.
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50 As can be seen the absorbance signal for inorganic standard of the 3 analytes
51 studied in microemulsion medium remained constant until the fourth day of analysis.
52 On the other hand, the stability of the analytical signal was lower for the samples.
53 The most critical was Fe that showed one decrease of 81% for the sample M-04 on
54 the second day and 17% for sample M-02 in the third day. For Cu, there was a
55 decrease of 57% for the sample M-02 in the third day.
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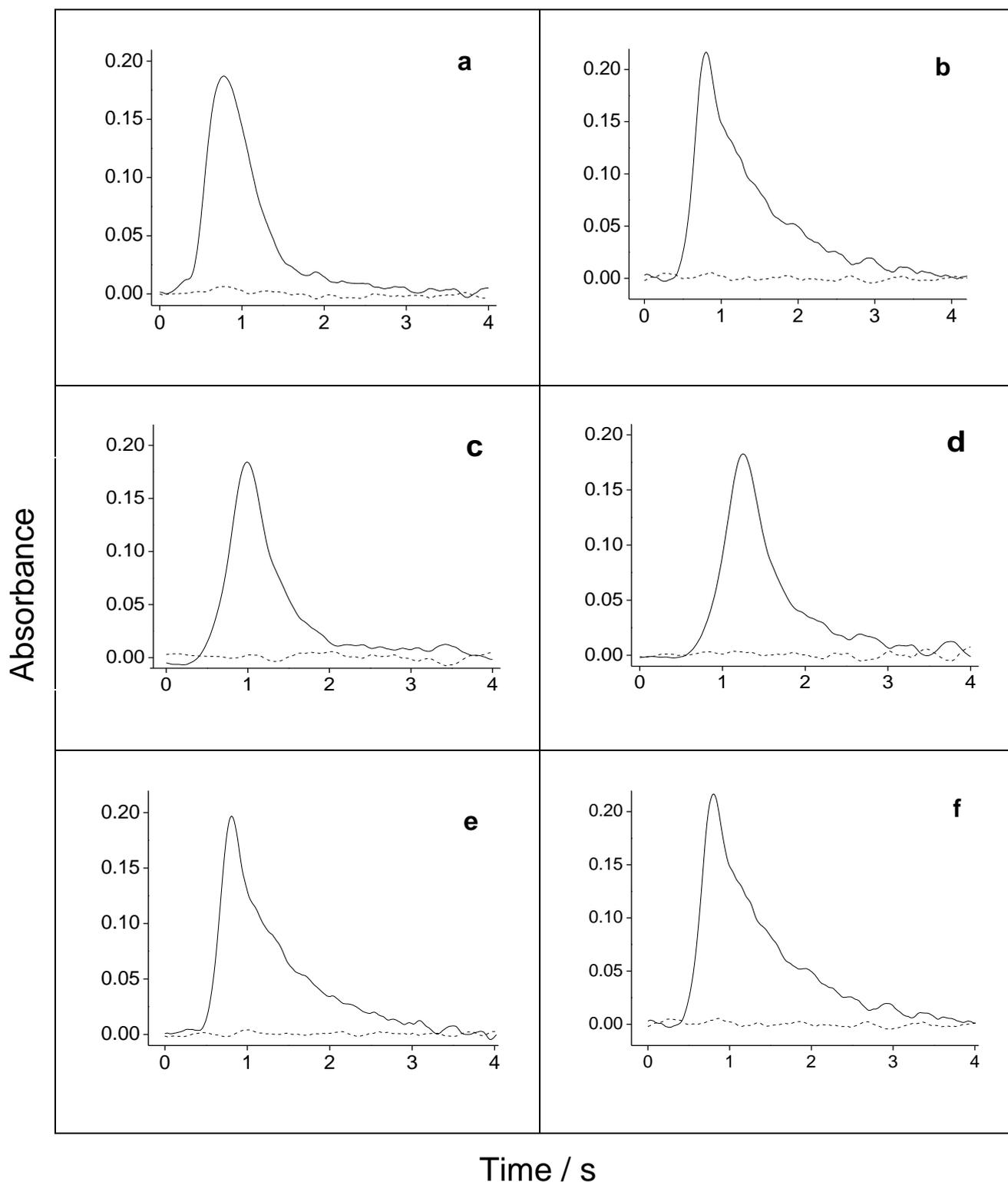


Figure 3. Absorbance signals for Fe (a and b), Cr (c and d) and Cu (e and f) in aqueous standards: 3.0 ng Fe (a); 0.1 ng Cr (c) and 0.2 ng Cu (e); used lubricating oils microemulsion: M-02, (b and d), M-01 (f). Full lines represent the atomic absorption (AA) and broken lines represent the background (BG) signal.

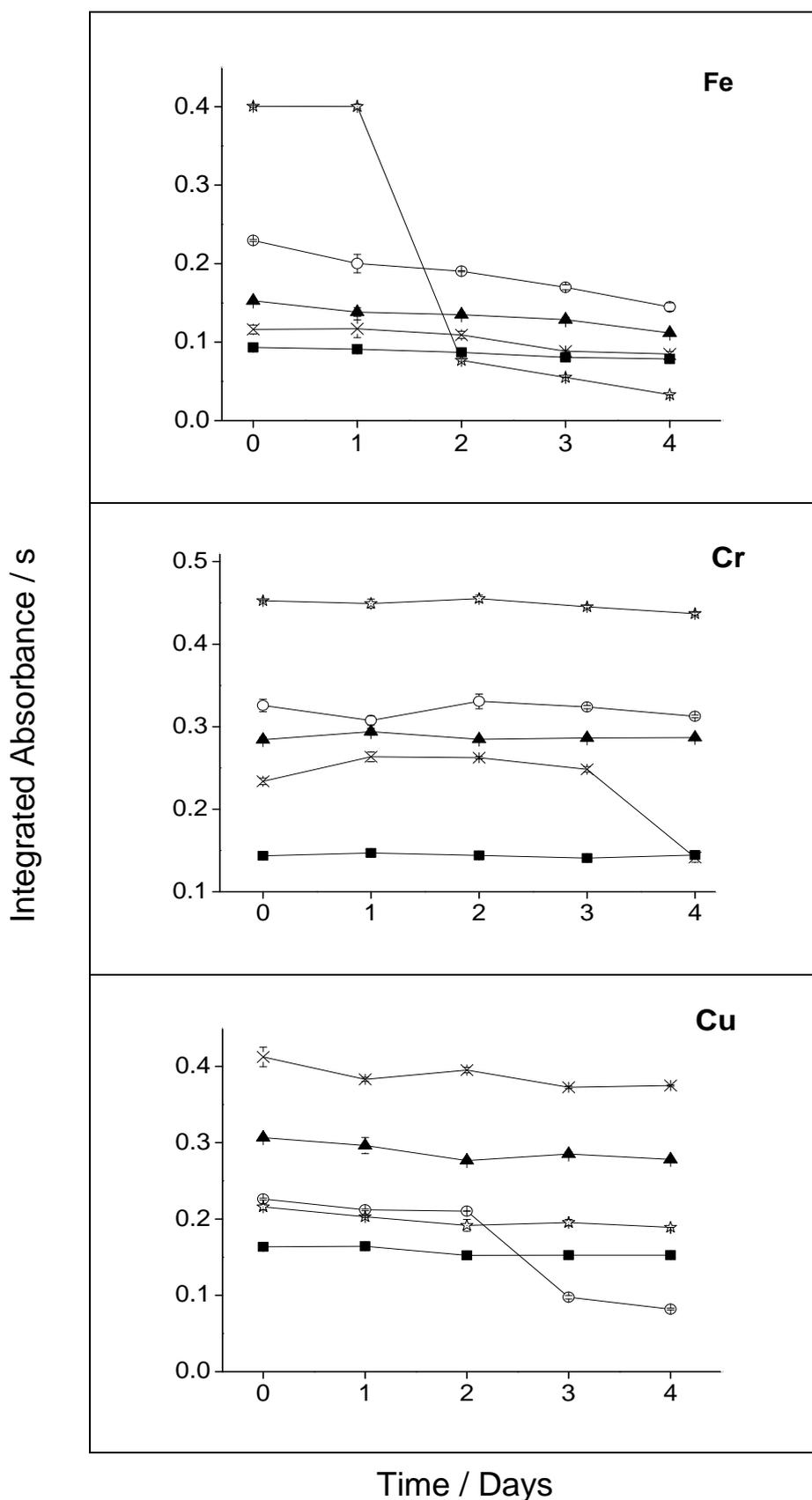


Figure 4. Variation of the absorbance over time for Fe, Cr and Cu in used lubricant oils microemulsions -x- Sample M-01; -o- Sample M-02; -▲- Sample M-03; -☆- Sample M-04 and -■- aqueous standards microemulsion (3.0 ng Fe, 0.1 ng Cr, 0.2 ng Cu).

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This may have been caused by the large amount of particulate formed after some period of time, as discussed before. For the sample M-04 for example, the particles was visually observed in 48 hours. Anyway, the stability was at least 24 hours for all analytes and samples investigated, that can be considerate adequate and higher then reported in other works with used lubricating oils.^{4,29,31} This higher stability, added to the fact of using aqueous inorganic standards for calibration, makes this sample preparation a suitable method for routine application.

3.4. Figures of merit

Calibration curves using aqueous standard in 0.014 mol L⁻¹ HNO₃ and inorganic standard in microemulsion medium were established using blank and five calibration solutions in the range of 50 - 400 µg L⁻¹ for Fe, 5 - 40 µg L⁻¹ for Cr and 10 - 50 µg L⁻¹ for Cu and the conditions optimized above. As can be seen in Table 3, the slope of the regression curves for the three elements obtained using the calibration curve prepared in 0.014 mol L⁻¹ HNO₃ or in microemulsion were very similar, indicating that simpler aqueous standards in 0.014 mol L⁻¹ HNO₃ could be used for calibration purposes. The correlation coefficient (R), the characteristic mass (m₀), the instrumental and sample limits of detection (LOD) and quantification (LOQ), obtained for Fe, Cr and Cu are also shown in Table 3.

The instrumental LOD and LOQ were calculated as the analyte concentration corresponding to an integrated absorbance signal equal to three times and ten times the standard deviation of the blank. To estimate the LOD and LOQ for the original sample, the mass used in the preparation of the sample (0.15 g) and final volume of the microemulsion (10 mL) was taken into account. The characteristic mass values, LOD and LOQ are lower than previously reported for Cr and Cu.^{31,39} For Fe the characteristic mass value using the line with 32% of sensitivity and gas flow during the atomization was approximately 12 times higher compared to the value obtained with its main line.³⁵ The relative standard deviation by the method (RSD%, n = 6) were very low (up to 5%) for all elements and samples, considering the complexity of the samples. For all elements analyzed the useful life time of the graphite tube was approximately 450 heating cycles.

Table 3 - Analytical figures of merit for Fe, Cr and Cu by ET AAS using microemulsion and aqueous standard

Parameters	Fe	Cr	Cu
Aqueous standard linear regression	$A_{\text{int}} = 0.02415(\text{ng}) + 0.02165$	$A_{\text{int}} = 1.47984(\text{ng}) + 0.01743$	$A_{\text{int}} = 0.68384(\text{ng}) + 0.00614$
Aqueous standard correlation coefficient (R)	0.9937	0.9989	0.9948
Microemulsion linear regression	$A_{\text{int}} = 0.02428(\text{ng}) + 0.01715$	$A_{\text{int}} = 1.35590(\text{ng}) + 0.01340$	$A_{\text{int}} = 0.71488(\text{ng}) + 0.00726$
Microemulsion correlation coefficient (R)	0.9922	0.9997	0.9938
Characteristic mass (pg)	150	3	6
Instrumental LOD (n=10) $\mu\text{g L}^{-1}$	0.28	0.01	0.03
Instrumental LOQ (n=10) $\mu\text{g L}^{-1}$	0.93	0.02	0.09
Sample LOD (n=10) mg kg^{-1}	1.85	0.04	0.2
Sample LOQ (n=10) mg kg^{-1}	6.18	0.12	0.6

3.5 Determination of Fe, Cr and Cu in lubricating oil

The accuracy of the proposed method was evaluated using NIST Certified Reference Material (SRM 1084a) and acid-digestion method. The CRM was analyzed using microemulsion as sample preparation and the results obtained using calibration with aqueous standards in $0.014 \text{ mol L}^{-1} \text{ HNO}_3$, are summarized in Tables 4. The Student's *t*-test was applied to the data of Table 4 and the calculated *t* values obtained for Fe (0.478), Cr (0.999) and Cu (1.343) were lower than *t*-critical obtained

for all elements (4.302), showing that the results obtained for the three analytes were not significantly different from the certified value at a 95% level of confidence.

Table 4 - Certified and measured concentration values of elements in the certified reference material (SRM 1084a) using microemulsion as sample preparation

Analyte	Certified value (mg kg ⁻¹)	Value found (mg kg ⁻¹)	RSD %
Fe	98.9 ± 1.4	99.7 ± 2.9	2.9
Cr	98.3 ± 0.8	99.6 ± 2.6	2.6
Cu	100.0 ± 1.9	103.8 ± 4.9	4.7

The results obtained with the proposed method and by the acid-digestion are shown in Table 5. For all elements the results have not shown significant difference at the 95% confidence level when a paired the Student's *t*-test was applied for the dataset of the obtained results. The calculated *t* values obtained were 1.323, 0.667 and 0.115 for Fe, Cu and Cr respectively, which were lower than *t*-critical obtained for all elements (4.302). The good agreement between the results supports that aqueous calibration standards can be used for the determination of Fe, Cr and Cu in used lubricating oils with the proposed method.

All samples showed higher levels of Fe (Table 5) than those found by Salvador *et al.*³⁹ and Gonçalves *et al.*⁴⁰ For Cr the values found in this study were similar to those reported by Gonçalves *et al.*⁴⁰ and Fischer *et al.*⁴¹ This may indicate that the oils analysed showed wear in the cooling system of the engine, since Cr is directly associated with this system in the automotive engine. The quantified values for Cu are similar to those found by Carballo *et al.*²⁹

Table 5 - Determination of iron, chromium and copper in used lubricating oils by electrothermal atomic absorption spectrometry using microemulsion as sample preparation

Samples	Fe concentration (mg kg ⁻¹) (mean±SD, n = 3)		Cr concentration (mg kg ⁻¹) (mean±SD, n = 3)		Cu concentration (mg kg ⁻¹) (mean±SD, n = 3)	
	ME	AD	ME	AD	ME	AD
M-01	23.0 ± 1.0	23.7 ± 3.7	1.02 ± 0.04	0.99 ± 0.08	4.63 ± 0.01	4.52 ± 0.11
M-02	86.0 ± 4.0	87.7 ± 4.3	2.82 ± 0.08	2.76 ± 0.06	11.5 ± 0.59	12.8 ± 0.82
M-03	59.3 ± 1.6	-	1.41 ± 0.06	-	5.75 ± 0.06	-
M-04	460 ± 8	473 ± 29	8.46 ± 0.30	8.88 ± 0.37	22.8 ± 0.85	21.9 ± 0.38

ME: microemulsion; AD: acid digestion.

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The presence of these metal in lubricating oils is associated to engine wearing, varying its content with the amount of kilometres, the type of engine and even the year of fabrication of the car.⁴² Unfortunately this information were not available for the samples analyzed in this work, but the sample M-04 (used oil of bus engine) was visually the most used lubricating oil considering the color and amount of particles. Confirming this information, this sample presented the higher concentration of all metals determined.

4. Conclusions

The analytical method developed in this work proved to be efficient for the determination of Cu, Fe and Cr in used lubricating oil samples by ET AAS. It's a simple, rapid, sensitive and accurate method. The use of the O/W microemulsion as sample preparation showed the following advantages of using inorganic aqueous standards for calibration and greater stability of the analyte in the medium. The method developed in this work is simpler and faster than other proposed in the literature. The construction of a phase diagram has shown the range of each component that could be used for obtaining the microemulsion. A comparison of the results obtained with the acid decomposition method and certified reference material showed that the method is accurate and can be safely applied in routine analysis.

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