Talanta 83 (2010) 637–643

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of calcium, magnesium and zinc in lubricating oils by flame atomic absorption spectrometry using a three-component solution

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ARTICLE INFO

Article history:
Received 2 August 2010
Received in revised form 5 October 2010
Accepted 6 October 2010
Available online 14 October 2010

Keywords:
Calcium
Magnesium
Zinc
Flame atomic absorption spectrometry
Lubricating oil
Three-component solution

ABSTRACT

Lubricating oils are used to decrease wear and friction of movable parts of engines and turbines, being in that way essential for the performance and the increase of that equipment lifespan. The presence of some metals shows the addition of specific additives such as detergents, dispersals and antioxidants that improve the performance of these lubricants. In this work, a method for determination of calcium, magnesium and zinc in lubricating oil by flame atomic absorption spectrometry (F AAS) was developed. The samples were diluted with a small quantity of aviation kerosene (AVK), *n*-propanol and water to form a three-component solution before its introduction in the F AAS. Aqueous inorganic standards diluted in the same way have been used for calibration. To assess the accuracy of the new method, it was compared with ABNT NBR 14066 standard method, which consists in diluting the sample with AVK and in quantification by F AAS. Two other validating methods have also been used: the acid digestion and the certified reference material NIST (SRM 1084a). The proposed method provides the following advantages in relation to the standard method: significant reduction of the use of AVK, higher stability of the analytes in the medium and application of aqueous inorganic standards for calibration. The limits of detection for calcium, magnesium and zinc were 1.3 $\mu g\,g^{-1}$, 0.052 $\mu g\,g^{-1}$ and 0.41 $\mu g\,g^{-1}$, respectively. Concentrations of calcium, magnesium and zinc in six different samples obtained by the developed method did not differ significantly from the results obtained by the reference methods at the 95% confidence level (Student's *t*-test and ANOVA). Therefore, the proposed method becomes an efficient alternative for determination of metals in lubricating oil.

1. Introduction

All mechanical equipment suffers wear due to the time of use and the exposure to contaminants that can damage its movable parts. One way to extend the lifespan of this equipment is through the use of suitable lubricating oils. The lubricating oils are widely used in engines in order to protect the movable parts, reducing friction and cleaning the engines inside [1]. The Brazilian annual consumption of lubricating oil is about 1,000,000 m^3 mainly in automobile use, representing diesel motors nearly 60% of the national consumption [2]. Lubricating oils are also used in hydraulic system industry, stationary engines, turbines, etc [1].

Due to the large diversity of equipment that uses lubricating oils special features of these oils should be improved according to the machine demands. That can be done by using specific additives, which have numerous functions such as antioxidants, dispersants and detergents [1]. The dialkyldithiophosphate zinc (ZDDP) is a multifunctional additive that acts as an antioxidant, an agent of extreme pressure and an anti-wearing agent [3]. Detergents such as alkarylsulphonates have compounds in their formula that contains calcium, magnesium, barium and their function is to reduce the deposit in the inner surfaces of combustion engines [4]. In Brazil, the National Petroleum Agency (ANP) is the responsible body for the control of quality of lubricating oils. The Program for Monitoring the Quality of Lubricants (PMQL) was created in 2006 by the ANP in order to monitor systematically the quality of lubricating oils marketed in Brazil. One of their control parameters is verifying the concentration of active components (Ca, Mg and Zn) that are in the form of organic compounds presented in additives. Monthly, the ANP publishes a newsletter with the results obtained in PMQL [5].

According to recent review published by Aucélio et al. [6], the majority of reported studies for determination of metals in lubricating oils are based on atomic spectrometry techniques. This fact is obviously due to the minimum pre-treatment of samples

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doi:10.1016/j.talanta.2010.10.013

Table 1
Aspiration rate and fuel/oxidant ratio optimized for the determination of calcium, magnesium and zinc in lubricating oil by F AAS using three-component solution and dilution with aviation kerosene methods.

Analyte	Fuel/oxidant		Fuel/oxidant ratio		Aspiration rate (mL min^{-1})	
	Dilution with kerosene	Three-component solution	Dilution with kerosene	Three-component solution	Dilution with kerosene	Three-component solution
Ca	C_2H_2/N_2O	C_2H_2/N_2O	0.391	0.415	2.4	1.5
Mg	C_2H_2/N_2O	C_2H_2/air	0.445	0.064	3.0	1.5
Zn	C_2H_2/air	C_2H_2/air	0.100	0.097	2.7	1.5

required by these spectrometric techniques, such as the dilution of lubricating oil in organic solvent, avoiding burning procedures for obtaining ash or digestion, which are lengthy and may be affected by the loss of analytes or by contamination. Inductively coupled plasma–optical emission spectrometry (ICP–OES) has been the most widely used technique, as these authors mentioned, probably because of its multi-element determination and its low detection limit. Despite the advantages, the difficulty of loading organic solvents in the ICP [6–10] is also known, requiring special accessories or conditions for dealing with diluted oil samples. Moreover, this technique has a relatively high cost for routine analysis. Despite presenting low sensitivity and mono-elementary characteristic, flame atomic absorption spectrometry (F AAS) continues to be an important technique for the determination of metals in lubricating oils. This is due to its low cost and robustness in relation to the tolerance of flames for most organic solvents. With regard to graphite furnace atomic absorption spectrometry (GF AAS), the number of applications is smaller probably due to the mono-elementary characteristics and the low sample consumption—that could lead to problems of non-representativeness.

Several other techniques have been used for the determination of metals in lubricating oils, though in lower scale, such as Anodic Stripping Voltammetry with a hanging mercury drop electrode [11], Square-Wave Anodic Stripping Voltammetry at thin film gold electrodes [12], Stripping Chronopotentiometry [13], High-Resolution Continuum Source Flame Atomic Absorption Spectrometry (HR-CS F AAS) [14,15], LASER-Induced Breakdown Spectroscopy (LIBS) [16,17], Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry (ETV ICP–MS) [18] and X-ray fluorescence spectrometry [19].

In terms of sample pre-treatment, there is a tendency of using methods to prevent its intensive manipulation [6]. The direct analysis of the diluted sample with organic solvent, due to its convenience and speed, has been widely used. However, organic standards, apart from being relatively expensive and difficult to prepare, can lead to erroneous results. It may be because of the alteration in the concentration caused by evaporation of solvent and metal deposition on the walls of the deposit containers [8,20,21]. Aucélio et al. [6] also pointed out problems of repetition and false results due to the presence of insoluble inorganic species in used lubricant oil. Alternatively, the water in oil (w/o) or oil in water (o/w) emulsions/microemulsions have proved to be a strong tendency to replace the methods of dilution [6,10,22,23]. Using emulsion, the main problem is its instability, which causes phase separation in a short period of time. The advantages of using microemulsions are the thermodynamic stability, the possibility of using inorganic standards for calibration and the acidification [24]. The acidification of the emulsion turns analyte species into an uniform chemical form [6,25], avoiding losses by adsorption as well.

The goal of this work was the development of a simple, fast, and accurate analytical method, which can be applied routinely in the determination of metals in lubricating oil samples by F AAS. The sample was introduced as a three-component solution (oil/water/alcohol). The target elements were Ca, Mg and Zn used by the National Petroleum Agency (ANP) for the PMQL. The formation, composition and stability of the three-component solution were investigated in details. The accuracy of the method was evaluated by comparison with the ABNT NBR 14066 standard method [26]. Acid digestion and the certified reference material (NIST SRM 1084a) were also investigated for validation. The expected advantages of the proposed procedure are the reduction of use of toxic solvents, replacement of liposoluble standards used by inorganic aqueous standards and greater stability of the analytes in the medium.

2. Experimental

2.1. *Instrumentation*

All measurements were carried out using an AAS 6 Vario atomic absorption spectrometer (Analytik Jena AG, Jena, Germany). Ca, Mg and Zn hollow cathode lamp (Photron, Australia) operating at 4 mA, 2 mA and 4 mA, respectively, were used as radiation source. The primary resonance lines of Ca (422.7 nm), Mg (285.2 nm) and Zn (213.9 nm) were used with a bandwidth of 1.2 nm, 1.2 nm and 0.5 nm, respectively. The fuel used was acetylene (White Martins, Brazil); nitrous oxide (White Martins, Brazil) and compressed air, obtained by an air compressor, model FIAC CDS 8/50 (Araraquara, São Paulo, Brazil), were used as oxidant. The acetylene flow rates, aspiration rate and the burner height were adjusted in order to obtain the maximum absorbance signal. The optimized aspiration rate and fuel/oxidant ratio for the determination of Ca, Mg and Zn are shown in Table 1.

An analytical balance (Gibertini, Italy) with an accuracy of 0.0001 g was used for weighing the samples and reagents. An open system (digester block model 324 A 242, Quimis, Brazil) operated at a frequency of 60 Hz with a potency of 2000 W and glass tubes with “cold finger” were used for sample digestion.

2.2. *Reagents and samples*

All reagents used were of analytical grade. The water was distilled in a glass water distillation system (Fisatom, São Paulo, Brazil) and additionally purified by a Milli-Q water purification system (Millipore, Bedford, MA, USA) resulting in a specific resistivity of 18.2 MΩ cm. All containers and glassware were soaked in 3 mol L^{-1} nitric acid for at least 24 h and rinsed three times with purified water before its use.

Nitric acid (Merck, Darmstadt, Germany), *n*-propanol (Merck, Darmstadt, Germany) and mineral-based oil (High Purity Standards, Charleston, USA) were employed in the preparation of the three-component solutions. The nitric acid was purified by sub-boiling in a quartz distiller (Kürner Analysentechnik, Rosenheim, Germany). Mineral oil was used in the three-component solution and in the dilution with solvent technique to simulate the oleic phase in the calibration standards. Aqueous stock solutions of 1000 mg L^{-1} of Ca, Mg and Zn, were prepared from $Ca(OH)_2 \cdot 2H_2O$, $MgCl_2$ and $ZnCl_2$ (all from Merck, Darmstadt, Germany), respectively, and acidified with nitric acid (0.014 mol L^{-1}).

The Ca, Mg, Zn and K liposoluble standards, dissolved in mineral oil, from calcium cyclohexanebutyrate ($1000 \pm 0.008\,mg\,g^{-1}$), magnesium 2-ethylhexanebutyrate ($997\,mg\,g^{-1} \pm 0.003$) zinc 2-ethylhexanoate ($1000 \pm 0.006\,mg\,g^{-1}$) and potassium cyclohexanebytirate ($1001 \pm 0.003\,mg\,g^{-1}$) salts, all from SpecSol (Quimlab, São Paulo, Brazil), were used in the ABNT NBR 14066 [26] standard method. Metal-free aviation kerosene (REFAP, Canoas, Brazil) was used as a solvent for liposoluble standards and for lubricating oil samples.

Sulfuric acid, distilled nitric acid and hydrogen peroxide, all from Merck, Darmstadt, Germany, were used in the acid digestion method.

The certified reference material SRM 1084a (wear-metals in lubricating oil, $100\,mg\,g^{-1}$), from the National Institute of Standards & Technology (NIST, Gaithersburg, MD, USA) was used for validation purpose. Six different lubricating oil samples purchased in local markets in Porto Alegre (RS, Brazil) were analyzed in this work: LO1 (Automatic Transmission Fluid—ATF); LO2, LO3 and LO5 (Engine oil—SAE 20W-50); LO4 (Automatic Transmission Fluid—ATF-Type A); LO6 (Two Strokes Engine—PAI-TC).

2.3. Preparation of the three-component solution

To prepare the three-component solution, the lubricating oil sample was first mixed with aviation kerosene in order to reduce its viscosity, then with the aqueous phase (analyte aqueous standard in/or $1.4\,mol\,L^{-1}$ HNO_3), and finally with the *n*-propanol. After the addition of all components, the system was shaken manually for a few seconds. Various proportions of lubricating oil, aviation kerosene, *n*-propanol and diluted nitric acid were mixed until the formation of a clear and stable solution. Through the different proportions of mixed reagents, a pseudo-ternary diagram phase was built, which will be shown afterwards. This procedure was performed at 25 °C, maintained by refrigeration of the laboratory. The composition adopted in the preparation of the three-component solution for later analysis was 0.1 g sample, 2.5 g aviation kerosene, 0.1 g of water with nitric acid ($1.4\,mol\,L^{-1}$) and the volume completed to 10 mL with *n*-propanol. All samples were prepared in triplicate. The three-component solutions for calibration were prepared in the same way as the sample, replacing the sample by 0.1 g of mineral oil to simulate the lubricating oil. Standards were prepared from calcium, magnesium and zinc aqueous stock solutions described above, pipetting the volume into the aqueous phase to give concentration in the range of $0.0–6.0\,mg\,L^{-1}$ for calcium, $0.0–0.5\,mg\,L^{-1}$ for magnesium and $0.0–2.0\,mg\,L^{-1}$ for zinc, in 10 mL volumetric flasks.

2.4. Determination of calcium, magnesium and zinc by the ABNT NBR 14066 standard method

The standard method ABNT NBR 14066 [26]—which consists on diluting the sample with aviation kerosene (AVK) and quantification by F AAS—was employed to evaluate the accuracy of the developed method. Standards were prepared from a liposoluble standard stock solution of $100\,mg\,kg^{-1}$, pipetting the appropriate volumes to obtain a concentration range from 0.0 to $6.0\,mg\,L^{-1}$ for calcium, $0.0–4.0\,mg\,L^{-1}$ for magnesium and $0.0–1.0\,mg\,L^{-1}$ for zinc in 10 mL volumetric flasks, and mineral oil was added to adjust the viscosity. Samples were prepared by weighing 0.05 g for calcium and 0.2 g for magnesium and zinc in 10 mL volumetric flasks. Both standard and sample were diluted with a solution of 2.0 g of potassium per liter of AVK. All samples were diluted in triplicate. Standards and samples were analyzed immediately after dilution.

2.5. Acid digestion procedure

Three selected samples were submitted to an acid digestion for validation purpose. All steps were performed in a digester block under reflux using a "cold finger". A mass of 0.25 g of samples were weighed directly into an open glass tubes and 2.5 mL of concentrated sulfuric acid was added. The mixture was gradually heated up to 130 °C and then kept for 2 h. After that, the tubes were left to cool into room temperature. Secondly, 2.5 mL of concentrated sulfuric acid was added and the glass tubes were gradually heated up to a temperature of 160 °C, keeping that temperature during 30 min. After this period, they were left to cool into room temperature. Thirdly, 3.5 mL of distillated nitric acid was added drop by drop to avoid foam formation. Afterwards, the glass tubes were gradually heated up to a temperature of 170 °C then kept for 60 min. Finally, 2.5 mL of hydrogen peroxide (30% v/v) was added and the tubes were left to rest during an hour to complete the digestion. The digestion products were transferred to a volumetric flasks and the volume was completed up to 25 mL with ultrapure water. All samples were digested in triplicate. Standards were prepared by serial dilutions from aqueous stock solutions ($1000\,mg\,L^{-1}$) of calcium, magnesium and zinc in $0.014\,mol\,L^{-1}$ nitric acid.

3. Results and discussion

3.1. Three-component solution

As reported by Aucélio et al. [6], several authors have proposed the emulsification of the lubricating oil before analysis. As most of works are applied for used lubricating oil, the composition is normally based on the use of a relatively small volume of a strong mineral acid mixture (HNO_3/HF or HNO_3/HCl) in order to promote the dissolution of the small wear metal particles. The resulting mixture is further dissolved in an adequate organic solvent (e.g., kerosene), forming a w/o emulsion, or, alternatively, surfactant and water are added, forming an o/w emulsion, before its introduction into the atomizer. However, emulsions are instable and a phase separation takes place in a short period, requiring agitation in order to maintain the homogeneity of the system during the analysis.

An o/w emulsion/microemulsion system was proposed for analysis of used lubricating oil by Souza et al. [25], for determination of Cr, Mo, Ti, V and Ni by ICP–OES, and by Aucélio et al. [22], for determination of Sb and Sn by GF AAS. The emulsion was prepared following a specific sequence of addition of sample/HNO_3/xylene/Triton X-100 and water, with assistance of an ultrasonic bath, in order to guarantee its homogeneity. The authors reported that using up to 5% (in mass) of sample and 6% (in mass) of surfactant Triton X-100, the emulsion remained stable for 40 min, which was enough time to perform the analysis [25]. An o/w microemulsion system based on surfactants mixture, lubricating oil and co-surfactant (sec-butanol) was proposed by Burguera et al. [27] for aluminum determination in lubricating oils. A sequential injection (SIA) was applied for online sample preparation. The sonication and repetitive change of the flowing direction improve the stability of the system, allowing attaining the microemulsion.

In this work several experiments have been performed in order to obtain a homogeneous and stable system with lubricating oils, which could be used as sample preparation for calcium, magnesium and zinc determination in these samples. The immediate preparation, without using ultrasonic or other mechanical equipment for agitation, was also aimed in order to make the proposed procedure fast and handy. Different types of solvents, such as iso-pentanol, xylene, *n*-butanol, *n*-propanol, as well as the surfactants Triton X-100 and sodium dodecyl sulfate, in different proportions were investigated. The mixtures of the sample, water, solvent and sur-

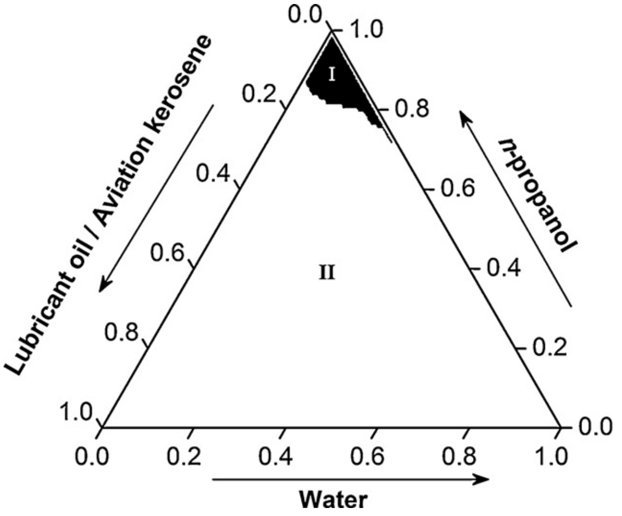

Fig. 1. Pseudoternary phase diagram of water, *n*-propanol and 1:15 (w/w) lubricant oil/kerosene mixture at 25 °C. Region I: stable and transparent mixture; region II: emulsion.

factant resulted in emulsions which are rapidly destabilized (phase separation). For the formation of the homogeneous system it was necessary the use of a small amount of AVK in order to reduce the viscosity of lubricating oils. The *n*-propanol alcohol was chosen because its solubility in water is 100% [28]. A system based on oil-in-water (o/w) microemulsion, mainly with a large amount of water, is very advantageous in order to reduce the costs and because it is similar to aqueous solutions, being much simpler to obtain optimized instrument parameters for analysis without drastic changes after aqueous solutions analysis. It also allows the acidification of the system to increase the stability of the analytes in the solution. Calibration against aqueous standards may also be expected. Therefore, we tried first to use large amount of water to obtain a microemulsion, but the hydrophobic phase (lubricating oil/AVK, fixed ratio 1:15 in mass) not exceeding 2% in mass was not stabilized when more than 20% in mass of water was used and the emulsion formation was achieved.

In order to obtain the region where a homogeneous and stable system could be achieved, a pseudoternary phase diagram (showed in Fig. 1) was built following these steps: first, it was prepared a fixed ratio (1:15 in mass) of lubricating oil/AVK. Different ratios for these two components were tested, from 1:1 to 1:16 (in mass). The minimum ratio that allowed the formation of three-component solution was 1:15. This mixture (oil/AVK) was treated as if it was only one component in the diagram, which has three components in its vertices: oil/AVK, water and *n*-propanol. Second, the points inside the triangle were plotted, as follows: fixing the quantity of one component and varying the others (the variations were 5% for each). The procedure ended when the whole interior of the diagram was plotted. Each point represents a mixture and, therefore, it must have its proper physical characteristics (emulsified or transparent mixture) identified for further delineation of the different regions. Fig. 1 shows two distinct regions: region I, where a homogeneous and transparent solution is found, and region II, where mixtures form an emulsion.

A dynamic light scattering (DLS) test was performed with homogeneous system formed and it showed a continuous system, not characterized as microemulsion. Thus, we decided to call it "three-component solution", as proposed by Silva et al. [8]. The composition that was adopted in the preparation of the three-component solution for later analysis was 0.1 g sample, 2.5 g aviation kerosene, 0.1 g of water with nitric acid (1.4 mol L^{-1}) and the volume completed to 10 mL with *n*-propanol. After the addition of all components, the system was shaken manually for a few seconds until the formation of a clear and stable solution. The standards for calibration were prepared in the same way, replacing the sample by 0.1 g of mineral oil to simulate the lubricating oil and adding the inorganic standards into the aqueous phase. Both three-component solution of standard and samples remained stable, without separation of phases, for at least 10 months.

3.2. Instrumental parameters optimization

Although the flames are quite tolerant for most organic solvents, the load of organic solvents in the flame requires a careful optimization of the instrumental parameters, in order to guarantee a good performance of the analysis. The instrumental conditions such as acetylene flow rates, aspiration rate and the burner height were optimized in order to obtain the maximum signal/BG ratio, using three-component solutions containing 3.0, 0.3 and 0.6 mg L^{-1} of inorganic standard of Ca, Mg and Zn, respectively. The same parameters were optimized for the liposoluble standards diluted with AVK (standard method). The optimized aspiration rate and fuel/oxidant ratio for the determination of Ca, Mg and Zn are shown in Table 1. As can be seen, the fuel/oxidant ratio was similar for the proposed method and dilution method, except for Mg, for which a different flame compositions were used in both method. In this work the stability of absorption measurements were not greatly affected by the presence of kerosene, as observed in a previous work of our group for biodiesel analysis using the dilution with xylene method [24,29]. However, regarding the three-component solution, the behavior was similar to that observed for biodiesel microemulsion, not affecting significantly the flame stability [24,29]. Even though, the best signal/BG ratio was obtained with fuel/oxidant ratio close to the minimum for Ca and Mg, for both methods. The aspiration rate that gave the best sensitivity for dilution with kerosene was also close to the minimum allowed in our equipment for this solution. On the other hand, for the three-component solution, which is more viscous than the kerosene solution, the aspiration rate of 1.5 mL min^{-1}, that is not the minimum, gave the best sensitivity. These optimized conditions were used in all subsequent studies.

3.3. Stability studies

In routine procedures, it is essential that the samples and calibration standards remain stable for at least a few hours to allow the accuracy of the analysis. The stability of the analytes in the three-component solution was tested through the hourly and daily monitoring of the analytical signal of standards and samples. The stability of the organic standards and samples diluted in AVK was also investigated for comparison purposes, and the results are shown in Fig. 2. Except for calcium, that remained stable for four days, the analytical signal for magnesium and zinc in the standard solution and in the sample decreased about 20% in 1 h for magnesium, reaching almost half of its initial value over 6 h for both elements. These results confirm the necessity of immediate analysis of standards and samples for these elements after the dilution.

On the other hand, the absorbance signal for inorganic standards and samples both prepared in the same way, i.e., as a three-component solution, did not change significantly over 2 days for magnesium and at least 4 days for calcium and zinc, as showed in Fig. 3. Higher stability for a number of elements in microemulsions have been reported in the literature [22,24,29], associated with the use of mineral acid. This high stability found in this work, together with the use of inorganic standard for calibration, make this sample preparation more suitable for routine application.

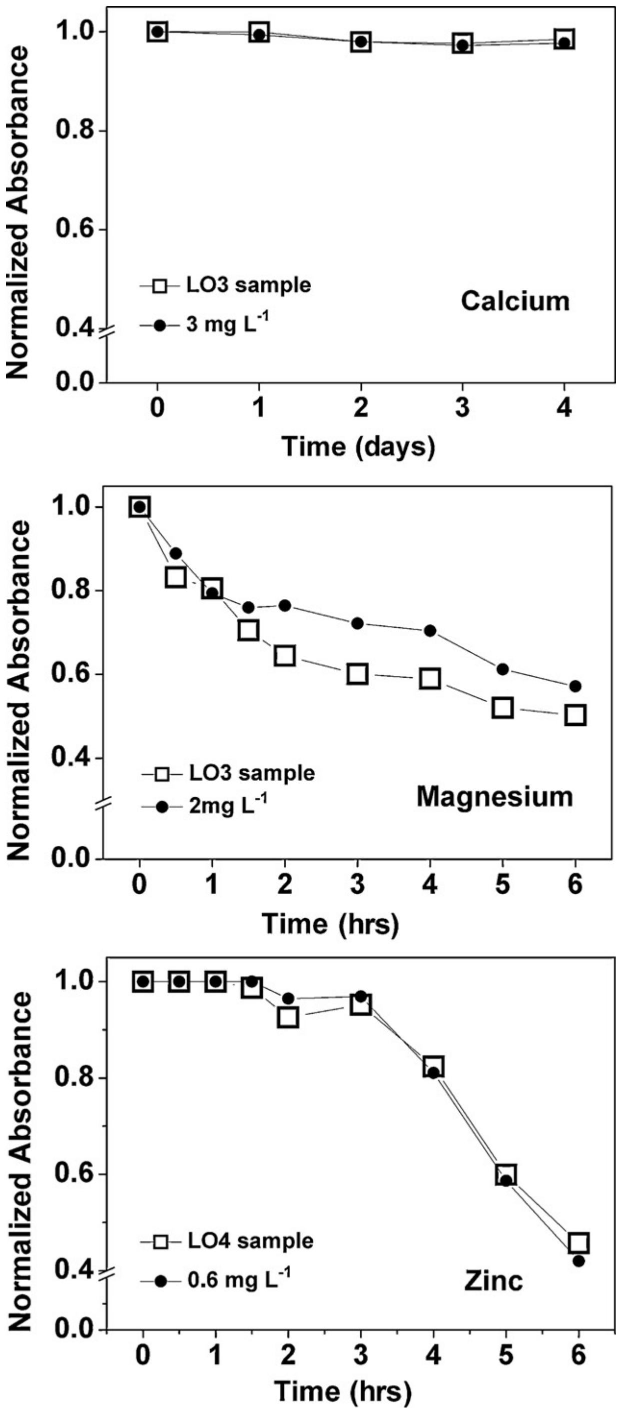

Fig. 2. Variation of the absorbance over time for calcium, magnesium and zinc in dilution with aviation kerosene method: (●) standard solutions and (□) lubricant oil samples.

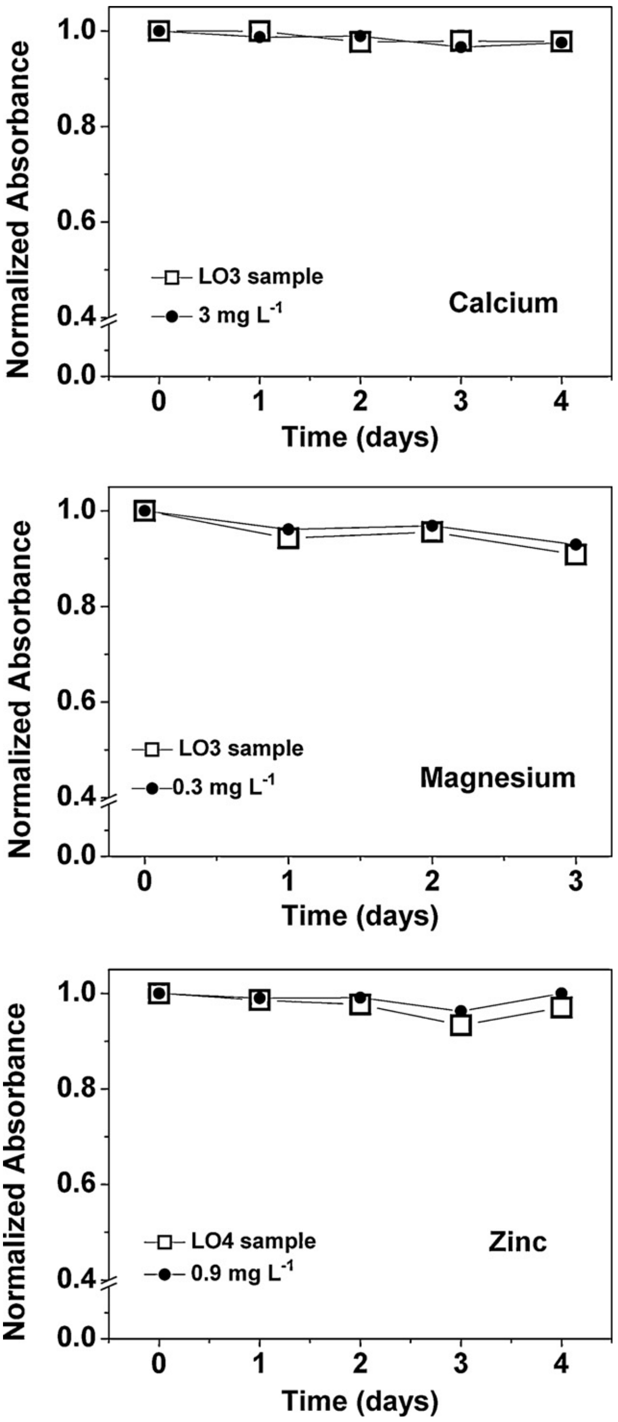

Fig. 3. Variation of the absorbance over time for calcium, magnesium and zinc in three component solution method: (●) standard solutions and (□) lubricant oil samples.

3.4. Figures of merit

Using the optimized instrumental conditions, calibration curves were constructed for inorganic standards in the three-component solution (proposed method) from which the analytical figures of merits were estimated (Table 2). For comparison purposes calibration curves and the figures of merits were also established for the liposoluble standards diluted in AVK, in accordance with the standard method ABNT NBR 14066 [26] (also showed in Table 2). The curves were linear up to 6.0 mg L^{-1} Ca, 0.5 mg L^{-1} Mg and 2.0 mg L^{-1} Zn for the proposed method and up to 6.0 mg L^{-1} Ca, 4.0 mg L^{-1} Mg and 1.0 mg L^{-1} Zn for the standard method.

As can be seen in Table 2, the sensitivity for calcium and zinc are similar for both methods as reflected by the characteristic mass and also by LOD and LOQ. The great difference obtained for magnesium in all figures can be related to the type of flame used for each method (see Table 1). According to Welz and Sperling, [30] interferences in the determination of metals can be avoided by using the C_2H_2/N_2O instead of the C_2H_2/air flame; however, losses in the sensitivity of analytes can occur with the former one, as observed

Table 2
Analytical figures of merit for calcium, magnesium and zinc by F AAS using three-component solution and dilution with aviation kerosene methods.

Analyte	Method	Linear regression equation	R	C_0 (μg L^{-1})	LOD (n = 10) (μg g^{-1})	LOQ (n = 10) (μg g^{-1})	RSD (n = 10) (%)	
							Standard	Sample[a]
Ca	Dilution with kerosene	$A = 0.1671c + 0.0201$	0.9987	24	2.0	6.5	1.4	4.3
	Three-component solution	$A = 0.1797c + 0.0123$	0.9981	23	1.3	4.3	1.3	0.7
Mg	Dilution with kerosene	$A = 0.2943c + 0.0166$	0.9983	14	0.21	0.71	2.5	4.3
	Three-component solution	$A = 1.2945c + 0.0056$	0.9992	3,0	0.052	0.17	1.0	1.0
Zn	Dilution with kerosene	$A = 0.3341c + 0.0037$	0.9976	12	0.23	0.76	1.8	4.1
	Three-component solution	$A = 0.2775c + 0.0093$	0.9970	13	0.41	1.4	0.7	0.9

[a] LO3 sample, R: correlation factor, C_0: characteristic concentration, LOD: limit of detection, LOQ: limit of quantification, RSD: relative standard deviation.

Table 3
Determination of calcium, magnesium and zinc in lubricant oil samples by F AAS.

Sample	Ca concentration (mg kg^{-1}) (mean ± SD, n = 3)			Mg concentration (mg kg^{-1}) (mean ± SD, n = 3)			Zn concentration (mg kg^{-1}) (mean ± SD, n = 3)		
	DK[a]	3CS[b]	Acid digestion	DK[a]	3CS[b]	Acid digestion	DK[a]	3CS[b]	Acid digestion
LO1	69 ± 1.5	61 ± 1.1	–	3.5 ± 0.04	3.3 ± 0.07	–	7.7 ± 0.30	5.2 ± 0.10	–
LO2	1967 ± 63	2011 ± 18	2055 ± 134	4.4 ± 0.2	4.3 ± 0.2	5.5 ± 0.5	1283 ± 23	1340 ± 38	1460 ± 34
LO3	1835 ± 134	1885 ± 65	1928 ± 148	23 ± 0.5	21 ± 1	19 ± 0.4	1105 ± 76	1008 ± 54	1232 ± 99
LO4	1489 ± 23	1497 ± 15	1448 ± 41	4.5 ± 0.06	4.5 ± 0.02	5.7 ± 0.2	652 ± 14	643 ± 27	777 ± 13
LO5	1756 ± 28	1806 ± 12	–	2.5 ± 0.03	2.9 ± 0.04	–	805 ± 41	860 ± 41	–
LO6	190 ± 1.4	190 ± 2.5	–	14 ± 0.3	16 ± 0.3	–	18.0 ± 0.10	16.8 ± 0.10	–

[a] DK = dilution with kerosene (ABNT NBR 14066 standard method [26]).
[b] 3CS = three-component solution.

in this work. It should be emphasized that the C_2H_2/N_2O flame was used because it was recommended by the standard method [26]. Ionization suppressor (2 g L^{-1} K) was also used as described in Section 2.4. However, from the results obtained in this work, we concluded that this hotter flame is not necessary for magnesium determination by the proposed method, as will be shown in the validation experiments. The last but not least, the precision of the results obtained with the proposed method was better for all elements investigated, as reflected by the RSD for standard and sample measurements. This feature is due to the lower fluctuation of the flame with the three-component solution.

3.5. Analytical results

The accuracy of the proposed method was evaluated through the comparison with the Brazilian Standard Method ABNT NBR 14066 [26]. The results obtained by both methods for calcium, magnesium and zinc in different kind of lubricating oil samples are summarized in Table 3. The paired *t*-test was applied to the data of Table 3, and showed that the results of both methods are not significantly different at the 95% confidence level.

Two other methods of validation were also employed: the use of reference material and acid digestion procedure. The certified reference material wear-metals in lubricating oil—NIST SRM 1084a—that has a certified value only for magnesium, was analyzed by the proposed method and the magnesium concentration found (94.9 ± 2.6 μg g^{-1}) did not differ significantly from the certified value (99.5 ± 1.7 μg g^{-1}) at a 95% confidence according to Student's *t*-test. Because no other reference material was available in our laboratory, in order to validate the results of the other elements we also investigated a digestion procedure, based on a procedure described by Amorim et al. [31]. In this work, the digestion was performed under reflux using a "cold finger" to avoid excessive evaporation of the acids and reduce the risk of contamination. The total time of digestion was approximately 6 h. The other details of the acid digestion were given in Section 2.5. The results of the three selected samples subjected to the acid digestion are presented in Table 3. These values did not differ significantly from the values obtained by three-component solution and dilution methods, according to the Analysis of Variance (ANOVA) at the 95% confidence interval. This shows that the proposed method provided accurate results, although it is very simple and fast. Another important point is that concentrations of Ca, Mg and Zn found in new lubricant oils are usually much greater than the limits obtained in this work. Thus, very low detection limits and high sensitivity techniques are not required for this application, as confirmed before [32]. The overall result was very satisfactory for routine analysis.

It should be emphasized that in Brazil there is no legislation establishing maximum or minimum values for concentrations of calcium, magnesium and zinc in new lubricating oils. However, the ANP controls whether the concentration of additives is consistent with the manufacturer information at the moment of the registration of the product in this agency [5].

4. Conclusion

The proposed method makes possible an accurate determination of calcium, magnesium and zinc in lubricating oil samples by F AAS. The sample preparation is very simple and fast, not requiring any equipment for homogenization or agitation. These features, allied to the higher stability of the standard and sample in the three-component solution and the possibility of using aqueous inorganic standards for calibration, makes the proposed method highly suitable for routine application. Therefore, it is an excellent alternative for monitoring the quality of lubricating oils within the Brazilian PMQL.

Acknowledgements

The authors thank to FAPERGS/CNPq (Programa PRONEX–process no. 10/0012-7) for financial support, CNPq (A.V.Z.—process no. 135999/2008-1; M.M.S. and M.G.R.V.) and CAPES (A.J.) for their scholarships. We thank Janaina A. Barbará for her careful experimental work. We also thank Refinaria Alberto Pasqualini—REFAP S.A. for the donation of AVK.

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