Determination of Zinc in Lubricating Oil by Flame AAS Employing Ultrasonic Extraction

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INTRODUCTION

The elements present in lubricating oils are generally classified as wear metals, contaminants, or additives (1). Organometallic compounds of some metals are usually added to the fresh oils as additives to improve some properties of the lubricating oils such as color, pour point, viscosity, antiwear, antifrictional, antifoaming, antioxidant, anticorrosive, dispersing, and others (2,3). Zinc (Zn) is one of the additive metals more frequently found in lubricating oils because it acts as an antioxidant and corrosion inhibitor, mainly in the form of zinc dialkyl-dithiophosphates (4). Therefore, the determination of Zn in lubricating oils is a relevant analytical task for quality control of the product (since performance of the oil is strictly dependent on the amount of additive) and also for evaluating wear and tear of the engine.

Among the spectrometric techniques available for Zn determination in lubricating oils, flame atomic absorption spectrometry (FAAS) is the oldest and most commonly used (5–7). However, the high levels of organic matter and the viscosity of the samples impair the direct analysis of lubricating oils by FAAS. Hence, sample pre-treatments are required which usually involve complicated and time-consuming procedures, such as ashing (8), dissolution in organic solvents

ABSTRACT

The determination of zinc in lubricating oils by line-source flame atomic absorption spectrometry (LS-FAAS) is proposed employing an alternative sample preparation procedure based on ultrasonic wave-assisted acid extraction. The chemometric optimization of the main parameters influencing the extraction provided the following conditions: 1.3 mL of HCl, 5.0 mL of H₂O₂, 120 seconds sonication time, 60 °C heating temperature, and 45% sonication amplitude of the ultrasound probe. Analytical curves in the 0.5 – 4.0 mg L⁻¹ Zn range were consistently obtained ($R = 0.9990$). Commercial unused lubricating oil samples were analyzed by the proposed method and by high-resolution continuum source flame AAS (HR-CS FAAS) as the comparative technique. A paired *t*-test showed that the results between the two techniques were in agreement at the 95% confidence level. The accuracy of the proposed method was evaluated using an alternative sample preparation method based on recovery tests. Recoveries in the 92 – 119% interval were found. The relative standard deviation was 4% and the limit of detection was 17.6 µg L⁻¹.

(9), emulsions (3,10), and acid decomposition (3,11). Thus, development of accurate analytical methods for oil analysis by exploring the present tendencies for minimum sample preparation, small amount of reagents and samples, and minimum generation of residue or waste, is attractive.

Ultrasound-assisted extraction is a simple, fast, inexpensive, efficient, and alternative sample preparation to conventional leaching processes for a variety of analytes and matrices. Sonication can be performed inside the sample flask, which prevents sample losses and minimizes the probability for sample contamination (12). On the other hand, quantitative extractions depend strongly on the interaction between the analyte and the matrix. Since optimization of the main parameters that influence the extraction is essential, chemometric techniques are more attractive for results evaluation and methods optimization than univariate approaches due to the high efficiency usually achieved in the shortest way, and requiring reduced consumption of reagents and sample, less time, and minimal effort (13).

This study reports on the evaluation of an alternative sample preparation based on ultrasonic wave-assisted acid extraction, employing multivariate optimization for the determination of Zn in lubricating oil by FAAS.

EXPERIMENTAL

Instrumentation

All measurements were carried out using a PerkinElmer® AAnalyst™ 100 flame atomic absorption spectrometer (Shelton, CT, USA), equipped with a deuterium lamp background corrector. A PerkinElmer® Lumina® hollow cathode lamp (HCL) was used for the determination of Zn at the analytical wavelength of 213.9 nm and a lamp current of 15 mA. High-purity acetylene

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(99.7%, Air Liquid, Brazil) was used as the fuel gas and an air-acetylene flame at the ratio of 4:2.

A Sonics & Materials titanium ultrasound probe (Newtown, CT, USA), connected to a Vibracell VC50-1 ultrasonic processor (50 W) controlled by a PerkinElmer USS-100 ultrasonic slurry sampler, was used for the extractions. For sample heating, a Tecnal TE 184 (Tecnal, SP, Brazil) thermostatic water bath was used.

A Multiwave® microwave oven (Anton Paar, Graz, Austria), equipped with 50-mL quartz vessels, was used for the microwave-assisted digestion of the lubricating oil samples as a comparative sample preparation procedure.

A Model AnalytikJena ContrAA 300 high-resolution atomic absorption spectrometer (Berlin, Germany), equipped with a Xenon short-arc lamp operating in a hot-spot mode as the continuum radiation source, was used as the comparative technique. The measurements were carried out at 213.8570 nm using a 5 mL min⁻¹ sample flow rate, the acetylene-air flow rates of 50 and 514 L h⁻¹, wavelength integrated absorbance equivalent to 1 pixel, and calibration within the 0.5 – 4.0 mg L⁻¹ Zn range.

Reagents and Standard Solutions

High purity de-ionized water (resistivity 18.2 MΩ cm) was obtained using a Millipore® RiOs™ 5 reverse osmosis and a Millipore® Milli-Q™ Academic system (Bedford, MA, USA). Nitric acid (E. Merck, Darmstadt, Germany), hydrochloric acid (Spectrum Chemical, New Jersey, USA,) and hydrogen peroxide 30% v/v (E. Merck, Darmstadt, Germany) were used to build the analytical curves and for sample preparation. All chemical reagents used were of analytical grade.

Analytical solutions containing 0.0, 0.5, 1.0, 2.0, 3.0, and 4.0 mg L⁻¹ Zn were prepared daily by appropriate dilution of the 1000 mg L⁻¹ stock standard solution (Normex, Carlo Erba, Italy) and acidifying to 1% (v/v) HNO₃.

All solutions and pre-treated samples were stored in high-density Nalgene® polypropylene bottles (Nalgene Nunc International, Rochester, NY, USA). Plastic bottles and all glassware used were cleaned by soaking in 10% (v/v) HNO₃ for at least 24 hours and rinsing abundantly in de-ionized water before use.

Sample Preparation

Two lubricating oil samples were purchased at a local market in Araraquara (São Paulo State, Brazil): Havoline Premium SL SAE 20W-50 (Chevron Brasil Lubrificantes, Ltda., Rio de Janeiro, Brazil) and VS Plus Supermultiviscoso SJ 20W-50 (Petrbras Lubrificantes Brasil, MG, Brazil). Both samples were analyzed using the proposed ultrasound extraction and microwave-assisted acid digestion method.

The chemometric study was carried out by applying Minitab®

software, Version 16 (Minitab Inc., State College, PA, USA). A two-step chemometric study was carried out to obtain the best conditions for Zn extraction: The first study with a fractional factorial design (2⁵⁻²) and the second study with a full factorial design (2³). In the first step, the parameters of hydrochloric acid volume, hydrogen peroxide volume, sonication amplitude, sonication time, and temperature were evaluated in two blocks, two levels (high and low), and without center point (Table I). This study resulted in eight experiments randomly carried out in triplicate.

After fixing the parameters (hydrogen peroxide volume and sonication time), the full factorial design was carried out for the parameters (and their interactions) of hydrochloric acid volume, sonication amplitude, and temperature in two blocks, with high, low, and center point (Table I). This full factorial design resulted in eight experiments, performed randomly in triplicate, and two additional experiments repeated at the central point, also in triplicate. After that, response surface graphs and contour plots were generated for evaluating in more detail near the center

TABLE I
Parameters and Levels of Experimental Design for Zinc Extraction

Design Type	Parameters	High Level	Center Point	Low Level
2 ⁵⁻²	Hydrochloric acid volume (mL)	1	–	5
	Hydrogen peroxide volume (mL)	1	–	5
	Sonication amplitude (%)	50	–	70
	Sonication time (s)	30	–	120
	Temperature (°C)	25	–	60
2 ³	Hydrochloric acid volume (mL)	0.5	1.0	1.5
	Sonication amplitude (%)	30	45	60
	Temperature (°C)	50	65	80
Surface Plot				
	Hydrochloric acid volume (mL)	0.8	1.0	1.2
	Sonication amplitude (%)	40	45	50
	Temperature (°C)	60	65	70

point and then finding the best condition for Zn extraction.

In all of these experiments, approximately 0.1 g of lubricating oil sample was weighed into 50-mL centrifuge polypropylene tubes with screw caps, and the corresponding volumes of hydrochloric acid and hydrogen peroxide were added. Some experiments required heating of the samples which was carried out in a thermostatic water-bath. After Zn extraction with the ultrasound probe, the tubes were filled to volume with de-ionized water, and the sample was analyzed by FAAS employing the proposed procedure. Calibration curves within the 0.5 – 4.0 mg L⁻¹ Zn range were built, and Zn was determined using the most sensitive analytical line for Zn (213.9 nm). All measurements were carried out in triplicate in single-element mode. The limits of detection (LOD) and limits of quantification (LOQ) for Zn were calculated according to IUPAC recommendations (14).

Based on the chemometric study, the best conditions for the Zn extraction were as follows: 0.1 g of lubricating oil, 1.3 mL of hydrochloric acid, 5 mL of hydrogen peroxide, temperature of 60 °C, sonication time of 120 seconds, and sonication amplitude of 45%. Using these parameters, the samples were analyzed by FAAS employing the same measurement procedure as described above.

For comparative studies, two commercial samples were also digested in a microwave oven by adding 2 mL H₂O₂ 30% (v/v), 2 mL concentrated HNO₃, and 2 mL deionized water to 0.1 g of sample placed in quartz flasks. Table II shows the optimized time-power program of the microwave oven for lubricating oil decomposition (3). The digests were transferred to a 50-mL volumetric flask and filled to volume with de-ionized water. The digested samples were analyzed by

line source FAAS and HR-CS FAAS.

Additionally, recovery tests were performed for two spiked samples of lubricant oil after adding 50 µL of a 1000-mg L⁻¹ Zn stock solution to 0.1 g of sample in a 50-mL volumetric flask in order to obtain solutions containing 1.0 mg L⁻¹ Zn.

RESULTS AND DISCUSSION

A sample amount of 0.1 g was preliminarily selected for extraction optimization after taking into consideration the Zn content usually found in unused lubricating oil. Hydrochloric acid plus hydrogen peroxide were evaluated since this mixture has been used in different procedures for Zn determination by different authors (4, 15). The extraction of Zn from lubricating oil using an ultrasound probe can be influenced by the reagent volume, sonication amplitude, sonication time and temperature. Taking into consideration these variables, it was decided to optimize them by means of a two-step chemometric study comprising a fractional factorial design (2⁵⁻²) and a full factorial design (2³). Minitab® software generated level combinations for all factors employed in the assays. Absorbance values were measured for all of these combination levels.

In the fractional factorial design (2⁵⁻²), the parameters cited above were evaluated in two levels (high and low), two blocks, and without

center point (Table I). After addition of H₂O₂ and HCl to a 0.1 g sample, the formation of foam was observed inside the centrifuge polypropylene tubes and subsequently the mixture clarified, which was intensified by the use of the ultrasound probe. The use of an oxidative process might probably help the release of Zn from the oil matrix.

The Pareto chart depicted in Figure 1 illustrates the more significant variables in the studied system, and the lengths of the bars are proportional to the absolute values of standardized effects. In this case, bars over the critical *t*-value at 2.110 represent the most significant variables on extraction. Analysis of the figure reveals that temperature is the most important variable, followed by HCl volume and sonication amplitude. The influence of the H₂O₂ volume and sonication time was insignificant. The effect of the temperature to release Zn should be more important for unused than used oils. The oxidation, thermal decomposition, and/or deterioration of oil inside the engine may produce more labile Zn species than those originally present as organometallic additives and are not easily extractable (4).

According to the results obtained by the main effects graphic for the 2⁵⁻² fractional factorial design (Figure 2), the high level at 60 °C was the most significant in the temperature parameter. The low levels for HCl volume (1 mL) and sonication amplitude (45%) were more significant, and the high levels for H₂O₂ volume (5 mL) and sonication time (120 seconds) were more significant.

After analyzing these results, it was possible to propose the second step based on a full factorial design (2³). In this design, the H₂O₂ volume and sonication time were fixed at 5 mL and 120 seconds,

TABLE II
Optimized Program of
Microwave Oven for
Lubricating Oil Decomposition

Step	Initial Power (W)	Final Power (W)	Time (min)
1	300	300	15
2	400	600	20
3	800	800	15
4	0	0	15

* Total time: 65 minutes.

respectively, and the remaining variables and their interactions were further investigated in two blocks, with high, low, and center point (Table I). The Pareto chart of the full factorial design (2^3) is depicted in Figure 3. The HCl volume-temperature interaction (AB) was the most significant answer, followed by temperature-sonication amplitude interaction (BC), HCl volume (A), HCl volume-sonication amplitude interaction (AC) and sonication amplitude (C). However, only temperature was not significant. The best answers were obtained in the center point condition taking into account the independent parameters or interactions between them. Therefore, the study of the neighborhood of the center point conditions was necessary to establish the best condition for Zn extraction. So, surface graphs were built according to the current values obtained for the conditions around the center point.

The surface graphs depicted in Figure 4 allowed the selection of the best conditions for Zn extraction. The maximum absorbance response for the interaction of HCl volume-temperature was 1.3 mL and 60 °C, respectively (Figure 4a). For the temperature-sonication amplitude interaction, the optimum values were 60 °C and 45%, respectively (Figure 4b). And for the HCl volume-sonication amplitude pair, 1.3 mL and 45% furnished the maximum response, respectively (Figure 4c). Therefore, the optimized conditions for Zn extraction from oil samples, using ultrasound probe, were 0.1 g of sample, 5.0 mL of H_2O_2 , 1.3 mL of HCl, 120 seconds sonication, 60 °C temperature, and 45% sonication amplitude.

The feasibility of the optimized method was checked after analysis of two commercial samples of unused lubricating oil (Table III). The determination of Zn at the most sensitive analytical line

(213.9 nm) was carried out by FAAS using calibration standards in the 0.5 – 4.0 mg L⁻¹ Zn range. For comparison purposes, the samples were also analyzed by HR-CS FAAS. Additionally, closed-vessel microwave-assisted acid digestion was carried out as a comparative sample preparation method, and the data are compiled in Table III. The concentrations of Zn in the lubricating oil samples by the proposed method were in agreement with those obtained by HR-CS FAAS at the 95%

confidence level (paired *t*-test). However, when the results by the proposed method were compared with those obtained by a comparative sample preparation method, a significant difference between them was observed. This may be attributed to the difficulty of releasing Zn quantitatively from the oil matrix by ultrasonic extraction. On the other hand, organic matrices are destroyed entirely during microwave digestion and the Zn present in the final digests are

Fig. 1. Pareto chart of effects obtained for the 2^{5-2} fractional factorial design for Zn extracted from an unused lubricating oil.

Fig. 2. Main effects graphic for the 2^{5-2} fractional factorial design for Zn extracted from an unused lubricating oil.

Fig. 3. Pareto chart of effects obtained for the 2^3 full factorial design for Zn extracted from an unused lubricating oil.

Parameters: A = HCl volume, B = temperature, and C = amplitude.

TABLE III
Results (Mean $\pm$ Standard Deviation) for Zn (in g kg^{-1}) Determined ($n = 3$) in Unused Lubricating Oils by the Proposed Method (FAAS) and Alternative Technique (HR-CS FAAS) After Ultrasound Extraction. Samples also analyzed after Microwave-Assisted Acid Digestion as Comparative Procedure (MAAD).

Sample	FAAS	FAAS*	HR-CS FAAS	MAAD
Havoline Premium SL	0.881 ± 0.034	0.957 ± 0.038	0.968 ± 0.043	0.976 ± 0.019
VS Plus Supermultiviscoso	0.671 ± 0.026	0.882 ± 0.017	0.873 ± 0.024	0.908 ± 0.02

* After 24 h interaction time between sample and reagents before ultrasound extraction.

chiefly as divalent cations which are easily atomized. Considering the microwave-assisted digestion as reference sample preparation procedure (100% Zn released), the efficiency of Zn extraction from the two samples obtained by ultrasound-assisted extraction was equivalent to 92% and 76%. This poor recovery may be attributed to the ineffective interaction between sample and reagents to produce an oxidative process to some extent before introducing the ultrasound probe. In order to improve the release of Zn, the time of interaction between the sample and reagents was increased to 24 hours. The efficiency of extraction was found to be

equivalent to 98% for both samples. The recoveries of the analyte added to the two samples were in the 92–119% range, suggesting that the proposed method is efficient for determining Zn in these samples. Relative standard deviations ($n=12$) were lower than or equal to 4.0%, and the limit of detection was $17.6 \mu\text{g L}^{-1}$.

CONCLUSION

The chemometric study was useful to optimize the main parameters that influence the ultrasonic extraction of Zn from lubricant oils: 1.3 mL of HCl, 5.0 mL of H_2O_2 , 120 seconds sonication time, 60°C heating tem-

perature, and 45% sonication amplitude of the ultrasound probe. Analytical curves ($0.5\text{--}4.0 \text{ mg L}^{-1}$ Zn) were consistently obtained ($R=0.9990$).

The results of the analysis of commercial unused lubricating oil samples by the proposed method were in agreement with high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) at the 95% confidence level. Good recoveries (92–119%) and precision ($\text{RSD}=4\%$) were obtained, and the limit of detection was $17.6 \mu\text{g L}^{-1}$. The sample pre-treatment proposed here is environmentally friendly because the consumption of reagents, the amount of residue and waste, and the consumption of energy are minimal. Although the probe requires individual sampling and a 24-hour waiting time, the proposed method is simple, low cost, and rugged for routine analysis of lubricating oil samples.

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Fig. 4. Surface graphs for (a) HCl volume - temperature interaction, (b) temperature - sonication amplitude interaction, (c) HCl volume - sonication amplitude interaction.

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