Microchim Acta 149, 199–204 (2005)
DOI 10.1007/s00604-005-0324-9

Microchimica Acta
Printed in Austria

Original Paper

Potentiometric Stripping Analysis for Simultaneous Determination of Copper and Lead in Lubricating Oils After Total Digestion in a Focused Microwave-Assisted Oven

Rodrigo A. A. Munoz, Cíntia S. Silva, Paulo R. M. Correia,
Pedro V. Oliveira, and **Lúcio Angnes***

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, São Paulo 05508-900, Brazil

Received August 20, 2004; accepted January 11, 2005;

Abstract. The determination of metals in lubricating oil has been used as an important means of preventing components failures, to provide environmental information, and to solve criminal issues. In this study derivative potentiometric stripping analysis (DPSA) was used for the simultaneous determination of copper and lead in lubricating oils of vehicular engines. The samples were completely digested in a focused microwave-assisted oven using a powerful oxidant mixture (HNO_3, H_2SO_4, H_2O_2). The optimized heating program to digest about 1 mL of lubricating oil takes 45 minutes. The residual carbon content after digestion was below 0.3% m/m for all samples. Copper and lead were also determined by graphite furnace atomic absorption spectrometry (GFAAS), and the results obtained were in good agreement with those obtained by electrochemical measurements. Recoveries of 94–109 and 93–103%, for copper and lead, respectively, were obtained for new and used lubricating oil samples.

Key words: Lead; copper; lubricating oil; potentiometric stripping analysis; focused microwave-assisted oven.

The determination of wear metals in used lubricating oils is an important means of preventing component failures of vehicular engines [1, 2]. Furthermore, the results can give valuable environmental information once these metals can also be found in vehicular exhaust particulate matter. In addition, metal content in oils is also utilized to solve criminal issues and to identify adulteration [2, 3].

Generally, wear metals in used lubricating oil can be determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after dissolution in adequate solvent to facilitate the samples' introduction into the torch [4, 5]. However, the sensitivity achieved by ICP-OES for trace element determination ($<100\,\mu g\,g^{-1}$) [6] cannot be adequate, and more sensitive techniques are necessary. In these cases, electrothermal atomic absorption spectrometry (ETAAS) is the technique of choice due to the low detection limits for several elements [4, 7]. The majority of ETAAS methods related to the determination of trace elements in lubricating oils involve emulsified oil-aqueous solutions [8] and dry or wet mineralization [9].

Sample preparation is an important step of trace-element determination in lubricating oils, especially when electroanalytical detection techniques are chosen. In general, these samples are digested using a hot plate system [10] or microwave-assisted ovens. However, the hot plate system is time-consuming, can introduce contamination and is less safe than microwave digestion. In spite of being a trend in sample

---

* Author for correspondence. E-mail: luangnes@iq.usp.br

preparation, the use of microwave heating for oil sample digestion has been insufficiently explored, and few procedures are described in the literature [11–13].

Sanz-Segundo et al. [11] described a procedure for lubricating oil digestion using a microwave oven with high-pressure vessels to determine wear metals. In this case 1 g of sample was digested with a mixture of concentrated nitric acid and hydrogen peroxide in a 110 minute program. It should be emphasized that the time required to reduce the pressure and the temperature of the high-pressure vessels is not taken into account. However, after the heating program has finished, it is necessary to wait for at least 3 hours before opening the high-pressure vessels containing the digested samples.

Alternatively to the high-pressure systems, focused microwave ovens also provide the possibility of performing digestion procedures at room pressure by using successive additions of oxidants [12–14]. In spite of the lower operation temperatures (restricted by the boiling point of some reagents), open systems are successfully used during the pre-treatment steps of complex samples with high organic content, e.g. lubricating oils. Recently, a focused microwave-assisted oven was used to digest diesel oil samples for the determination of some elements using a powerful oxidant mixture (HNO_3, H_2SO_4 and H_2O_2) [14, 15]. The performance of each one of the six cavities of the focused microwave oven showed differences, indicating an irregular radiation distribution [15], the residual carbon content determination being carried out by ICP OES with axial viewing.

The great majority of studies related to the determination of metals in petroleum and derivatives using microwave-assisted ovens for sample digestion employed spectrometric techniques for detection. A few papers described the detection of wear metals in lubricating oil by electrochemical techniques [10, 16]. In one of these studies [16], the authors employed the same digestion program for a microwave oven previously described in the literature [11].

The rare application of electrochemical techniques for the quantification of metals in lubricating oil samples can probably be attributed to the problems produced by the adsorption of organic molecules on the electrodes. Therefore, the use of digestion procedures capable of minimizing the organic content in the samples is mandatory to explore these techniques successfully. This problem is also observed for other samples with high organic content, such as clinical, environmental and food samples [17–19].

Other electrochemical methods for the determination of metals in oil samples are described in the literature. Pournaghi-Azar et al. [20] outline a method for lead determination in gaseous oil samples by extraction of lead (II) benzoylacetonate in chloroform, preceded by the decomposition of organic-lead compounds with concentrated nitric acid at 300 °C. Lo Coco et al. [21] developed a method for extracting lead (II) from oil products with hot concentrated hydrochloric acid in a proper extractor. The procedure (including all steps) took 60 min. In these cases, lead determination was performed using differential pulse anodic stripping voltammetry (DPSAV) and potentiometric stripping analysis (PSA), respectively.

In recent years, the use of PSA for trace metal determination in oil samples (detection limits at $ng\,g^{-1}$) has significantly increased [21–26]. PSA is a two-phase technique involving a deposition step where the metal ions are reduced at the working electrode by applying a constant potential, analogous to anodic stripping voltammetry, and a stripping step where the metals are reoxidized, resulting in an E versus t curve. The stripping time is proportional to the concentration of the metal and to the electrolysis time [27]. The transformation of E versus t curve into dt/dE versus E curve (derivative PSA) allows the charging current to be eliminated from the analytical signal, resulting in enhanced sensitivity and resolution [28]. All the PSA methods described above use the derivative PSA (DPSA).

Considering the potentialities of PSA, such as the remarkable specificity and sensitivity, the aim of this study was the simultaneous determination of copper and lead in lubricating oil by DPSA. Details about sample digestion and analysis will be discussed in the following sections.

Experimental

Reagents, Samples and Materials

Analytical reference solutions of copper and lead were prepared from stock Titrisol solutions containing $1000\,mg\,L^{-1}$ of each analyte (Merck, Darmstadt, Germany). All dilutions were performed with high-purity deionized water (Millipore, Bedford, MA, USA). Analytical-grade reagents were used throughout: HNO_3 (65%, $m\,v^{-1}$), H_2SO_4 (97%, $m\,v^{-1}$), H_2O_2 (30%, $m\,v^{-1}$), NaCl, CH_3COONa, and $(NH_4)_2HPO_4$ (Merck, Darmstadt, Germany).

Samples of new and used lubricating oil for automotive vehicles were obtained at local gas stations. These samples were stored in polyethylene bottles at room temperature until analysis. All glassy and polyethylene materials used for sample preparation and solution storage were decontaminated with nitric acid 10% v/v for

24 hours. The digested samples were stored in polyethylene vessels at 4 °C.

Instrumentation

A focused microwave-assisted oven with two cavities (Star System 2, CEM) was used for the digestion of the lubricating oil samples. Electrochemical measurements were performed with an Autolab PGSTAT20 potentiostat (EcoChemie, Utrecht, Netherlands). A ZEEnit® 60 model graphite furnace atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) was utilized for the determination of copper and lead for comparison with the electroanalytical results. Analysis of total organic content was performed in an Elemental Analyzer 2400 CHN (Perkin Elmer).

Electrochemical Cell and Electrodes

For copper determination, we employed the working gold electrode obtained from compact discs developed in our laboratory [29–33]. For simultaneous determination of lead and copper, a commercial glassy carbon electrode with a thin mercury film deposited on it was used. A voltage of -1.0 V was applied at the glassy carbon electrode for 5 min in a solution of 1 mmol L^{-1} mercury (II) and 0.1 mol L^{-1} hydrochloric acid. The reference and auxiliary electrodes were a miniaturized $Ag/AgCl_{(sat)}$ electrode [34] and a platinum wire, respectively. A 5 mL Plexiglas electrochemical cell was constructed for the quantification of lead and copper.

Microwave Oven Digestion

An aliquot of 1 mL of oil sample (0.860 ± 0.018 g, n = 20) was placed into a microwave vessel with 10 mL (both) of concentrated HNO_3 and H_2SO_4. The heating program used for the digestion is shown in Table 1. In a last step, 15 mL of H_2O_2 were added in aliquots of 1 mL. A recovery study to evaluate the optimized digestion procedure was performed using both new and used lubricating oil samples and adding 200 and 20 µg L^{-1} of copper and lead, respectively, to the digestion vessels before starting the heating program. All samples were digested in duplicate.

The solution obtained after the sample decomposition was diluted up to 50 mL with deionized water. A blank was obtained by performing the same digestion program with all the reagents except the sample.

DPSA Determination

The copper determination used for initial experiments was performed by DPSA with a constant stripping current using a gold electrode. After optimizing the digestion procedure, DPSA with a chemical stripping agent (dissolved oxygen) at a glassy carbon electrode featuring a thin mercury film was used for simultaneous determination of copper and lead.

Table 1. Focused microwave-assisted oven heating program for lubricating oil samples

Step	Ramp time (min)	Hold time (min)	T (°C)
Addition of 1 mL of sample + 10 mL HNO_3 + 10 mL H_2SO_4			
1	5	0	100
2	2	3	110
3	2	5	130
4	10	3	180
5	5	3	220
Addition of 15 mL H_2O_2			
6	0	7	220

Table 2. Parameters of DPSA measurements for the analysis of the digested samples

PSA parameters	Chemical stripping (Hg^0 thin film electrode)	Constant current (Au electrode)
Conditioning potential (mV)	0	650
Conditioning time (s)	20	20
Deposition potential (mV)	−800	0
Deposition time (s)	60–120	15–60
Equilibrating time (s)	12	12
Potential limit (mV)	0	650
Stripping current (µA)	–	0.4

The DPSA parameters are listed in Table 2. One mL of oil sample was digested and the digestion product was quantitatively transferred to a 50 mL volumetric flask, where the volume was completed. A small amount of this solution (typically 50 or 100 µL) was transferred to the electrochemical cell and diluted 10 or 20 times with 20 mM sodium chloride. This large dilution was possible due to the high sensitivity of the stripping techniques. The final pH of the solutions after dilution was 1.0. The standard addition method was used for quantification of both metals.

GFAAS Determination

The GFAAS parameters for the determination of copper and lead are listed in Table 3. For both determinations, 20 µg of $(NH_4)_2HPO_4$ was used as matrix modifier. The digested solutions were diluted 5–10 times for both metal determinations. Analytical curves were constructed with standard solutions containing 1% v/v nitric acid (instrumental blank) in both cases. The estimated detection limits of copper and lead were 314 and 330 ng g^{-1}, respectively.

Table 3. Operating and heating program parameters for GFAAS

Spectrometer setup

	Cu	Pb
Wavelength (nm)	324.8	283.3
Bandpass (nm)	0.5	0.5
Lamp type	HCL*	HCL*
Lamp current (mA)	230	450
Reading time (s)	5	5

Heating program for the atomizer

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow rate (mL min^{-1})
Drying	130	10	5	250
Pyrolysis	500	10	30	250
Atomization	1500	0	4	0
Cleaning	2200	1	4	250

* *HCL* Hollow cathode lamp.
Total heating program time: 64 s.
Sample volume: 12 µL; injection temperature: 100°C.

Results and Discussion

Sample Digestion Procedure

One of the most significant advantages of the open-vessel microwave assisted oven is the speed at which a sample can be digested. Additionally, the sample can be digested virtually without any safety problems. Despite the low temperature and operation pressure, good efficiency can be achieved for organic and inorganic samples digestion [35].

Concentrated nitric acid alone was not able to destroy hydrocarbon molecules at atmospheric pressure. To overcome the temperature limitation and improve the efficiency of the lubricating oil digestion, a mixture of $HNO_3 + H_2SO_4$ was used to reach a temperature as high as 220 °C. After the fifth step in the heating program (Table 1), a carbonaceous residue was formed on the bottom of the digestion flask. Then the carbonaceous residue was completely dissolved by addition of 15 mL of H_2O_2 in the 1 mL aliquots. This yielded a clear solution. The use of a microwave oven with two cavities allows simultaneous digestion with good precision and accuracy, improving the analytical throughput. The residual carbon content in the digested sample was lower than 0.3% m/m for all samples.

Electrochemical Determinations

In the initial experiments, copper determinations were performed by PSA using a constant stripping current on gold electrodes. The results were excellent. The signals were reproducible and the results in good agreement with the GFAAS determinations. For this reason, it was concluded that no interference from organic compounds was found during the stripping step when using this technique. When the same electrode was employed for simultaneous determination of copper and lead, the results obtained for the latter metal were not satisfactory with respect to sensitivity.

Square-wave stripping voltammetry (SWSV) using gold electrodes was also evaluated for the same purpose. Good results were obtained in previous studies for the determination of copper and lead in rainwater and ethanol fuel [29, 36]. The same methodology was tested here for the digested lubricating oil samples, but it was not possible to detect lead under the same conditions. The lead signal was depressed, and by addition of increasing lead concentrations to the cell containing the diluted digested sample (even in the presence of chloride ions which are required for good performance of the gold electrode [29]), no increase in signal was observed.

The suspicion that the presence of sulfate ions was responsible for the anomalous response verified in these experiments made us investigate this aspect. Under the same SWSV conditions and in the absence of the digested sample, the response to lead ions was not affected by increasing sulfate concentrations. The reason for this phenomenon observed in the presence of the digested sample remains unclear.

Faced with the failure of using gold electrodes, copper and lead were simultaneously determined in the digested solutions utilizing mercury film plated on a glassy carbon electrode. On this electrode, the best response for simultaneous determination of lead and copper was obtained at a potential of −800 mV. The selection of less negative deposition potentials led to smaller signals, whereas the adoption of more negative values provoked the formation of hydrogen gas, biasing the deposition step. The behavior of both metals for different deposition times at −800 mV was also verified. A linear response was recorded for copper up to 600 s deposition time, while the lead signals did not increase with deposition times higher than 120 s. Therefore, 60 or 120 s was used for subsequent analysis, depending on the amount of metals in the solution.

DPSA with a chemical stripping agent (dissolved oxygen) was successfully applied to the simultaneous determination of copper and lead in all digested samples. Figure 1 presents derivative potentiometric

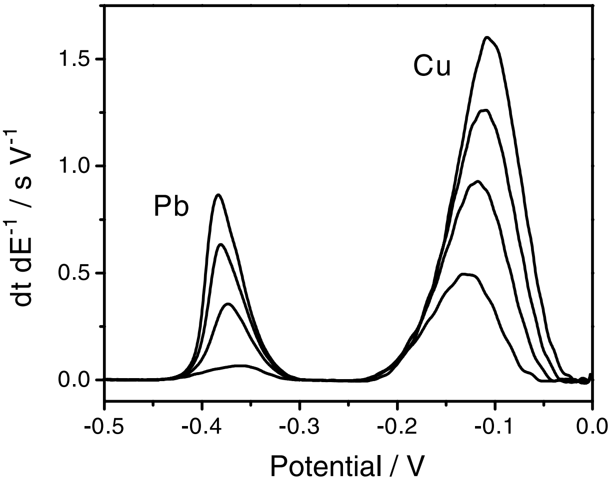

Fig. 1. Copper and lead derivative potentiometric stripping curves obtained under the experimental conditions described in Table 2 (120 s deposition time). The digested sample (no. 2) diluted 20 times plus three additions of 5 μg L^{-1} (aliquots of 10 μL of 1000 μg L^{-1} of each metal in 2000 μL of sample + electrolyte)

Table 4. Concentrations of Cu and Pb obtained by the proposed and comparative method in non-used and used lubricating oil samples

Samples*	Proposed method (DPSA) ($\mu g\,g^{-1}$)		Comparative method (GFAAS) ($\mu g\,g^{-1}$)	
	Cu	Pb	Cu	Pb
1	17.5 ± 0.1	0.9 ± 0.1	17.5 ± 0.2	1.0 ± 0.1
2	11.7 ± 0.1	1.8 ± 0.1	14.7 ± 0.1	1.8 ± 0.1
3	15.6 ± 0.9	7.6 ± 0.2	17.1 ± 0.1	7.6 ± 0.2
4	23.0 ± 0.1	0.9 ± 0.1	21.5 ± 0.1	0.78 ± 0.01
5	0.12 ± 0.02	<LD	<LD	<LD

* Samples 1–4 correspond to used oils (n = 3), sample 5 to non-used oil (n = 5).

stripping curves for a typical analysis. Addition of chloride ions improved the sensitivity of the technique for copper detection. Table 4 shows both metal concentrations for some samples of used and non-used lubricating oil samples obtained by DPSA and GFAAS techniques. The content of lead ions in the four analyzed samples of non-used lubricating oil was below the detection limits. It was possible to quantify copper in just one of them (under the conditions adopted). This result is included in Table 4 (sample 5), while results corresponding to the other three samples (numbers 6–8) were omitted because they were below the detection limit of both the proposed and the GFAAS method.

The recovery of 94–109% and 93–103% for copper and lead, respectively, was obtained by our sample digestion procedure. The detection limits [37] for copper and lead were 92 and 115 $ng\,g^{-1}$ of sample (S/N = 3), respectively, using a deposition time of 120 seconds at −800 mV. These detection limits can be improved by using other oxidant agents in the electrolyte, such as mercury (II) or acidic permanganate. The disadvantage of using mercury or permanganate is the generation of highly toxic waste which requires special treatment.

Conclusions

The focused microwave-assisted oven was successfully applied to lubricating oil digestion. The total carbon content was below 0.3% m/m, allowing the use of electroanalytical techniques such as stripping potentiometry without any apparent interference from organic molecules at the working electrode. The possibility of performing digestions under atmospheric pressure has important advantages for routine analysis. These include reduction of time when compared to traditional digestions and high-pressure systems (additional time for depressurization), and more safety for the analyst. The combination of an efficient sample digestion procedure and sensitive stripping analysis is an attractive methodology for solving several analytical problems in environmental, biological, and industrial fields.

Improvements on the detection limits for both metals can be reached using higher deposition times and/or by addition of oxidants such as mercury (II) [21–24] or potassium permanganate [38]. For the application proposed in the present study, attaining lower limits is not mandatory if the content of both metals in non-utilized oils is very low, whereas in the case of utilized lubricants the content grows to the $\mu g\,g^{-1}$ level and is easily detected under the conditions adopted here. The minimization of reagents and waste is an increasing concern when developing analytical procedures. When using only the dissolved oxygen present in the solutions, the detection limits of DPSA were not so favorable, but it was still possible to perform metal determination at low concentrations. Now studies utilizing the same approach for crude oil and diesel fuel are in the course of being developed in our laboratory.

Acknowledgements. The authors acknowledge the fellowships received from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP – Processo 01/11271-8) and Conselho Nacional de Pesquisa (CNPq – Processo 304031/1985-2). This study was also supported by a grant from the project CNPq/CT-Petro – Processo 502452/2003-0. L. Angnes and P. V. Oliveira are also grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the research fellowship provided.

References

[1] Ekanem E J, Lori J A, Thomas S A (1997) Talanta 44: 2103
[2] Zieba-Palus J (1998) Forensic Sci Int 91: 171
[3] Zieba-Palus J, Koscielniak P (2000) Forensic Sci Int 112: 81
[4] Fassel V A, Peterson C A, Abercrombie F N, Kniseley R N (1976) Anal Chem 48: 516
[5] Bangroo P N, Jagga C R, Arora H C, Rao G N (1995) Atom Spectrosc 16: 118
[6] Vandecasteele C, Block C B (1993) Modern methods for trace element determination. John Wiley & Sons, Chichester
[7] Burrows J A, Heerdt J C, Willis J B (1965) Anal Chem 37: 579

[8] Goncalves I M, Murillo M, Gonzalez A M (1998) Talanta 47: 1033
[9] Turunen M, Peraniemi S, Ahlgren M, Westerholm H (1995) Anal Chim Acta 311: 85
[10] Tamrakar P K, Pitre K S (2002) Bull Electrochem 18: 35
[11] Sanz-Segundo C, Hernandez-Artiga M P, de Cisneros J L, Bellido-Milla D, Naranjo-Rodriguez J (1999) Mikrochim Acta 132: 89
[12] Jin Q H, Liang F, Zhang H Q, Zhao L W, Huan Y F, Song D Q (1999) Trends Anal Chem 18: 479
[13] Luque-Garcia J L, de Castro M D L (2003) Trends Anal Chem 22: 90
[14] Nóbrega J A, Costa L M, Santos D M (2002) Analytica 1: 32
[15] Costa L M, Silva F V, Gouveia S T, Nogueira A R A, Nóbrega J A (2001) Spectrochim Acta B 56: 1981
[16] Sanz-Segundo C, Hernandez-Artiga M P, de Cisneros J L, Bellido-Milla D, Naranjo-Rodriguez I (2002) Bull Electrochem 18: 165
[17] Dunemann L, Meinerling M (1992) Fresenius J Anal Chem 342: 714
[18] Schramel P, Hasse S (1993) Fresenius J Anal Chem 346: 794
[19] Karadjova I, Girousi S, Iliadou E, Stratis I (2000) Mikrochim Acta 134: 185
[20] Pournaghi-Azar M H, Ansary-Fard A H (1998) Talanta 46: 607
[21] Lo Coco F, Monotti P, Rizzotti S, Ceccon L (1999) Anal Chim Acta 386: 41
[22] Dugo G, La Pera L, La Torre G L, Giuffrida D (2004) Food Chem 87: 639
[23] La Pera L, Saitta M, Di Bella G, Dugo G (2003) J Agric Food Chem 50: 1125
[24] La Pera L, Lo Curto S, Visco A, Dugo G (2002) J Agric Food Chem 51: 3090
[25] Lo Coco F, Ceccon L, Ciraolo L, Novelli V (2003) Food Control 14: 55
[26] Lo Coco F, Monotti P, Rizzoti S, Ceccon L (2000) Italian J Food Sci 12: 477
[27] Jagner D (1978) Anal Chem 50: 1924
[28] Town R M, Van Leeuwen H P (2001) J Electroanal Chem 509: 58
[29] Richter E M, Pedrotti J J, Angnes L (2003) Electroanalysis 15: 1871
[30] Richter E M, Augelli M A, Magarotto S, Angnes L (2001) Electroanalysis 13: 760
[31] Angnes L, Richter E M, Augelli M A, Kume G H (2000) Anal Chem 72: 5503
[32] Munoz R A A, Matos R C, Angnes L (2001) J Pharm Sci 90: 1972
[33] Munoz R A A, Matos R C, Angnes L (2001) Talanta 55: 855
[34] Pedrotti J J, Angnes L, Gutz I G R (1996) Electroanalysis 8: 673
[35] Nóbrega J A, Trevizan L C, Araújo G C L, Nogueira A R A (2002) Spectrochim Acta Part B 57: 1855
[36] Munoz R A A, Angnes L (2004) Microchem J 77: 157
[37] Miller J C, Miller J N (1992) Statistics for analytical chemistry. Harwood, Chichester
[38] Soares H M V M, Almeida A A N, Castro M P O, Pinho S C, Vasconcelos M T S D (1998) Analyst 123: 1377