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Combination of ultrasonic extraction and stripping analysis: An effective and reliable way for the determination of Cu and Pb in lubricating oils

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Abstract

The determination of metals in lubricating oil has been used as an important way to prevent components failures, to provide environmental information and in some cases, to identify adulteration. In this work, an effective and simple procedure is proposed for Cu and Pb determination in lubricating oils. An ultrasonic bath was employed for extraction of these elements from oil samples in a mixture 1:1 (v/v) of concentrated HCl and H_2O_2. A very efficient extraction of Cu and Pb (∼100%) was attained after 30 min of ultrasound, allowing the simultaneous determination of both metals using square-wave anodic stripping voltammetry at thin-film gold electrodes. The extraction procedure was performed in 4 mL polypropylene closed vessels and dozens of samples could be treated simultaneously in the same ultrasonic bath. The regions of the ultrasonic bath, where the maximum efficiency of extraction was attained were evaluated. Over the optimized region, 30 samples can be treated simultaneously. Used lubricating oils from automotive engines were analyzed by using the optimized extraction procedure.

Keywords: Ultrasonic extraction; Anodic stripping voltammetry; Gold electrodes; Lubricating oil; Copper; Lead

1. Introduction

Ultrasound-assisted (US-assisted) extraction is an effective procedure for removing a number of analytes from different types of samples. It is possible due to several combined effects: (a) extremely high effective temperatures, which result in a huge increase of solubility and diffusivity; (b) high pressures, which favor penetration between insoluble interfaces or between a solution and a solid matrix; (c) the oxidative energy of radicals created during sonolysis of the solvent (e.g. hydroxyl and hydrogen peroxide from water) [1]. Due to these characteristics, ultrasound energy has been used as an efficient procedure for sample preparation. In many situations, US-assisted treatment is a fast, inexpensive, and efficient alternative to conventional leaching processes. There are a number of applications to both organic and inorganic analytes in a wide variety of samples [1].

Several applications associating horns with electrochemical detectors for the determinations of elements in different kind of samples are described in the literature. These specific applications have been collectively named sonoelectroanalysis [2,3]. Lead in wine [4] and petrol [5], copper in beer [6], cadmium [7], copper [8], and zinc [9] in blood are some examples of US-assisted extraction using horns for stripping analysis. In most of examples, the US-assisted extractions were performed in situ during the metal deposition step at the working electrode. Matysik et al. [10] described with more details the principle and advantages of this technique.

Ultrasonic probes were also extensively applied for the metals extraction from biological [11–16], plant [17–20], and sediment samples [15,21,22] associated with atomic absorption spectrometry determinations using electrothermal or flame atomizers. Some important parameters were considered in these studies, such as sonication amplitude, exposure time, type and concentration of extractor, sample mass, and particle size. There is one application of ultrasonic extraction to environmental samples in which was used electroanalysis

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for metals determination. An important advantage of the methodology emphasized in this work was the possibility of in situ measurements [23].

A few papers describing the use of US-assisted treatment for metals extraction in ultrasonic baths can be found in the literature [22,24–28]. This small number of studies using ultrasonic bath can, probably, be attributed to its less efficient ultrasound irradiation and distribution in comparison to ultrasonic horns [10]. On the other hand, metallic horns (normally titanium) can also contain impurities, which would introduce contaminations into the solution, after long sonication periods [12].

The wear metals determination in lubricating oils has been used as an important way to prevent components failures of vehicular engines [29,30], to control the quality of engines [31,32], and to identify some specific adulteration. Additionally, these determinations can provide valuable environmental information.

Sample preparation is a step of capital importance in oil analysis, mainly when electroanalytical techniques are chosen for the detection. In general, oil samples have been completely decomposed using dry ashing [33] and wet digestion in hot plate [34], or microwave-assisted oven [35,36]. On the other hand, some procedures for the extraction of metals from oil samples can be found in the literature [37–43]. These procedures were used for metals extraction in different oil products with hot concentrated hydrochloric acid in a proper extractor for 60 min. A mixture of hydrochloric acid (37%) and hydrogen peroxide (30%) was used for metals extraction from oils in a Teflon beaker under stirring at 90 °C for about 30 min [41–43]. In all these studies [37–43], metal determination was carried out, using potentiometric stripping analysis (PSA) using an oxidant agent in the stripping step. In another study [44], an efficient US-assisted extraction (>90%) of lead from waste oils was attained in 1.50 mol L^{-1} of nitric acid. This recovery was possible using temperatures higher than 40 °C and sonicating power of 90 W in a batch cell or 60 W in a flow cell. Madigan et al. [45] described sonochemical deposition of copper particles in organic suspensions onto a gold electrode followed by anodic stripping voltammetry in a separated aqueous solution. Results indicating the possibility for oil analysis were also presented.

In this work, a reliable US-assisted extraction procedure for copper and lead determination in lubricating oil samples using anodic stripping voltammetry (ASV) is proposed.

2. Experimental

2.1. Reagents, samples, and materials

Copper and lead reference solutions were prepared from titrisol standard solutions (Merck, Darmstadt, Germany). High-purity deionised water ($R \geq 18\,\mathrm{M\Omega\,cm^{-1}}$) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all solutions and samples. Analytical grade concentrated hydrochloric (37%, m/v), nitric (65%, m/v), and sulfuric acids (97%, m/v), hydrogen peroxide (30%, m/v), sodium chloride, and ammonium monohydrogen phosphate (Merck, Darmstadt, Germany) were used without further purification. Used lubricating oil samples were obtained at local gas stations and were collected during oil changing operation in automotive vehicles. These samples were stored in polyethylene bottles at room temperature. All the glassy and plastic materials used for preparation and storage of samples and solutions were decontaminated with nitric acid (10%, v/v) during 24 h. The digested samples were stored in polyethylene vessels at 4 °C. The extractions were performed in 4 mL polypropylene closed vessels.

2.2. Instrumentation

A Microsonic SX-20 (Eurosonic, Brazil) ultrasonic bath operating at 20 kHz was used for extractions. The different regions in the ultrasonic bath were mapped to select the best irradiation positions. For comparative studies, a focused microwave-assisted oven CEM Star System 2 (Matthews, NC, USA) with two cavities was used for the digestions of the lubricating oil samples. Electrochemical measurements were performed with an Autolab PGSTAT20 potentiostat (Eco-Chemie, Utrecht, The Netherlands). A ZEEnit® 60 model (AnalytikjenaAG, Jena, Germany) graphite furnace atomic absorption spectrometer was employed for determination of copper and lead to compare with the electroanalytical results.

2.3. Electrochemical cell and electrodes

A homemade small Plexiglas cell (1 mL) was used for the electrochemical measurements. The determination of copper and lead in the extractor solutions was performed using thin-film gold electrodes manufactured from compact discs (Mitsui Gold Standard), which were developed in our group [46–50]. The electrode area was approximately 5 mm^2, delimited with enamel. For the simultaneous determination of copper and lead in the microwave digested samples, a thin mercury film plated onto a glassy carbon electrode (working electrode) was used. The mercury thin-layer film was obtained applying −900 mV for 5 min in a solution containing 1 mmol L^{-1} mercury(II) and 100 mmol L^{-1} HCl. A larger Plexiglas electrochemical cell (3 mL) was used for electrochemical measurements using the glassy carbon electrode. The reference and auxiliary electrodes were a miniaturized $\mathrm{Ag/AgCl_{(sat)}}$ [51] and a platinum wire, respectively.

2.4. Procedure

2.4.1. US-assisted extraction

Concentrated nitric and hydrochloric acids, hydrogen peroxide 30% (m/v) and a mixture of 1:1 (v/v) concentrated hydrochloric acid ($\mathrm{HCl_{conc}}$) and H_2O_2 were evaluated as extractor solutions. Aliquots varying from 20 μL (17 mg) to 100 μL (85 mg) of lubricating oil samples were used for method development in a fixed extractor solution (2.0 mL). The ultrasound exposure time was varied between 5 and 130 min. The extraction procedure could be performed for dozens of vessels simultaneously. The extractor solutions were taken from their flasks with a micropipette and transferred to decontaminated polypropylene vessels. After that, the vessels containing the extractor solutions were only opened partially and placed in a boiling water bath for 15 min to decompose the excess of hydrogen peroxide and to eliminate the gas bubbles, which prejudiced both, the transference of reliable aliquots for analysis, and consequently, the reproducibility of the measurements. The temperature of the solutions during the US-assisted extraction was monitored.

Additional studies were carried out to evaluate the metals extraction in different regions of the ultrasonic bath. This study was performed to corroborate a previous study [52], which indicated that the region over the piezoelectric crystals presented the higher ultrasound intensity. Therefore, this region was explored in the initial optimization studies, before the verification of the optimal region of the bath.

2.4.2. *Microwave digestion*

For the digestion of lubricating oil in the microwave oven, a program similar as the one described in a previous study [35] was adopted. It consists in transferring an aliquot of 1 mL (0.85 g) of the sample to be digested to the microwave vessel, adding 10 mL of (both) sulfuric and nitric acids and applying a sequence of ramps of temperature (100–220 °C, total time: 38 min). After that, 15 mL of hydrogen peroxide 30% is added together and the temperature is maintained at 220 °C for 7 min. From this treatment, a very clean solution was obtained.

2.4.3. *Stripping analysis*

Square-wave stripping voltammetry (SWSV) at gold electrodes was applied for the simultaneous determination of copper and lead in the extractor solutions. The initial copper determinations in extractor solutions were performed using chronopotentiometric-stripping analysis (CSA) at gold electrodes. The SWSV and CSA parameters are presented in Table 1.

Microwave oven digestion solutions were diluted at least 10 times before the determinations. Due to the different concentration of copper and lead in the diluted lubricating oil samples, the deposition time was studied. The standard addition method was applied for determination of copper and lead, using PSA at a mercury film plated onto a glassy carbon electrode [35].

Table 1
The SWSV and CSA parameters for the electrochemical measurements

Electrochemical parameters	SWSV	CSA
Conditioning potential (mV)	600	600
Conditioning time (s)	20	20
Deposition potential (mV)	−250	0
Deposition time (s)	30–120	15–60
Equilibrating time (s)	14	14
Step potential (mV)	40	–
Amplitude (mV)	4	–
Frequency (Hz)	20	–
Potential limit (mV)	–	600
Stripping current (μA)	–	0.4

2.4.4. *GFAAS determinations of the digested samples*

The determinations of copper and lead in electrothermal atomic absorption spectrometry were performed as previously described in the literature [35]. For lead determination, an aliquot of 20 μL of sample was co-injected with 5 μL of chemical modifier (20 μg of $(NH_4)_2HPO_4$) into the graphite tube atomizer. For copper determination, an aliquot of 20 μL of sample was just introduced into the graphite tube without chemical modifier. The digested solutions were diluted 5–10 times. In this study, the analytical reference solutions (0–40 $\mu g\,L^{-1}$ for copper and 0–60 $\mu g\,L^{-1}$ for lead) were prepared in 1% (v/v) nitric acid. The estimated detection limit of copper and lead were 314 and 330 $ng\,g^{-1}$, respectively.

3. Results and discussion

3.1. *US-assisted extraction*

Before reaching the optimal extractor for metals extractions from lubricating oils, different oxidant mixtures were evaluated. The use of concentrated nitric acid for US-assisted metal extractions led to undesirable results, probably, due to the generation of organic nitro-compounds that caused interferences on voltammetric measurements [53]. Concentrated hydrochloric acid alone did not extract copper with the same efficiency as in presence of an oxidant. The best extractor found was the combination of H_2O_2 (30%) and HCl_{conc}. During our preliminary experiments, the strong oxidant (aqua-regia) media was also tested. However, it cannot be used because it attacked the gold electrode. Moreover, hydrogen peroxide was more convenient than HNO_3 due to its easy elimination before the electrochemical measurement.

During the US-assisted extraction using H_2O_2 (30%) and HCl_{conc}, intense formation of bubbles inside the mini-vessels and the clarification of oil solution due to the H_2O_2 action in acid medium could be observed. These effects suggest the occurrence of an oxidative process on the oil by the oxidant extractor, which was necessary to liberate the metals from the organic matrix. This clarification was only observed using the mixture of the concentrated HCl and H_2O_2 as the extractor.

It was also observed the formation of a thin-layer of oil along the entire polypropylene tube wall, probably, due to the hydrophobic characteristics of the polymeric material. This behavior enhances significantly the superficial area between the oil and oxidant solution. Two favorable situations were created with this phenomenon: (a) the improvement of the extraction efficiency caused by the increase in the superficial contact area between organic and inorganic medias and (b) the

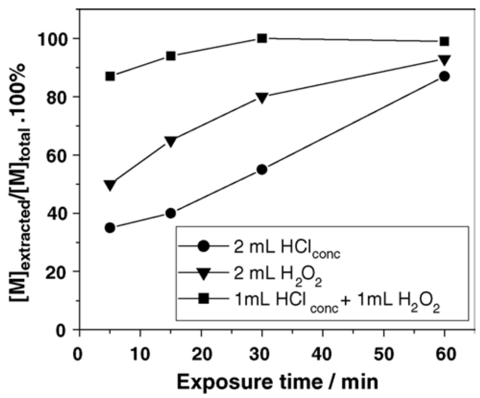

Fig. 1. Copper extraction performance from a lubricating oil sample during different ultrasonic exposure times in HCl_{conc}, H_2O_2 (30% w/v), and in a mixture 1:1 (v/v) of HCl_{conc} and H_2O_2.

near-total absence of residual oil in the aqueous medium facilitating the transference of a reproducible (and clean) volume of extractor solution directly to the cleaned vessels. There was no need to pass the extracted solutions through a carbon-retaining column to eliminate organic compounds that would interfere on electroanalysis.

Fig. 1 shows the extraction performance of concentrated hydrochloric acid, hydrogen peroxide and a mixture 1:1 (v/v) of HCl_{conc} and hydrogen peroxide (30% w/v), in function of sonication time. The mixture produces a synergetic extraction of copper.

The composition of the oxidant mixture chosen was evaluated (see Fig. 2). Two parallel experiments were performed: (a) 1 mL of HCl_{conc} was added to 20 μL of sample and (b) 1 mL of H_2O_2 was added to 20 μL of sample in another vessel. Aliquots of H_2O_2 were added in the first one, while aliquots of HCl_{conc} were added in the second, until 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2 were present in both vessels. The ultrasonic exposure time was fixed at 15 min. Near 100% efficiency was obtained using 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2 as extractor.

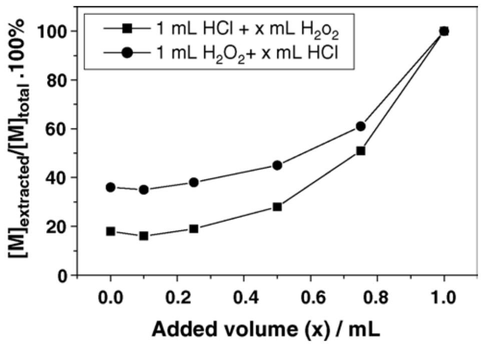

Fig. 2. Copper extraction performance from a lubricating oil sample in two parallel experiments; 1 mL of HCl_{conc} was added to 20 μL of sample in one vessel and 1 mL of H_2O_2 was added to 20 μL of sample in another vessel. Aliquots of H_2O_2 were added in the first one while aliquots of HCl_{conc} were added in the second, until 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2 were contained in both vessels. The ultrasonic exposure time was 15 min.

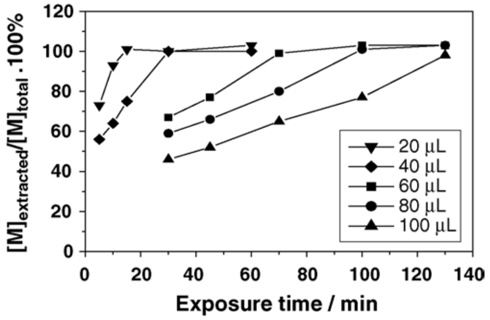

Fig. 3. Copper extraction performance for 20, 40, 60, 80, and 100 μL of a lubricating oil sample using 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2.

Fig. 3 shows the performance of copper extraction from 20, 40, 60, 80, and 100 μL of sample using 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2 as extractor for different exposure times in the ultrasonic bath. This figure demonstrates a good relation between the amount of sample and the time necessary for the complete liberation of the metal. So, for samples containing low levels of metals, it can be interesting to use larger amounts of sample, while for samples with higher concentrations, 20 μL of sample significantly abbreviates the sonication time necessary for the complete liberation of the metals.

The ultrasound energy accelerated intensively the extraction promoting an efficient stirring, but it is necessary to point out that the ultrasonic process was not the process primarily responsible for releasing the metal ions associated with the organic matrix.

The temperature in the vessels during an extraction process was monitored. When the vessels were put into the bath and the sonication process started, the solution temperature increased gently (2–4 °C) during 15 min of sonication. The increase was more accentuated during the first 5 min. Therefore, this slight heating cannot be a considerable factor that would be responsible for improving the extraction efficiency.

As previously demonstrated by other authors [52], the maximum sonochemical intensity was obtained at the region over the two crystals and the efficiency decayed with the distance. This was confirmed by extractions of copper and lead in different regions of the ultrasonic bath. Table 2 presents the recoveries of copper and lead after extractions performed in different regions of the ultrasonic bath. The ultrasonic exposure time was fixed at 30 min. The numbers in the first column of Table 2 indicate the different positions of the bath, as being 5a and 5b exactly over the crystals, 4a and 4b between the crystals whose position is exactly on the centre of the bath, while the other numbers represent different positions on the extremities of the bath, which are, respectively, more distant from the crystals in accordance with the copper recovery values.

More than 200 tubes (1.25 mm diameter, 8.1 cm length) could be submitted to sonication simultaneously. Exploring the optimal region designated as exactly over the piezoelectric crystals of the bath only 30 tubes (15 in each crystal) would be situated in this region. At the same time, many other samples

Table 2
Respective copper and lead recoveries for extractions performed in the different regions of the ultrasonic bath ($n = 3$)

Position	Pb ($\mu g\,g^{-1}$)	Recovery (%)[a]	Cu ($\mu g\,g^{-1}$)	Recovery (%)[a]
1a	0.664 ± 0.06	37 ± 3	5.8 ± 0.6	39 ± 4
1b	0.572 ± 0.05	32 ± 3	6.4 ± 0.6	43 ± 4
2a	0.966 ± 0.07	54 ± 4	7.1 ± 0.6	48 ± 4
2b	0.722 ± 0.06	40 ± 3	9.5 ± 0.8	64 ± 5
3a	1.19 ± 0.08	66 ± 4	9.6 ± 0.9	65 ± 6
3b	0.986 ± 0.06	55 ± 3	9.6 ± 0.9	66 ± 6
4a	1.24 ± 0.08	69 ± 5	14.2 ± 1.0	97 ± 8
4b	1.19 ± 0.09	66 ± 5	14.0 ± 1.4	95 ± 9
5a	1.74 ± 0.09	97 ± 5	14.2 ± 1.3	97 ± 9
5b	1.95 ± 0.14	108 ± 8	15.3 ± 1.4	104 ± 9

[a] Compared with Pb and Cu concentrations obtained after the total digestion of the sample.

can be also sonicated in a less effective condition, reducing the time necessary at the optimum region (the tubes from other positions can be moved to the best region every time that a tube is taken off to perform the respective analysis). A special type of ultrasonic bath should be designed to extend the region in which improved extractions could be performed in large scale for routine applications. Hence, it was easy to conclude that the metals determination sequence was the determinant step of the analysis frequency.

To evaluate the efficiency of metals US-assisted extraction from a lubricating oil sample, the copper and lead determination in the extraction solutions was carried out and in the same sample digested in the focused microwave oven.

3.2. Electrochemical determinations

Due to the presence of organic compounds in the extractor solutions (after US-assisted extraction), the initial optimization experiments were done using CSA for copper determination with gold electrodes. This technique is less susceptible to the interference of organic compounds adsorption onto the working electrode than stripping voltammetry [54]. After initial optimization of the extraction procedure, it was thought to extend the same technique for lead determination in the same conditions. Unfortunately, the sensitivity of this technique for lead is very poor, and for this reason, it was necessary to explore other ways to get the simultaneous determination of lead and copper.

In earlier studies done in our group, good results for copper and lead determination in rainwater and ethanol fuel were attained using square-wave stripping voltammetry at gold electrodes [46,55]. In these studies, we also observed the improvement of the signal and good peaks resolution, especially, for lead, when chloride ions were added in the electrolyte. Hence, the best electrolyte for SWSV using gold electrodes was obtained by diluting the extractor solutions. Therefore, SWSV was applied for the simultaneous determination of copper and lead in the extractor solutions using the same extraction conditions optimized for copper.

The choice of the deposition potential for SWSV determination of copper and lead was limited by the hydrogen overpotential, which specially affected the lead signal.

The application of −400 mV in diluted hydrochloric acid solutions resulted in good signals for lead. However, in present study, the extractors containing the analytes were diluted only 10 times, resulting in a very acidic electrolyte ($\sim 0.6\,mol\,L^{-1}$ of HCl). There was not observed any hydrogen bubble on the working electrode when −250 mV was applied in such acidic electrolytes. This potential was adopted in further measurements.

The deposition time was varied from 30 to 300 s (at −250 mV) for solutions containing copper and lead at concentrations similar to that typically found in lubricating oils. Generally, the copper content in the analyzed samples was much higher than the lead content. The satisfactory results were attained using 60 or 120 s. The copper signal behavior was always linear until 300 s, while for lead only until 120 s. Even so, some increase of the lead signal was verified when deposition times higher than 120 s were applied, but this enhancement was a non-linear one.

The results obtained for copper and lead extraction from 20 and 40 μL of sample, using 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2 as extractor, for different exposure times in the ultrasonic bath are shown in Fig. 4. There, the best extraction performance for copper is evident. This behavior suggests that copper was more labile than lead in this situation because it was more easily liberated from the oil matrix.

Lubricating oil samples were analyzed after the optimized US-assisted extraction of copper and lead by SWSV. Table 3 shows the elements concentrations obtained by both PSA and GFAAS after the total microwave digestion and by SWSV after the ultrasonic extraction procedure applied to four different used motor oil samples. The US-assisted extraction condition for 20 μL (17 mg) of oil sample with 30 min exposure time and 2 mL of mixture 1:1 (v/v) HCl_{conc} and H_2O_2 was the best one. This time (30 min) was necessary for the total lead extraction, while for copper only 15 min were necessary.

The voltammograms for an aliquot of an extracted sample diluted 10 times, plus three additions of standard solutions

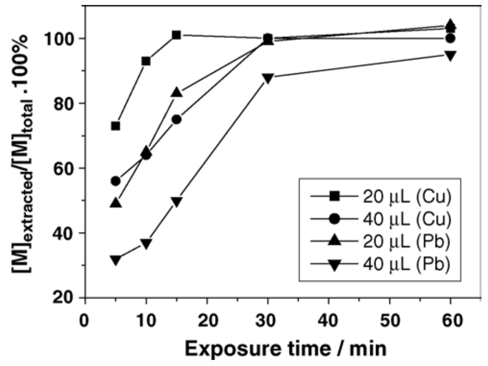

Fig. 4. Copper and lead extraction performance for 20 and 40 μL of a lubricating oil sample using 2 mL of 1:1 (v/v) HCl_{conc} and H_2O_2.

Table 3
Concentrations of copper and lead obtained by SWSV after the proposed extraction method and by PSA and GFAAS after the total digestion of samples in used lubricating oil samples (µg g^{-1} of sample, $n = 3$)

Samples	Proposed method (SWSV)		Comparative method (PSA)		Comparative method (GFAAS)	
	Cu	Pb	Cu	Pb	Cu	Pb
1	17.5 ± 0.2	0.90 ± 0.10	17.4 ± 0.1	0.91 ± 0.03	17.5 ± 0.2	0.97 ± 0.05
2	14.8 ± 0.6	1.74 ± 0.14	11.7 ± 0.1	1.76 ± 0.06	14.7 ± 0.13	1.80 ± 0.04
3	15.6 ± 0.9	7.5 ± 0.5	15.6 ± 0.9	7.59 ± 0.15	17.1 ± 0.1	7.6 ± 0.2
4	21.1 ± 0.1	0.82 ± 0.09	23.0 ± 0.1	0.85 ± 0.08	21.5 ± 0.1	0.78 ± 0.01

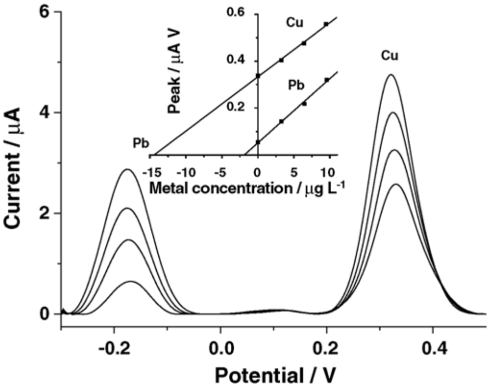

Fig. 5. Voltammograms for an aliquot of an extracted sample diluted 10 times (60 µL in 600 µL), plus three additions of 10 µL of 200 µg L^{-1} standard solution of copper and lead. The respective calibration curves are presented. SWSV conditions are listed in Table 1.

of copper and lead (3.3 µg L^{-1}) are shown in Fig. 5. The respective calibration curves are also presented.

The detection limit for SWSV determination of lead and copper was 67 and 23 ng g^{-1} of lubricating oil (S/N = 3), respectively, calculated for the extraction of 17 mg of sample, and considering the dilution (10 times) of the extracted solutions. The deposition time utilized in these measurements was 120 s. For samples with lower concentrations of metals, this time can be increased and the detection limits that can be obtained will be lower than the ones calculated here.

4. Conclusions

The association of ultrasonic extraction (using an ultrasonic bath) for copper and lead liberation from lubricating oil samples, and stripping techniques (such as ASV) for their posterior determination, provides a very interesting possibility for routine analysis. The required instrumentation presents advantages because of the low cost of acquisition and maintenance, and because such instrumentation is easily found in many laboratories. Another great advantage is that the sample pretreatment can be performed for dozens of samples simultaneously, at room temperature, and at atmospheric pressure, instead of requiring individual samples, as happens in cases when a horn is utilized. The same method of sample treatment can also be utilized for the quantification of other metals. Currently, our group has initiated studies to establish conditions for trace metals quantification in crude oil. These aspects are very important in refineries, such as the ones in Brazil, which receives crude oil from many regions of the world.

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