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## Simultaneous determination of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry using a glassy carbon–mercury-film electrode

Received: 15 April 2004 / Revised: 15 June 2004 / Accepted: 16 June 2004 / Published online: 20 July 2004  
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**Abstract** A new, versatile, and simple method for quantitative analysis of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry is described. These metals can be quantified by direct dissolution of fuel ethanol in water and subsequent voltammetric measurement after the accumulation step. A maximum limit of 20% (v/v) ethanol in water solution was obtained for voltammetric measurements without loss of sensitivity for metal species. Chemical and operational optimum conditions were analyzed in this study; the values obtained were pH 2.9, a 4.7- $\mu\text{m}$  thickness mercury film, a 1,000-rpm rotation frequency of the working electrode, and a 600-s pre-concentration time. Voltammetric measurements were obtained using linear scan (LSV), differential pulse (DPV), and square wave (SWV) modes and detection limits were in the range  $10^{-9}$ – $10^{-8}$  mol L $^{-1}$  for these metal species. The proposed method was compared with a traditional analytical technique, flame atomic absorption spectrometry (FAAS), for quantification of these metal species in commercial fuel ethanol samples.

**Keywords** Alternative fuel · Ethanol · Heavy metals · Mercury film electrode · Anodic stripping voltammetry

### Introduction

Fuel ethanol

Several petroleum crises from 1970–1980 resulted in a substantial increase in the price of petroleum per barrel and stimulated research into alternative sources

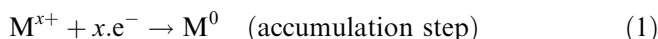
of energy in various countries. As a result, ethyl alcohol obtained from sugar cane has been successfully used as an alternative fuel for national automobiles in Brazil since 1975. It was initially used as an additive in gasoline and subsequently as a new fuel option with economic and ecological advantages [1, 2].

Despite generating less pollution than petroleum derivatives [3–6], ethyl alcohol does contain contaminants, for example organic compounds (methanol, aldehydes, esters, etc.) and inorganic species, for example metals (zinc, copper, cadmium, iron, chromium, nickel, cobalt, lead, etc.). These contaminants can arise from production process, transport, or fuel storage [7, 8]. In this context, analysis of metallic contaminants in fuel ethanol is a relevant research field in Brazil; conventional techniques such as chromatography and spectrometry are used [7–9].

### Electroanalytical applications

Electrochemical methods of analysis have been extensively employed for determination of trace metals in a wide range of matrixes of human interest, for example food [10, 11], beverages [12, 13], biological fluids [14], and others; the practicability, precision, and selectivity of these methods are comparable with those of traditional techniques of analysis such as spectrometric and chromatographic methods, besides utilizing more accessible equipment.

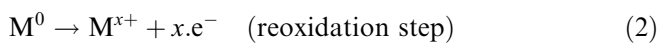
A frequently used electroanalytical procedure for metal trace determination is anodic stripping voltammetry; reported detection limits (DL) are in the ppb range for various metals. This experimental procedure consists in accumulation of reduced metallic species on the working electrode surface by applying a reduction potential for a pre-established interval of time:



and subsequent potential sweep at oxidation range,

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being obtained a resulting anodic current with linear dependence to metal concentration in a broad range of analysis.



### Mercury film electrodes (MFEs)

Chemical modification of electrode surfaces by mechanical or electrochemical inclusion of analytes has several advantages in terms of selectivity, sensitivity, and efficiency in the determination of metallic species by electroanalytical techniques [15–17], including metal analyses of petroleum-derived fossil fuels [18, 19].

In this context, a successful electrode for metal analysis is an MFE comprising a thin layer of metallic mercury electrodeposited on a conventional solid and inert surface such as glassy carbon. This kind of electrode has experimental advantages such as a high surface area/volume ratio, resulting in a higher concentration of amalgam during the deposition step, which increases the sensitivity. Additionally, MFEs have high mechanical resistance, being stable to vigorously stirring or coupled with flow systems [20, 21]; this increases their applicability.

Despite the importance of quality control of fuel ethanol, the literature contains no reports of studies of voltammetric determination of these metallic species in this fuel. So, the aim of this work was to develop an electrochemical method for simultaneous determination of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry using a glassy carbon–mercury-film electrode.

## Experimental

### Reagents

#### *Supporting-electrolytes*

Hydrochloric acid from Merck, lithium chloride from Mallinckrodt, and lithium hydroxide from Vetec were used to prepare lithium chloride solutions of different pH to act as supporting electrolytes. All reagents were of analytical grade purity. Lithium chloride was chosen because of its high solubility in ethyl alcohol. Two groups of stock solutions of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  of these reagents were prepared separately, one in deionized water and the other in HPLC-grade ethyl alcohol from Aldrich.

#### *Metal standard solutions*

Standard solutions of zinc, copper, lead, and cadmium were prepared by dilution of corresponding analytical purity-grade sulfate and chloride salts in the supporting-

electrolyte solutions described above; the solutions were standardized by complexometric titration according to the literature [8]. Two groups of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  solutions containing each metal were prepared, one in water and the other in alcohol. A  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  mercury nitrate stock solution in  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  aqueous lithium chloride solution was used for mercury film preparation.

### Equipment

#### *Cell and electrodes*

Voltammetric measurements were obtained in a conventional electrochemical cell with a 2-mm diameter glassy carbon electrode (working electrode), a  $0.25\text{-cm}^2$  platinum plate (auxiliary), and a saturated calomel reference electrode (SCE). Oxygen was removed from the solutions of interest by nitrogen gas flow, through a coupled Teflon tube in the cell.

#### *Apparatus*

A potentiostat from PAR EG&G, model 273A, coupled to a microcomputer was used to obtain the voltammograms. During the deposition step electrode rotation was achieved by using a rotation generator from PAR EG&G, model 616RDE.

pH was measured by using a pH meter from Corning, model 455, with a coupled temperature corrector.

Flame atomic absorption spectroscopy (FAAS) experiments were carried out by using a spectrometer from Perkin–Elmer, model A Analyst 100, coupled to a printer. Hollow cathode lamps from Perkin–Elmer were utilized for each metallic species.

### Procedure

#### *Preparation of the MFE*

Electrochemical deposition of a mercury film on the glassy carbon electrode surface was achieved according to a conventional procedure reported in the literature [22]. The electrochemical cell contained  $30 \mu\text{L}$   $1.0 \times 10^{-2} \text{ mol L}^{-1}$  mercury nitrate solution diluted to a final volume of 15 mL with an aqueous solution of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  lithium chloride, resulting to a  $2.0 \times 10^{-5} \text{ mol L}^{-1}$  solution in mercury ions. After de-aerating this solution with nitrogen flow for 15 min, a potential of  $-0.9 \text{ V}$  vs. SCE was applied to the system for 20 min, with a rotation value of 200 rpm for the working electrode, and the resulting electrical current was recorded as a function of the time. After film formation the electrode was rinsed with deionized water and stored in an aqueous supporting-electrolyte solution.

### Optimization of the composition of the reaction medium

The best reaction medium for analysis was investigated by using different alcohol/water compositions from 0 to 100% *w/w*, prepared by mixing aqueous supporting electrolyte solution, as previously described, with ethyl alcohol. To each 15 mL of studied solution was added 30  $\mu\text{L}$  of each metal standard solution, to give metal solutions of concentration  $2.0 \times 10^{-6} \text{ mol L}^{-1}$ . Voltammetric measurement of the different solutions was performed by linear sweep voltammetry (LSV) with a scan rate of  $100 \text{ mV s}^{-1}$ , a potential interval from  $-1.4$  to  $0 \text{ V}$  versus SCE, a  $-1.4 \text{ V}$  versus SCE potential value for the stripping step at a 10-min time interval, and a 200-rpm rotation for the MFE.

### Optimization of experimental conditions

The optimum pH for analysis was investigated. Ten 15-mL aliquots of the previously optimized reaction medium were prepared at pH ranging from 2 to 11 and fixed ionic strength. Standard solutions of the metal species were added to these solutions in the same way as described above and LSV was again used for voltammetric measurements, under the same conditions as described above. Film thickness was also investigated. Mercury films of different thickness were obtained by the procedure described above for different deposition times from 2 to 30 min. The optimum value of the rotation frequency for MFE was obtained by variation of the frequency from 0 to 1,000 rpm. Finally, the best value for deposition time stripping step was studied from 1 to 30 min.

### Zinc, copper, lead, and cadmium analysis in commercial samples of fuel ethanol

After optimization of experimental and voltammetric conditions for the three different modes of voltammetry, three commercial samples of fuel ethanol from different

gas stations in Araraquara city were analyzed. Each 3 mL sample was initially diluted to a final volume of 15 mL with supporting electrolyte. Further 100-fold dilution to furnish second and third samples was also necessary. Quantitative analysis of these metals by flame atomic absorption spectrometry (FAAS) was also performed to enable comparison between a conventional technique and the new proposed methodology; FAAS was performed in accordance with experimental conditions reported in the literature [8] and the concentration of the metallic species was obtained by use of a calibration curve in the interval from  $1.0 \times 10^{-7}$  to  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ .

## Results and discussion

Optimization of the composition of the reaction medium and other experimental conditions

Voltammograms obtained for zinc, copper, lead, and cadmium at different water/alcohol compositions were analyzed in terms of anodic peak current ( $i_{\text{ap}}$ ) and anodic peak potential ( $E_{\text{ap}}$ ) for each metallic species; the results are reported in Table 1.

According to these results  $i_{\text{ap}}$  values decrease when the concentration of alcohol is increased, indicating more difficult accumulation of metal on the mercury film. An explanation for these results might be 13 times higher cell resistance [23] for ethanol and lower dielectric constant. Table 1 indicates that 80% water and 20% ethanol (*w/w*) gives the best results, i.e. this is the maximum percentage of ethanol which does not lead to loss of sensitivity. For solutions with alcohol concentrations above 80%, amperometric response is observed for cadmium only. It was also shown that voltammetric speciation of these metals is not possible for ethanol concentrations higher than 80%.

Optimized experimental conditions, i.e. pH, film thickness, rotation, and deposition time, for voltammetric analysis are reported at Table 2.

**Table 1** Influence of the composition of the reaction medium on  $i_{\text{ap}}$  and  $E_{\text{ap}}$  for analysis of zinc, copper, cadmium, and lead by anodic stripping voltammetry in LS mode

Composition (% water)	Zinc		Cadmium		Lead		Copper	
	$i_{\text{ap}}$ ( $\mu\text{A}$ )	$E_{\text{ap}}$ (V) vs. SCE	$i_{\text{ap}}$ ( $\mu\text{A}$ )	$E_{\text{ap}}$ (V) vs. SCE	$i_{\text{ap}}$ ( $\mu\text{A}$ )	$E_{\text{ap}}$ (V) vs. SCE	$i_{\text{ap}}$ ( $\mu\text{A}$ )	$E_{\text{ap}}$ (V) vs. SCE
100	7.2	-1.10	61.6	-0.54	18.4	-0.41	21.4	-0.06
90	1.7	-1.12	37.0	-0.57	10.6	-0.43	23.0	-0.16
80	1.6	-1.05	36.2	-0.49	16.4	-0.34	19.6	-0.16
70	1.2	-1.06	28.8	-0.56	11.5	-0.42	12.5	-0.16
60	1.3	-1.11	20.9	-0.60	13.8	-0.49	15.9	-0.17
50	1.3	-1.10	11.2	-0.63	8.7	-0.52	16.1	-0.20
40	1.3	-1.11	5.6	-0.66	7.2	-0.53	16.5	-0.22
30	1.2	-1.10	4.3	-0.70	6.7	-0.57	17.2	-0.27
20	-	-	3.7	-0.78	-	-	-	-
10	-	-	-	-	-	-	-	-
0	-	-	-	-	-	-	-	-

$v$  100  $\text{mV s}^{-1}$ ,  $t_{\text{dep}}$  10 min,  $E_{\text{ap}}$  -1.4 V vs. SCE

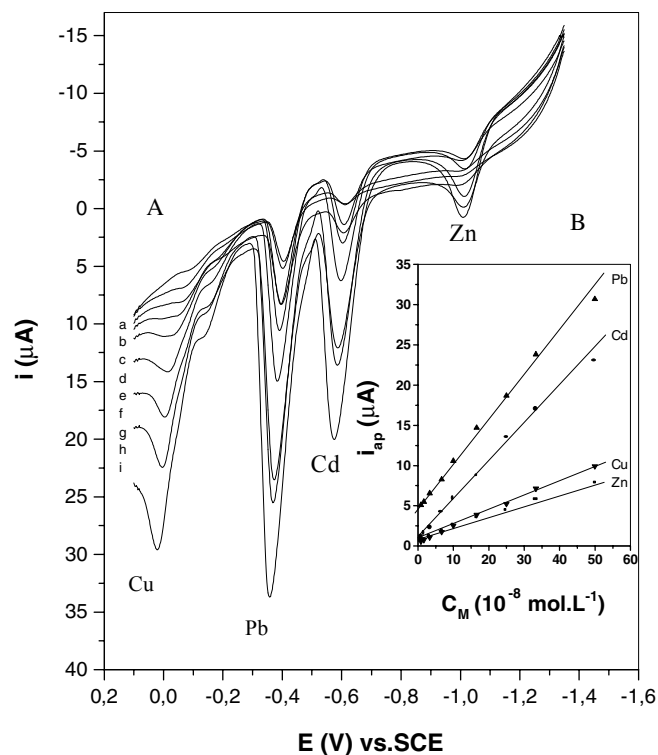
**Table 2** Optimized experimental conditions for voltammetric analysis of metallic species in fuel ethanol

pH	L $\mu\text{m}^{-1}$	r rpm <sup>-1</sup>	t <sub>dep</sub> s <sup>-1</sup>
2.9	4.7	1,000	600

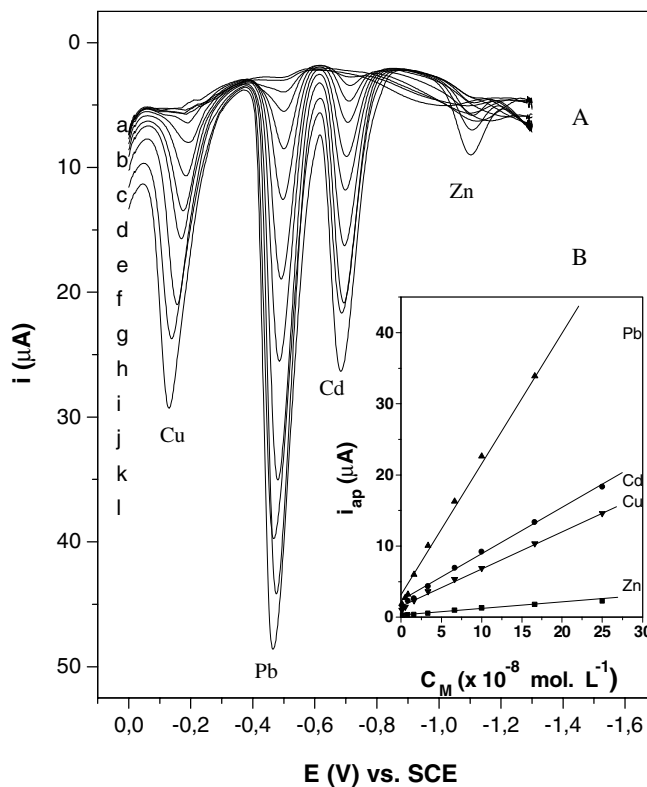
### Optimization of conditions for voltammetry

An important condition in LSV is the scan rate. In this study it was observed that  $E_{ap}$  values were disturbed at high positive values of the scan rate and that the linear dependence of  $i_{ap}$  on the square root of scan rate ( $v$ ) enables important information to be obtained about mass transport and about the reversibility of the chemical reaction [24, 25]. An initial value of the scan rate of 100 mV s<sup>-1</sup> was established for voltammetric measurements.

After optimization of the voltammetric conditions, concentrations of zinc, copper, lead, and cadmium from  $8.0 \times 10^{-9}$  to  $5.0 \times 10^{-7}$  mol L<sup>-1</sup> were investigated; the voltammograms obtained are reported in Fig. 1A and the respective calibration curves for these metals are reported in Fig. 1B.



**Fig. 1** A Voltammograms obtained in LSV mode for different concentrations of zinc, copper, lead, and cadmium in a solution of 0.01 mol L<sup>-1</sup> lithium chloride in 80/20% water/ethanol at pH 2.9 as supporting electrolyte;  $t_{dep}$  10 min,  $r$  1,000 rpm. Concentrations: (a) 0.83 (b) 1.66 (c) 3.33 (d) 6.66 (e) 10.0 (f) 16.6 (g) 25.0 (h) 33.3 (i)  $50.0 \times 10^{-8}$  mol L<sup>-1</sup>. B Respective calibration curves for the metallic species

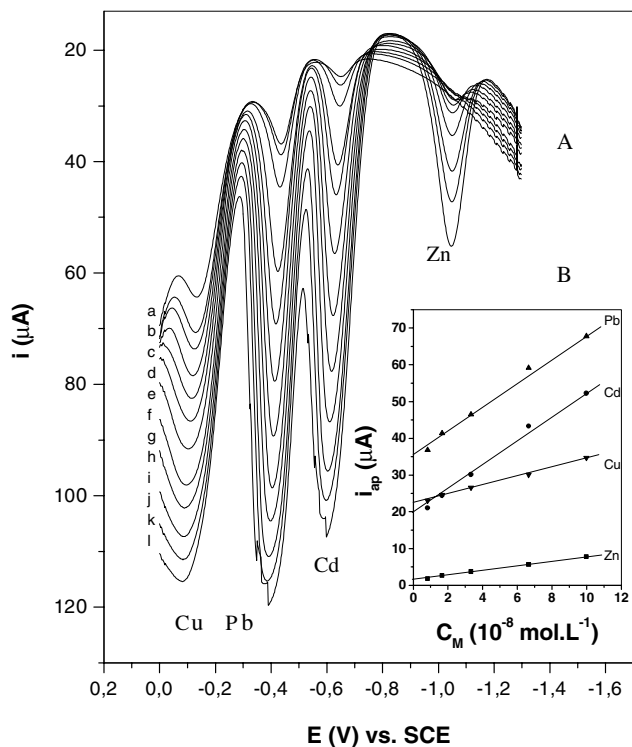


**Fig. 2** A Voltammograms obtained in DPV mode for different concentrations of the metallic species.  $t_{dep}$  10 min,  $r$  1,000 rpm. Concentrations: (a) 0.10 (b) 0.20 (c) 0.50 (d) 0.83 (e) 1.60 (f) 3.33 (g) 6.66 (h) 10.0 (i) 16.6 (j) 25.0 (k) 33.3 (l)  $50.0 \times 10^{-8}$  mol L<sup>-1</sup>. B Respective calibration curves for the metallic species

Use of differential pulse voltammetric (DPV) mode resulted in optimized potential scan rate and pulse magnitude of 5 mV s<sup>-1</sup> and 100 mV, respectively. Concentrations of the metallic species from  $8.0 \times 10^{-9}$  to  $5.0 \times 10^{-7}$  mol L<sup>-1</sup> were investigated using this mode of voltammetry. The voltammograms obtained are reported at Fig. 2A and respective calibration curves for these metals are reported in Fig. 2B. Similar behavior in terms of affinity was obtained for this modality, i.e. Pb > Cd > Cu > Zn.

For square wave voltammetry (SWV) the optimized pulse magnitude ( $E_{sw}$ ) and pulse frequency ( $f$ ) were established as being 100 mV and 75 Hz, respectively. The range of concentrations studied was from  $8.0 \times 10^{-9}$  to  $5.0 \times 10^{-7}$  mol L<sup>-1</sup>. The voltammograms obtained are reported in Fig. 3A and respective calibration curves are shown in Fig. 3B.

The calibration curves obtained for the metallic species using the three modes of voltammetry enabled determination of important electrochemical properties such as amperometric sensitivity ( $a$ ), linear correlation coefficient ( $r$ ), standard deviation (SD), and detection limit (DL). The values obtained are reported at Table 3. For DL calculation a theoretical procedure was followed according to the literature [22].



**Fig. 3** **A** Voltammograms obtained in SWV mode for different concentrations of the metallic species.  $t_{\text{dep}} = 10$  min,  $r$  1,000 rpm. Concentrations: (a) 0.10 (b) 0.20 (c) 0.50 (d) 0.83 (e) 1.60 (f) 3.33 (g) 6.66 (h) 10.0 (i) 16.6 (j) 25.0 (k) 33.3 (l)  $50.0 \times 10^{-8}$  mol L $^{-1}$ . **B** Respective calibration curves for the metallic species

Zinc, copper, lead, and cadmium analysis in commercial samples of fuel ethanol

#### Voltammetric analysis

Because of its good DL values and better working concentration range, DPV mode was employed for voltammetric analysis of zinc, copper, lead, and cadmium in commercial fuel ethanol samples.

**Table 3** Voltammetric data obtained from analysis of zinc, cadmium, lead, and copper by use of LSV, DPV and SWV modes

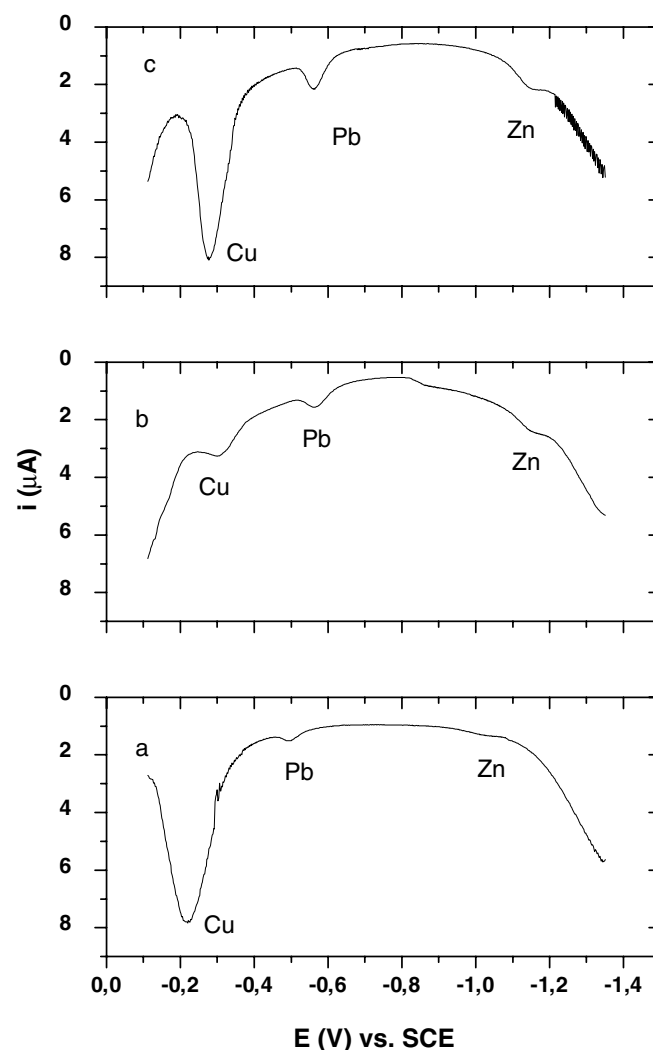
	$a$ ( $10^7 \mu\text{A mol}^{-1} \text{L}$ )	$r$	SD ( $\mu\text{A}$ )	DL ( $10^{-9} \text{mol L}^{-1}$ )
Zn				
LSV	1.45	0.9957	0.40	25.9
DPV	0.87	0.9964	0.16	19.8
SWV	6.3	0.9981	0.16	8.06
Cd				
LSV	4.63	0.9974	0.40	25.9
DPV	6.68	0.9977	0.44	19.7
SWV	34.5	0.9972	1.12	9.70
Pb				
LSV	5.35	0.9975	0.68	38.0
DPV	19.6	0.9971	0.94	14.5
SWV	33.7	0.9961	1.31	16.0
Cu				
LSV	1.92	0.9991	0.15	23.4
DPV	5.37	0.9980	0.31	17.3
SWV	12.2	0.9978	0.35	8.58

Three different samples of conventional fuel ethanol were studied, each one in triplicate. Examples of the voltammograms obtained for each sample are reported in Fig. 4.

Traces of zinc, copper, and lead were found in the commercial samples studied. Despite use of one of the highest amperometric sensitivities, no traces of cadmium were found in these samples. Mean values and standard deviations for these trace metals are reported in Table 4.

#### Spectroscopic analysis

For determination of metal concentrations in the commercial samples by FAAS, sensitivity for cadmium was highest, with an  $a$  value of  $3.17 \times 10^4 \text{ mol}^{-1} \text{L}$ , an  $r$ -value of 0.9968, and an SD value of 0.0099. These results resulted in a DL value of  $8.98 \times 10^{-6} \text{ mol L}^{-1}$ .



**Fig. 4** Voltammetric analysis in DPV mode of zinc, copper, lead, and cadmium in commercial fuel ethanol samples.  $t_{\text{dep}} = 10$  min,  $r$  1,000 rpm, LiCl 0.01 mol L $^{-1}$  as supporting electrolyte. **a** Sample 1: 3.0 mL of added sample; **b** Sample 2: 300  $\mu\text{L}$  of added sample **c** Sample 3: 300  $\mu\text{L}$  of added sample

**Table 4** Concentrations of trace metals in commercial fuel ethanol samples measured by DPV and by FAAS

Sample	$C_{Zn}$ ( $\times 10^{-7}$ mol L $^{-1}$ )		$C_{Cu}$ ( $\times 10^{-7}$ mol L $^{-1}$ )		$C_{Pb}$ ( $\times 10^{-7}$ mol L $^{-1}$ )	
	DPV	FAAS	DPV	FAAS	DPV	FAAS
1	ND	ND	4.78 $\pm$ 0.20	ND	12.1 $\pm$ 0.57	13.4 $\pm$ 0.73
2	7.40 $\pm$ 0.28	8.23 $\pm$ 0.53	8.31 $\pm$ 0.39	8.71 $\pm$ 0.48	24.1 $\pm$ 1.10	26.3 $\pm$ 1.30
3	1.04 $\pm$ 0.04	ND	6.42 $\pm$ 0.31	ND	8.10 $\pm$ 0.39	7.4 $\pm$ 0.42

ND not detected

Zinc resulted in the second highest absorptive sensitivity,  $2.67 \times 10^4$  mol $^{-1}$  L, with an  $r$ -value of 0.9983, an SD value of 0.002 and a DL of  $2.36 \times 10^{-7}$  mol L $^{-1}$ . Copper and lead resulted in the lowest of sensitivity,  $7.37 \times 10^3$  and  $1.55 \times 10^3$  mol $^{-1}$  L, respectively. The  $r$ -values for the calibration curves for these metals were 0.9992 and 0.9732, respectively, and the SD values 0.0019 and 0.0003. DL values for these metals were  $8.78 \times 10^{-7}$  and  $6.57 \times 10^{-7}$  mol L $^{-1}$ , respectively. According to the results obtained by use of this technique, without an accumulation step, DL values for the metals studied were between  $10^{-7}$  and  $10^{-6}$  mol L $^{-1}$ , so the technique was less sensitive than voltammetry. Results obtained from analysis of metals in commercial samples by FAAS are also reported at Table 4; this enables comparison of the spectroscopic and voltammetric techniques.

## Conclusions

According to the results obtained it is possible to conclude that electrochemical deposition of a mercury film on glassy carbon electrodes enables use of the electrode as a transducer for determination of zinc, copper, lead, and cadmium in fuel ethanol samples by anodic stripping. The optimum pH was 2.9 and the best supporting electrolyte was 20/80 ethanol/water.

Furthermore, the voltammetric modes LSV, DPV, and SWV when employed with an accumulation step enabled simultaneous analysis of zinc, copper, and lead species in commercial fuel ethanol samples with DL values from  $10^{-9}$  to  $10^{-8}$  mol L $^{-1}$ , approximately ten to 100 times more sensitive than FAAS. Voltammetric techniques also have experimental advantages, for example no need for an atomization step, use of specific reagents for the accumulation step, and low cost of cell and equipment.

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