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# On-site fuel electroanalysis: Determination of lead, copper and mercury in fuel bioethanol by anodic stripping voltammetry using screen-printed gold electrodes

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## HIGHLIGHTS

- Screen-printed gold electrodes for fuel bioethanol analysis.
- Stripping voltammetric determination of Pb, Cu and Hg in fuel bioethanol.
- Routine and on-site determination of metals in fuel bioethanol.
- Promising applications of screen-printed electrodes for fuel analysis.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The potential application of commercial screen-printed gold electrodes (SPGEs) for the trace determination of lead, copper, and mercury in fuel bioethanol is demonstrated. Samples were simply diluted in  $0.067 \text{ mol L}^{-1}$  HCl solution prior to square-wave anodic stripping voltammetry (SWASV) measurements recorded with a portable potentiostat. The proposed method presented a low detection limit ( $<2 \mu\text{g L}^{-1}$ ) for a 240 s deposition time, linear range between 5 and  $300 \mu\text{g L}^{-1}$ , and adequate recovery values (96–104%) for spiked samples. This analytical method shows great promise for on-site trace metal determination in fuel bioethanol once there is no requirement for sample treatment or electrode modification.

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## 1. Introduction

Bioethanol is the largest volume biofuel used in the transportation sector, mainly produced from sugarcane in Brazil and from corn in the US. Its use has contributed to the decrease in pollutant emissions and has brought economic advantages over fossil fuels. In Brazil, fuel bioethanol is consumed either in the hydrated form (95% (v/v) ethanol) as a car fuel or in the anhydrous form, added to gasoline (25% (v/v) ethanol) to act as an antiknock agent. The

production and commercialization of bioethanol for use as a vehicular fuel depends on rigorous quality control. American, Brazilian and European norms establish upper limits in bioethanol for some contaminants in bioethanol, including chloride, sulphate, sodium, and copper [1,2]. The presence of copper in anhydrous bioethanol form gums in contact with gasoline, which clogs engine pipes and injectors. Due to the depletive effects of copper as a catalyst for oxidation processes in fuels, the Brazilian norm establishes a more stringent limit in fuel bioethanol ( $0.07 \text{ mg kg}^{-1}$ ) than the American and European norms ( $0.1 \text{ mg kg}^{-1}$ ). Nevertheless, other metallic impurities at low concentrations, such as Fe, Ni, Mn, Co, Pb, and Zn, can degrade biofuels by catalysing oxidation processes in gasoline or biodiesel [3–6]. The determination of trace

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metals in fuel bioethanol can provide evidence on metallic corrosion occurring during transport and storage and can give an indication of emission levels of metals to the environment [2,7–9]. Highly toxic metals such as lead and mercury can be incorporated into bioethanol due to the intensive use of fertilizers, vinasse, and sewage sludge in the cultivation of the sugarcane and corn used for biofuel production [10,11].

Considering the requirements for quality control of bioethanol, the development of sensing devices capable of determining trace metals rapidly and accurately is in great demand for fast on-site analysis. Screen-printed electroanalytical sensors are inexpensive, disposable, easily operated by portable mini-potentiostats, and provide sensitive and accurate determinations of a large variety of analytes, as highlighted in recent reviews [12,13]. The use of screen-printed electrodes (SPEs) for trace metal determination has been widely reported in the recent literature [13–20]. However, few applications of SPEs involve the analysis in water-miscible organic solvents such as methanol or ethanol [21]. Therefore, other types of electrodes have been previously explored for biofuel analysis. Modified (carbon-paste or composite) electrodes as well as a gold microelectrode were reported for copper determination in fuel bioethanol [22–24]. The simultaneous determination of copper and lead at a gold disc electrode [25] and of cadmium, copper, lead and zinc at a mercury-film electrode [26] were also reported. Simultaneous determinations are appropriate for fast screening of the biofuel sample in order to reveal the nature of contamination (once different metals indicate corrosion of storage tanks or contamination by natural sources or during production) and to verify if deleterious metals may be in contact with gasoline, accelerating degradation processes (once anhydrous ethanol is used as an additive in gasoline), or expelled to the atmosphere (an environmental issue) [1,2,9]. Reviews on biofuel analysis by electrochemical methods reveal that stripping analysis is the main technique employed for metal determinations in biofuels and that other metals can be determined by stripping analysis, including Fe(III), Mn(II) and Sn(IV) [2,9].

This work presents for the first time the use of SPEs for trace metal determination of lead, copper and mercury in fuel bioethanol. Organic-resistant screen-printed gold electrodes (SPGEs) provided the simultaneous determination of copper, lead, and mercury in fuel bioethanol.

## 2. Experimental

### 2.1. Reagents, stock solutions and bioethanol samples

High-purity deionized water ( $R \geq 18 \text{ M}\Omega \text{ cm}$ ) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. Concentrated hydrochloric acid (37%, m/v) was obtained from Vetec (Rio de Janeiro, Brazil). Ethanol (99.5%, v/v) was acquired from Synth (Diadema, Brazil). Copper, lead and mercury stock solutions ( $1000 \text{ mg L}^{-1}$ ) were purchased from Quimlab (Jacareí, Brazil). Working standard solutions were prepared just before use by appropriate dilution of the stock solution acidified with 1% (v/v)  $\text{HNO}_3$ . All reagents were used without further purification (analytical grade). Fuel bioethanol samples were purchased from ethanol factories and gas stations installed in the Triângulo Mineiro region, in the state of Minas Gerais, Brazil.

### 2.2. Instrumentation, electrochemical cell and electrodes

Anodic stripping square-wave voltammetry (SWASV) measurements were performed on a hand-held, battery-powered DropSens  $\mu\text{STAT}200$  bipotentiostat (DropSens, Oviedo, Spain) equipped with a sensor connector (BICAST model, DropSens, Oviedo, Spain) for

connecting the screen-printed gold electrode (SPGE) strip electronically to the bipotentiostat. A laptop with DropView 2.0 software for Windows XP<sup>®</sup> was used to control the instrument, plot measurements and treat experimental data.

SPGEs with high and low temperature curing ink strips (SPGE-HT and SPGE-LT, respectively) were purchased from DropSens (Oviedo, Spain). The average roughness values of the HT and LT-SPGEs are 0.695 and 2.10  $\mu\text{m}$ , respectively (according to information provided by DropSens). They are designed in a three-electrode configuration printed on the same planar platform consisting of a gold disc-shaped working electrode ( $\varnothing$  4 mm), a gold counter electrode, and a silver pseudo-reference electrode. An organic-resistant insulating layer (DropSens domain) is printed over the electrode system in such a way that only the electric contacts and electrode areas are uncovered.

A homemade cell (with internal volume of 10 mL) made of glass was used for the measurements.

### 2.3. Activation of screen-printed gold electrode

The conditioning of the SPGE before analysis (fresh electrodes) was performed according to the procedures previously described [15–17,20]. Baseline stabilization was obtained by cycling the potential over the 0.0–0.7 V range at  $50 \text{ mV s}^{-1}$  (15 cycles) in  $0.1 \text{ mol L}^{-1}$  HCl. After this conditioning, the electrode response remained stable for about 15 analytical runs in 25% (v/v) hydroethanolic solution (optimized condition), and then a new electrode was needed.

### 2.4. Electrochemical measurements

The initial experiments were performed in hydroethanolic solutions with the addition of HCl as electrolyte evaluating different types of SPGEs. Subsequently, the percentage of ethanol and the concentration of HCl in the mixture were varied, in order to obtain the best signal response. The optimized electrolyte composition consisted of 25% (v/v) hydroethanolic solution containing  $0.05 \text{ mol L}^{-1}$  HCl (final concentration of HCl in the mixture).

Fuel bioethanol samples were analyzed after a 4-fold dilution in aqueous  $0.067 \text{ mol L}^{-1}$  HCl in order to result in the same composition of the optimized electrolyte (considering that fuel bioethanol samples are close to 100% ethanol). Recovery tests were performed by the analysis of three fuel bioethanol samples spiked with a hydroethanolic standard solution containing Pb, Cu and Hg at two concentration levels (50 and  $100 \mu\text{g L}^{-1}$ ). The percentage of recovery (%) was calculated as the ratio between the found concentration and added (spiked) concentration multiplied by 100 (considering that the concentration of Pb, Cu and Hg were below the respective LOD values).

SWASV was used for simultaneous determination of lead, copper and mercury in fuel bioethanol. The optimized SW parameters were 20 Hz (frequency), 38 mV (amplitude), and 4 mV (step potential). The cleaning and deposition conditions of ASV were 0.7 V for 60 s and  $-0.5 \text{ V}$  for 240 s, respectively, whilst an equilibrating time of 20 s and stirring speed of 2000 rpm were applied.

All electrochemical measurements were carried out in the presence of dissolved oxygen and at room temperature. The standard addition method was used for all analyses.

## 3. Results and discussion

### 3.1. Optimization of the method

The first experiments were carried out using 50% (v/v) hydroethanolic solution in  $0.1 \text{ mol L}^{-1}$  HCl in order to investigate

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