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Batch-injection stripping voltammetry of zinc at a gold electrode: application for fuel bioethanol analysis

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A B S T R A C T

This article reports for the first time the anodic stripping voltammetric (ASV) detection of Zn at a gold disk macroelectrode for the analysis of fuel bioethanol. The accurate determination of Zn at gold macroelectrodes was only possible with the aid of batch injection analysis (BIA) associated with ASV; this statement was proved by comparison with a conventional three-electrode system. The BIA system consisted of injections of bioethanol sample plugs (up to 1 mL) at $28.3\,\mu L\,s^{-1}$ directly onto a working (gold disc) electrode immersed in $0.04\,mol\,L^{-1}$ Britton-Robinson buffer (pH 7) solution through an electronic micropipette and the Zn deposition occurs simultaneously. The highest analytical response for Zn was obtained for a deposition time of 90 s, which indicated that Zn deposition also occurred from diffusion after the injection ended. The proposed method presented a low detection limit ($5\,\mu g\,L^{-1}$), a linear range between 25 and $250\,\mu g\,L^{-1}$, and adequate recovery values (88–104%) for spiked samples, but no sample treatment was required. Such remarkable analytical features associated with the portability characteristics of BIA demonstrated the promising application of the proposed method for routine and on-site determination of metals in fuel bioethanol.

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1. Introduction

The reduction in petroleum reserves worldwide and the environmental pollution by fossil fuels has accelerated the production and consumption of biofuels such as biodiesel and bioethanol. Worldwide, one of the most widely used transportation fuel is bioethanol. Production of bioethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution [1,2]. Most of the bioethanol produced in the world derives from plant juice containing sucrose from sugarcane in Brazil and starch from corn in the United States [3]. Bioethanol is consumed in Brazil as automotive fuel in two forms: in its hydrated form (95% (v/v) ethanol) or in its anhydrous form added to gasoline (25% (v/v) ethanol) to act as an antiknock agent [4,5].

Bioethanol fuel can contain inorganic contaminants such as zinc, cadmium, copper, lead, nickel, and anions (chloride, sulphate and nitrate). The production process, transport and storage of biofuels are the likely sources of trace metals to fuel [6,7]. The presence of trace metals in biodiesel induces and accelerates oxidative processes resulting in the formation of gums [7–9]. A similar effect is verified in gasoline especially when metals are present in anhydrous bioethanol that is mixed with gasoline to produce gasohol (E25 in Brazil and E5-E15 in USA and Europe, in which E25 corresponds to 25% v/v of anhydrous ethanol). Special attention is given to copper, which is the most deleterious metal for catalyzing oxidation reactions in fuels; for this reason, this metal has been controlled by regulatory agencies. However, similar effects can occur due to the presence of other metals, such as zinc. It is also important to consider the deleterious effect of metals present in hydrated bioethanol as this fuel is commonly mixed with gasoline due to the popular use of flex-fuel engines in Brazil. Metals can also lead to additional corrosion and deposit in different parts of the engine, which perturbs fuel performance.

The determination of zinc in fuel samples has been reported in the literature using techniques such as energy dispersive X-ray fluorescence after pre-concentration on chromatography paper [10] and flame atomic absorption spectrometry using on-line preconcentration system [11]. An electrochemical method for the determination of zinc in bioethanol was described in a previous work using anodic stripping voltammetry and glassy-carbon mercury-film electrode [12]. However, the use of carbon-mercury-film electrodes can cause environmental and health problems. A few papers reported the detection of zinc in a negative potential

window using gold electrodes [13–15]. Garnier et al. [13] employed a 25-μm gold microelectrode for Zn detection; however, poor resolution of the peak was observed for concentrations below than 10 μg L^{-1}. Gibbon-Walsh et al. [14] demonstrated the very low detection limit ($\sim$20 ng L^{-1}) for Zn using a vibrating 10-μm gold microelectrode and 300 s deposition time. Wang et al. [15] evaluated the modification of a gold microelectrode with gold nanoparticles (GNP) followed by a thin film of different elements such as Sn, Bi and Sb. The electrochemical system Sn/GNP gold microelectrode provided higher sensitivity for Zn with a detection limit of 5 μg L^{-1} using a 300 s deposition time [15].

Batch injection analysis (BIA) with electrochemical detection represents an alternative way of performing rapid assays. This technique involves the injection of a sample plug through a micropipette tip directly onto the working electrode surface (wall-jet configuration) which is immersed in a large-volume blank solution [16,17]. The association of BIA with electrochemical techniques provides additional precision and rapidness for the development of electroanalytical methods. Moreover, BIA eliminates the need for a stirrer in stripping analysis since the deposition step occurs simultaneously with sample injection by the micropipette, and then facilitates the development of a portable analytical method. Some works describing the association of BIA with stripping analysis employing conventional or electronic micropipettes were described in the literature [18–23].

For the first time, this work presents the anodic stripping voltammetric detection of Zn at a gold disk macroelectrode using a BIA system and its comparison with a conventional three-electrode system for the analysis of bioethanol fuels.

2. Experimental

2.1. Reagents, stock solutions and bioethanol samples

High-purity deionised water (R $\geq$ 18 MΩ cm) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. Concentrated acetic (99.7% m/v), hydrochloric (37.0% m/v), and nitric (64.0% m/v) acids were obtained from Vetec (Rio de Janeiro, Brazil). Sodium acetate (98.0% m/v) and ethanol (99.5% v/v) were acquired from Synth (Diadema, Brazil). Sodium hydroxide (97.0% m/m) was obtained from Dinâmica (Diadema, Brazil). Stock solutions of 1000 mg L^{-1} zinc, arsenic, cadmium, chromium, copper, manganese, nickel, lead and mercury were purchased from Quimlab (Jacareí, Brazil). Hydroethanolic standard solutions of zinc containing 95% (v/v) ethanol (analytical grade) and 5% (v/v) water (similar composition of commercially available bioethanol) were prepared for all experiments. All standard solutions (aqueous and ethanolic ones) and bioethanol samples were acidified with 1% HNO$_3$ (v/v). All reagents were used without further purification (analytical grade). Fuel bioethanol samples were purchased from ethanol factories and gas stations.

2.2. Instrumentation, electrochemical cell and electrodes

Electrochemical recordings were conducted using a μ-Autolab Type III potentiostat (EcoChemie, Utrecht, The Netherlands). The reference and auxiliary electrodes were a miniaturised Ag/AgCl (saturated KCl) [24] and a platinum wire, respectively. A commercial gold electrode (Metrohm) was used as a working electrode (diameter = 3 mm). Cleaning of the gold surface was performed mechanically on a felt-polishing pad using an alumina powder suspension (0.3 μm) and copiously rinsing with deionized water. For continuous measurements of standard solutions of Zn (II), the gold electrode was just polished before the experiment started. For fuel bioethanol analysis, the gold electrode was

polished before the zinc determination in a new bioethanol sample.

A homemade BIA cell (with internal volume of 180 mL) was constructed from a polypropylene rod, in which the working electrode is placed at the bottom of the cell (inverted position). The top cover contains four holes to adapt counter and reference electrodes, a micropipette tip, and a stirrer powered by a battery (portable characteristics), which was used for the measurements. The design of the BIA cell used in this work was described previously [25,26]. A 0.04 mol L^{-1} Britton-Robinson (BR) buffer solution with pH = 7 was used as a supporting electrolyte.

Injections of standard or sample solutions in the homemade BIA cell were performed using an Eppendorf electronic micropipette (multipette® stream). This micropipette (using a 1 mL tip) permits injections from 10 to 1000 μL at programmable dispensing rate (from 28 to 345 μL s^{-1}). The distance of combitip® from the working electrode was maintained at a constant ($\approx$2 mm), as recommended in a previous work [16].

The performance of the proposed BIA cell for zinc determination in bioethanol samples was compared with a conventional electrochemical cell (internal volume of 10 mL) containing the three-electrode system. During the deposition time in the BIA system, the samples or standards solutions were directly added to the cell (without dilution in electrolyte).

2.3. Electrochemical measurements

Square-wave (SW) anodic-stripping voltammetry (ASV) was used for zinc determination in bioethanol. The parameters for electrochemical measurements in hydroethanolic and aqueous media using SWASV associated with BIA are listed in Table 1. All conditions presented for the BIA-ASV system were also applied for zinc determination in the conventional cell (except for specific BIA parameters, such as dispensing rate, injection volume, and stirring steps). In the BIA system, the conditioning step was performed under stirring supplied by an external stirrer coupled to the cell (280 rpm by the application of 4.5 V on the micro DC motor) [25]. The deposition step (BIA system) was performed during the injection (total time of 35 s) of standard or sample solutions, thus the deposition (preconcentration) still occurred after the end of injection (analyte transfer by diffusion). Fig. 1 presents a scheme illustrating how the BIA-ASV method is applied for the determination of zinc in bioethanol. The conditioning and deposition steps in the conventional cell were carried out under constant stirring of a magnetic bar (2500 rpm).

An interference study was performed using different interfering/Zn(II) ratios (1:1 and 1:10), keeping the Zn(II) concentration at

Table 1
Parameters of BIA-SWASV measurements for zinc determination in bioethanol samples.

	Electrochemical parameters	Value	External stirring (280 rpm)
Conditioning step	Conditioning potential	500 mV	Yes
	Conditioning time	90 s	
Deposition step	Deposition potential	−900 mV	No
	Deposition time	90 s	
	Dispensing rate	28.3 μL s^{-1}	
	Injected volume	1000 μL	
SWASV scanning	Initial potential	−900 mV	No
	End potential	0 mV	
	Step potential	8 mV	
	Amplitude	50 mV	
	Frequency	50 Hz	