



Batch-injection stripping voltammetry of metals in fuel bioethanol



Thiago F. Tormin, Laiz C.D. Narciso, Eduardo M. Richter, Rodrigo A.A. Munoz*

Instituto de Química, Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Uberlândia, MG, Brazil

HIGHLIGHTS

- Batch injection analysis with stripping voltammetry for bioethanol analysis.
- Trace Cd, Cu and Pb in fuel bioethanol using 1-mL aliquot.
- Estimation of the labile fraction of metals in bioethanol samples.
- Routine and on-site determination of metals in bioethanol.

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ABSTRACT

This article reports for the first time the application of batch injection analysis (BIA) with anodic stripping voltammetry (ASV) for determination of metals in fuel bioethanol. An aliquot of bioethanol plug (up to 1 mL) is directly injected onto a working (mercury-film) electrode immersed in electrolyte through an electronic micropipette and simultaneously metal deposition occurs. Stripping peaks for cadmium, lead, and copper were obtained at the same voltammetric scan under optimized conditions (electrolyte, deposition time and potential, injected volume, and dispensing rate). The proposed method presented low detection limit ($\leq 1 \mu\text{g L}^{-1}$) for a 90 s deposition time, a linear range between 12.5 and 200 $\mu\text{g L}^{-1}$, and adequate recovery values (87–109%) for spiked samples. Estimation of the labile fraction of metals in bioethanol samples was also attained. Such remarkable analytical features associated with the portability characteristics of BIA attest the promising application of the proposed method for routine and on-site determination of metals in bioethanol.

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1. Introduction

The production and consumption of biofuels are constantly increasing due to their environmental and economic advantages over fossil fuels. The use of bioethanol (or fuel ethanol) has been stimulated in Brazil 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) acting as an antiknock agent. Consequently, regulatory agencies responsible for production and commercialization of fuels (including biofuels) require a rigorous quality control [1]. For instance, the presence of inorganic contaminants in bioethanol is associated with the formation of insoluble salts and corrosion of metallic components inside the engine, which results in clogging of nozzles and fuel deterioration [2].

Trace metals in bioethanol can be an indicative of metallic corrosion during storage and their presence can accelerate oxidation processes resulting in the formation of gums [3]. Therefore, analytical methods for the sensitive determination of metals in bioethanol are required. The portability of analytical methods is also a

demanding task in quality control of fuels taking into consideration the need for on-site analysis.

Electrochemical techniques fulfill such characteristics and stripping voltammetry is the most popular technique for the determination of trace in several samples including fuels such as diesel oil [4], biodiesel [5,6], and bioethanol [7–9]. The stripping analysis technique generally involves a deposition step, in which the solution containing sample or standards is kept under stirring (forced mass transfer), prior to the voltammetric or potentiometric scanning (stripping step).

Batch injection analysis (BIA) with electrochemical detection 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 [10]. 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. The pioneer work describing the association of BIA with stripping analysis employed a conventional micropipette [11], but electronic

* Corresponding author. Tel.: +55 34 3239 4143x213; fax: +55 34 3239 4208.
E-mail address: raamunoz@iqufu.ufu.br (R.A.A. Munoz).

micropipettes were also applied for this purpose [12–15]. Typically, BIA with stripping analysis was employed using mercury-based electrodes for the determination of different metals in water samples [12–15].

This work presents for the first time the application of BIA with anodic stripping analysis (ASV) for the determination of metals in bioethanol employing a mercury-film electrode. Using an electronically propelled micropipette, a sample or standard plug (1 mL) was precisely injected onto a mercury-film electrode (pre-concentration step) immersed in electrolyte and just after the voltammetric scan (stripping step) was performed.

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 acetic (97.8% m/v), hydrochloric (37.0% m/v), nitric (65.0% m/v) acids were obtained from Vetec (Rio de Janeiro, Brazil). Sodium acetate (98.0% m/v) and ethanol (99.5% v/v) acquired from Synth (Diadema, Brazil). Stock solutions (1000 mg L^{-1} cadmium, copper, lead, and mercury) were purchased from Quimlab (Jacareí, Brazil). Hydroethanolic standard solutions containing 95% (v/v) ethanol (analytical grade) and 5% (v/v) aqueous metal solution (similar composition of commercially-available bioethanol) were prepared for initial optimization experiments and calibrations. The latter solutions were acidified with 1% (v/v) HNO_3 . All reagents were used without further purification (analytical grade). Bioethanol samples were purchased at local fuel stations. Samples were analyzed *in natura* and after acidification with 1% (v/v) HNO_3 .

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 miniaturized Ag/AgCl (saturated KCl) [16] and a platinum wire, respectively. A mercury-film electrode (MFE) was used as the working electrode. The preparation of the *ex situ* MFE involves the electrochemical deposition of a mercury-film on a glassy-carbon electrode surface (3-mm diameter) according to a conventional procedure reported in the literature (-800 mV for 300 s in a solution contained 100 mg L^{-1} mercury(II) and 0.1 mol L^{-1} HCl) [4]. The mercury-film formation was performed in a conventional electrochemical cell once in the beginning of the workday. Before the mercury-film formation, the glassy-carbon electrode was dry-polished using alumina powder with $0.1 \mu\text{m}$ particles and then rinsed with Milli Q water.

Injections of standard solutions or samples were conducted using an Eppendorf electronic micropipette (multipette® stream). This micropipette (using a 1 mL tip) permits injections from 10 to $1000 \mu\text{L}$ at programmable dispensing rate (from 28 to $345 \mu\text{L s}^{-1}$). The distance of combitip® from the working electrode was constant ($\approx 2 \text{ mm}$), as recommended in a previous work [10]. A homemade BIA cell (with internal volume of 180 mL) was used for the measurements as described previously [17]. A 0.1 mol L^{-1} acetate buffer solution (supporting electrolyte) was added in the BIA cell before insertion of the three-electrode system.

2.3. Electrochemical measurements

Square-Wave (SW) anodic stripping voltammetry (ASV) was used for simultaneous determination of cadmium, lead, and copper

in bioethanol. The optimized SW parameters were 50 Hz (frequency), 50 mV (amplitude), and 7 mV (step potential). The cleaning and deposition conditions of ASV were 0.1 V for 5 s and -1.0 V for 90 s, respectively. The deposition step was performed during the injection of standard solutions or samples through the BIA system, which takes approximately 45 s, thus the deposition still occurred after the end of injection.

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

The association of BIA with ASV (BIA-ASV) for metal determinations using MFEs was already reported and optimized in the literature for the analysis of aqueous solutions [11–15]. Previous papers described the use of acetate buffer as supporting electrolyte for metal determination at a MFE using BIA-ASV [11,15], and the selection of SW parameters was based on these works. Initially the deposition step was kept constant (-1.0 V for 90 s). The deposition potential of -1.0 V was selected for the determination of cadmium, lead, and copper because a more negative potential can contribute to hydrogen evolution. The deposition time of 90 s, which is around 3-fold the time of injection (35 s), was selected based on previous works that often reported the use of higher deposition times than injection times [11–15]. Under these conditions, the BIA parameters (injected volume and dispensing rate) were studied based on the analytical responses of each metal.

The analytical response of the three metals increased almost linearly for injected volumes from 200 to $1000 \mu\text{L}$. Similar behavior (increase in signal for higher injected volumes) was observed in previous studies [11–15]. The increase in injected volumes provides higher contact time between the metals and electrode surface and also a higher mass amount of metals is injected and preconcentrated, which would explain the linear increase in current. Therefore, injections of $1000 \mu\text{L}$ hydroethanolic standard solutions were selected in further experiments.

The analytical response for the three metals was measured when the dispensing rate was evaluated. Fig. 1 presents the analytical signals for cadmium, lead and copper obtained by injections in the BIA system of $1000 \mu\text{L}$ of $75 \mu\text{g L}^{-1}$ of each metal in hydroethanolic solutions (95% v/v ethanol) onto a MFE immersed in the

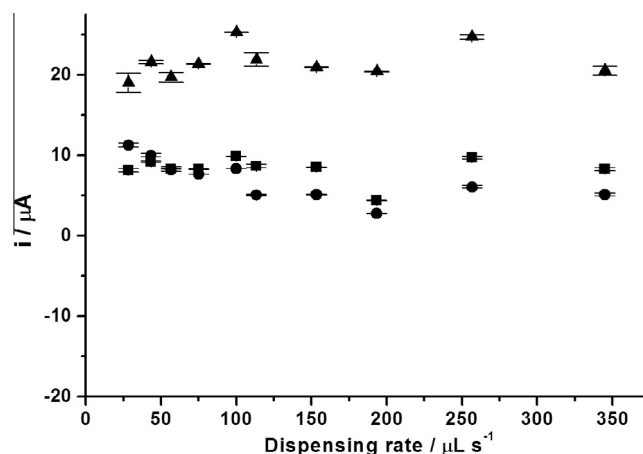


Fig. 1. Optimization of dispensing rate ($28.3\text{--}345.0 \mu\text{L s}^{-1}$) hydroethanolic medium (95% v/v ethanol) containing $75 \mu\text{g L}^{-1}$ of cadmium (■), lead (●) and copper (▲). Conditions: -1.0 V deposition potential; 90 s deposition time; $1000 \mu\text{L}$ injected volume; electrolyte: 0.1 mol L^{-1} acetate buffer (pH 4.5).

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