Analytical Methods

Rapid voltammetric method for quinine determination in soft drinks

Mihaela Buleandra, Andreea A. Rabinca, Mihaela C. Cheregi, Anton A. Ciucu*

University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, 90-92 Panduri Avenue, 050663 Bucharest, Romania

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A B S T R A C T

A novel voltammetric assay for quinine (QN) determination using an electrochemically pretreated pencil graphite electrode is described. The detection limit of QN was 2×10^{-7} M. The method possesses some obvious advantages including extreme simplicity, rapid response, and low cost.

1. Introduction

Quinine (QN) is a plant alkaloid with medicinal use having anti-pyretic, anti-malarial, anti-inflammatory, analgesic and muscle relaxant properties (Dar, Brahman, Tiwari, & Pitre, 2012; Geto, Amare, Tessema, & Admassie, 2012); it was found effective as additional therapy for acquired immune deficiency syndrome, and neurodermatitis (Paton & Aboulhab, 2005). If taken excessively, QN can induce side-effects; the clinical manifestations of overdose include gastrointestinal problems, cinchonism, visual disturbances, central nervous system effects, and cardiac dysrhythmias (Huston & Levinson, 2006). The therapeutic plasma concentration range of QN is 3 to $7\,\mu g\,mL^{-1}$, and blood concentration higher than $10\,\mu g\,mL^{-1}$ can cause adverse effects and might be lethal (Samanidou, Evaggelopoulou, & Papadoyannis, 2005; Zaugg & Thormann, 2001). In beverage industries, it is applied as a bitter flavoring agent in soft drinks (tonic water, bitter lemon) which may contain usually approximately $80\,mg\,L^{-1}$ of QN (Awasthi, Srivastava, & Singla, 2011).

Due to its potential toxicity, analytical methods like liquid chromatography (Mirghani, Ericsson, Cook, Yu, & Gustafsson, 2001; Samanidou et al., 2005), gas chromatography (Bannon, Yu, Cook, Roy, & Villeneuve, 1998), capillary electrophoresis (Zaugg & Thormann, 2001), isotachophoresis (Reijenga et al., 1985), fluorimetry (Ortega-Algar, Ramos-Martos, & Molina-Diaz, 2004), chemiluminescence (Li, Zhang, & Wu, 2000), atomic (Yebra & Cespon, 2000) and mass spectrometry (Shrivas & Wu, 2007) have been reported for QN quantitative determination. Few electrochemical techniques, involving potentiometry (Kamel & Sayour, 2009; Zareh, Malinowska, & Kasiura, 2001), polarography (Dar et al., 2012; Thomas & Gierst, 1983), and voltammetry (Awasthi et al., 2011; Geto et al., 2012; Liu et al., 2012; Zhan, Liu, & Gao, 2011) have been described.

A survey of the literature reveals that there is no report regarding the direct voltammetric determination of QN content in soft drinks without previous separation, using a pencil graphite electrode (PGE). The paper presents the electrochemical behavior of QN and a novel rapid voltammetric method for QN selective determination making use of a disposable and cheap electrochemically pretreated pencil graphite electrode (PGE*).

2. Materials and methods

2.1. Reagents and solutions

Quinine sulfate and sulfuric acid were Sigma–Aldrich (Germany) reagents. For voltammetric measurements a stock solution of 1×10^{-2} M QN was freshly prepared in 1 mL 0.1 M H_2SO_4 diluted with deionized water in a 25 mL volumetric flask. Working solutions were prepared by adding Britton-Robinson buffer (BRB) solution of adequate pH value. A stock solution of 1×10^{-3} M QN prepared in 0.05 M H_2SO_4 was used for fluorescence measurements.

2.2. Equipment

A PGSTAT 128N (Ecochemie B.V., Netherlands) controlled by Nova 1.8 software was used for voltammetric studies. Pencil graphite (PG) and electrochemically pretreated pencil graphite (PG*) were used as working electrodes in a 10 mL voltammetric cell including a Pt wire and Ag|AgCl as auxiliary and reference electrodes. The PGEs were prepared and electrochemically pretreated as described elsewhere (Buleandra et al., 2017). Fluorescence measurements were carried out on a FP-6500 PC spectrofluorimeter (Jasco, Japan). Wavelength calibration was performed by measuring excitation and emission wavelengths at
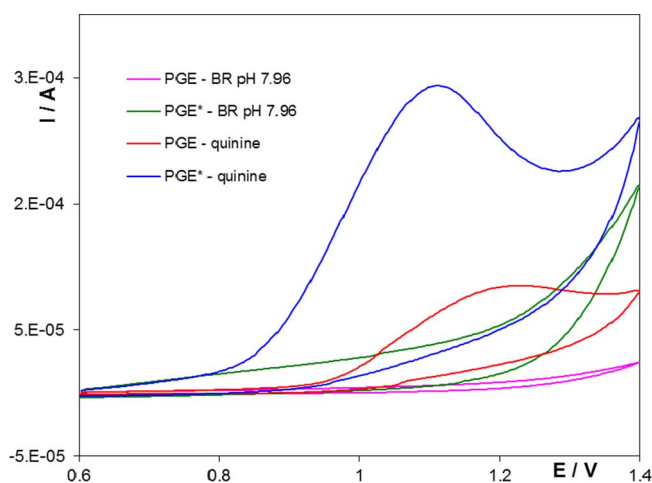
Fig. 1. CVs for 0.5 mM QN in pH 7.96 BRB solution and for supporting electrolyte (BRB solution pH 7.96) obtained at the PGE* and PGE; scan rate 100 mV s^{-1}.
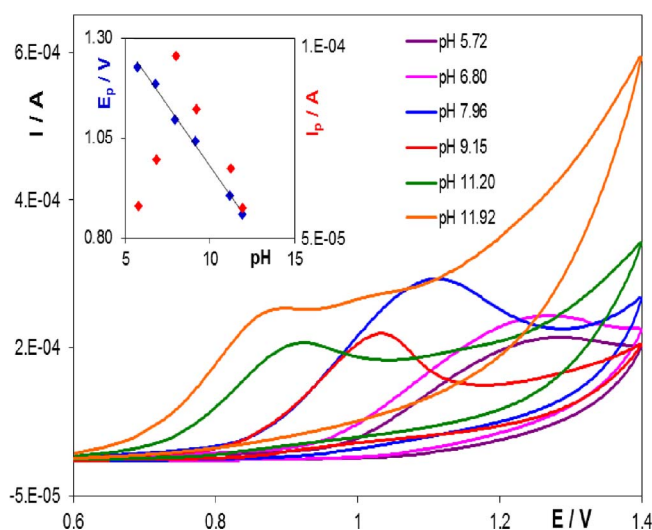

Fig. 2. CVs for 0.5 mM QN in BRB solution of different pH values at PGE*; scan rate 100 mV s^{-1}. Inset the plots of E_p vs. pH (blue) and of I_p vs. pH (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
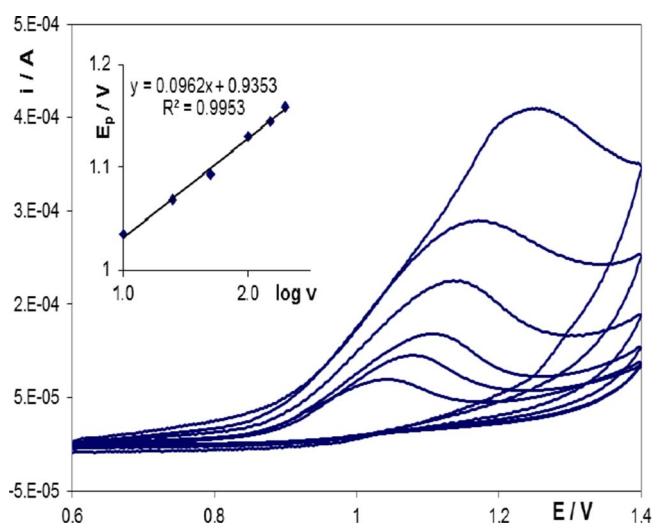

Fig. 3. CVs for 0.5 mM QN in pH 7.96 BRB solution on PGE* at different scan rates (10, 25, 50, 100, 150 and 200 mV s^{-1}). Inset the plot of E vs. logarithm of scan rate.
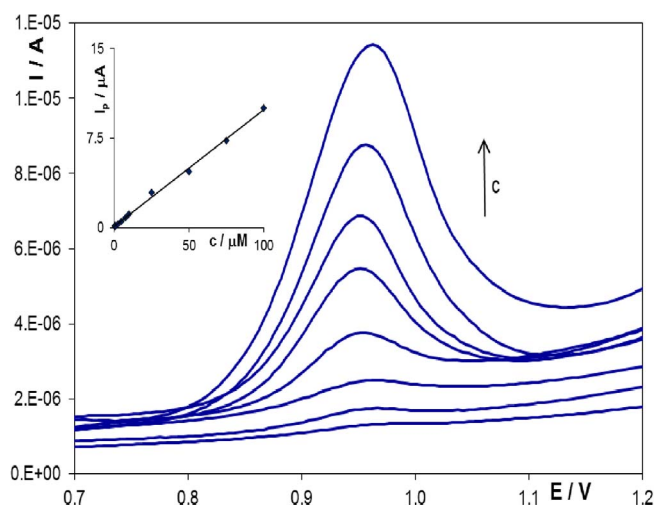

Fig. 4. DPVs recorded in BRB solution pH 7.96 at PGE* for different QN concentrations (0.5×10^{-6}; 1×10^{-6}; 5×10^{-6}; 1×10^{-5}; 2.5×10^{-5}; 5×10^{-5}; 7.5×10^{-5} and 1×10^{-4} M). Inset the calibration graph.

350 nm and 450 nm respectively.

2.3. Procedures

Cyclic voltammetry (CV) studies were done in the potential range +0.6 V to +1.4 V, at a scan rate of 100 mV s^{-1}. Differential pulse voltammograms (DPVs) were recorded between +0.7 V and +1.2 V under optimized instrumental parameters (scan rate 10 mV s^{-1}, pulse amplitude 25 mV, sampling width 17 ms, pulse width 100 ms, pulse period 500 ms). The oxidation peak potential at +0.95 V resulted in DPV method was used for QN quantitative determination in soft drinks and data were compared with those from a fluorimetric method (Pungor, 1995).

2.4. Sample preparation

The soft drinks were purchased from a local supermarket. Before analysis, carbon dioxide was removed from the samples; 1.0 mL of each sample was diluted ten times with BRB solution pH 7.96 and analyzed without any further treatment. The DPV peak currents of QN were recorded on the PGE* for diluted samples before and after three standard additions of 0.1 mL of 1×10^{-3} M QN solution. For fluorescence measurements 50 μL of soft drinks were transferred into a 10 mL volumetric flask and diluted with H$_2$SO$_4$ 0.05 M to the mark. QN concentration was determined from a calibration graph (fluorescence intensity (I) vs. QN concentration (C$_{QN}$)) having the regression equation I = 242.8 C$_{QN}$ (μM) − 8.8137 (R^2 = 0.9938). Each measurement was done in triplicate and the presented results are an average of the data.

3. Results and discussion

Surface characterization of PGE and PGE* by atomic force microscopy and their electrochemical behavior in a solution of 1×10^{-3} M K$_3$[Fe(CN)$_6$] prepared in 1 M KCl were presented in a previous paper (Buleandra et al., 2017). The electrochemical results indicated an easier electronic transfer at the PGE* surface compared with PGE due to the pre-treatment of the electrode.

3.1. Electrochemical behavior of quinine on PGEs

The CVs at the PGE* (Fig. 1) shows a well defined irreversible oxidation peak for QN at +1.1 V, while in case of PGE the oxidation peak appears at +1.2 V, and a smaller oxidation current is observed also. This behavior indicates an easier electronic transfer at the PG* electrode