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Analytical Methods

Nafion covered lead film electrode for the voltammetric determination of caffeine in beverage samples and pharmaceutical formulations

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ABSTRACT

This paper presents a sensitive, selective and low-cost voltammetric method for the determination of caffeine using a Nafion covered lead film electrode. The sensor was prepared on a glassy carbon electrode modified with lead film recovered by a Nafion layer. Caffeine was accumulated and then oxidised at the modified electrode surface to produce two anodic peaks at 0.86 and 1.40 V (vs. Ag/AgCl) in 0.1 mol L^{-1} H_2SO_4 medium. The obtained detection limits for caffeine following 120 s of accumulation time were equal to 1.7×10^{-8} mol L^{-1} (for peak 1) and 2.2×10^{-7} mol L^{-1} (for peak 2). The method was successfully applied to determination of caffeine in tea, coffee, soft and energy drink samples as well as pharmaceutical formulation and the contents closely corresponded to those quoted by the manufacturer and those obtained by the reported spectrophotometric method.

1. Introduction

Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) is an alkaloid from xanthine group that is widely distributed in various kinds of beverages and food, such as coffee, tea, coca-cola, cola nuts and chocolate. It can also be purchased in capsules and tablets for treatment of asthma, nasal congestion, and headache or to improve athletic endurance and facilitate weight lost (Cauli & Morelli, 2005). The popularity of caffeine-containing products is connected with her physiological effects, such as stimulation of the central nervous system, diuresis and gastric secretion (Spătaru, Sarada, Tryk, & Fujishima, 2002). However, it can cause adverse mutation effects when excessively consumed, such as inhibition of DNA repair and cyclic AMP phosphodiesterase activity. Furthermore, it can be a cause of cancer, heart diseases and complications in pregnant women and ageing (Sun, Huang, Wei, Wu, & Ren, 2011). For these reasons, it is very important to control the concentration of caffeine in its different sources.

Many methods have been developed for the determination of caffeine, including ultraviolet visible (UV–VIS) spectrophotometry (Belay, Ture, Redi, & Asfaw, 2008; Hajian & Soltaninezhad, 2013), thin-layer chromatography (TLC) (Abourashed & Mossa, 2004), high-performance liquid chromatography (HPLC) (El-Shahawi, Hamza, Bahaffi, Al-Sibaai, & Abduljabbar, 2012; Hadad, Salam, Soliman, & Mesbah, 2012; Lino & Pena, 2010; Sik, 2012), FT-Raman spectrometry (Armenta, Garrigues, & de la Guardia, 2005), FT-IR spectrometry (Paradkar & Irudayaraj, 2002), near-infrared spectroscopy (NIRS) (Zhang et al., 2013) and capillary electrophoresis (CE) (Sultan et al., 2013). Usually, these methods are more expensive and time-consuming as compared to electroanalytical methods.

Till now, only a few papers dealing with an electroanalysis of caffeine at the conventional bare electrode materials (e.g. glassy carbon) have been published (Švorc, 2013). The major drawback of the electrochemical determination of caffeine at such electrode materials is that its oxidation occurs at a very positive potential, overlapping with oxidation of the background medium (Spătaru et al., 2002), which gives the analysis a low reproducibility. Various chemically modified electrodes have been developed to solve this problem, especially cation-exchanger Nafion has been largely used. In particular, the Nafion showed a good affinity towards caffeine because of its substantial improvements of sensitivity in acidic conditions (Schrenk, Villigram, Torrence, Brancato, & Minteer, 2002). In this frame, Brunetti, Desimoni, and Casati (2007) developed a differential pulse voltammetric method based on a Nafion-covered glassy carbon electrode for the quantitative determination of caffeine in cola beverages: the approach allowed quantifying the analyte in the 9.95×10^{-7}–1.06×10^{-5} mol L^{-1} range, with a detection limit of 7.98×10^{-7} mol L^{-1}. Nafion has been also used as a modifier of boron-doped diamond electrode, and the achieved detection limit of 1.0×10^{-7} mol L^{-1} enables reducing matrix effects by working in highly diluted solutions (Martínez-Huitle, Suely Fernandes, Ferro, De Battisti, & Quiroz, 2010).

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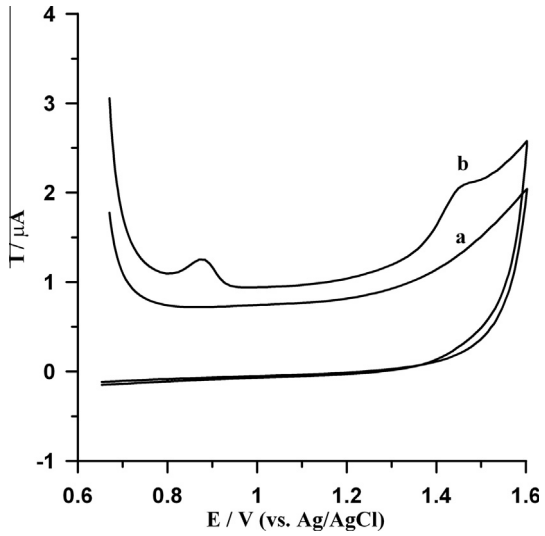

Fig. 1. Cyclic voltammograms obtained at the Nafion covered lead film electrode in the absence (a) and presence (b) of 5×10^{-6} mol L^{-1} caffeine in 0.1 mol L^{-1} H_2SO_4 solution (scan rate of 100 mV s^{-1}). Caffeine was accumulated for 30 s at −1.55 V.

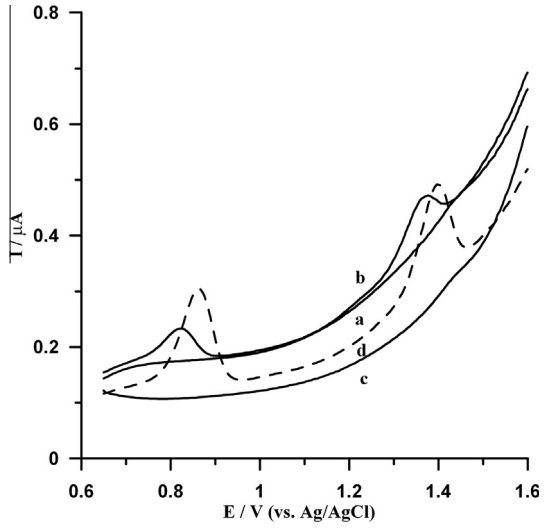

Fig. 2. Differential pulse adsorptive stripping voltammograms obtained at: (a) a bare glassy carbon electrode (GCE), (b) the Nafion covered glassy carbon electrode (Nafion/GCE), (c) the lead film electrode (PbFE) and (d) the Nafion covered lead film electrode (Nafion/PbFE). The lead film plating solution contained 0.1 mol L^{-1} HNO_3 and 7.5×10^{-5} mol L^{-1} Pb(II). The lead film was deposited at −1.4 V for 30 s. In the case of (b) and (d) the glassy carbon surface and lead film plated on the glassy carbon surface were covered by applying 0.5 μL of 1% Nafion solution. Caffeine at concentration of 5×10^{-6} mol L^{-1} was accumulated in 0.1 mol L^{-1} H_2SO_4 solution for 30 s at −1.55 V. Stripping parameters: amplitude of 50 mV, modulation time of 4 ms, scan rate of 50 mV s^{-1}.

In 2005, the lead film electrode (PbFE) was introduced for the first time for adsorptive stripping voltammetric determinations of inorganic ions such as Co(II) and Ni(II) (Korolczuk, Tyszczuk, & Grabarczyk, 2005). Till now, the electrochemistry of PbFE and its advantages compared to other bare and modified carbon electrodes have been reported for determination of several important biologically active compounds (caffeic acid, thiamine, betulinic acid etc.). The versatility of this electrode material has also been utilised for development of sensors (Tyszczuk, Skalska-Kamińska, & Woźniak, 2011; Tyszczuk-Rotko, 2012).

The main aim of this paper was to optimise and develop a simple and sensitive adsorptive striping voltammetric method with the use of Nafion covered lead film electrode (Nafion/PbFE) for determination of caffeine in pharmaceutical formulations and food samples. In the present study we tried to point out the advantages of using the Nafion and lead film as modifiers of a glassy carbon electrode.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of analytical grade and were used without further purifications. Caffeine, Nafion 5% were obtained from Sigma–Aldrich (Germany), while HCl 37%, HNO_3 65%, H_2SO_4 95%, $Pb(NO_3)_2$, and C_2H_5OH 96% were obtained from POCh (Poland). A stock standard solution of caffeine (10^{-2} mol L^{-1}) was prepared daily by dissolving a reagent in water and was stored in a refrigerator in the dark until used. Working solutions were prepared by appropriate dilution of a stock standard solution in 0.01 mol L^{-1} H_2SO_4. Nafion (5% w/v solution) was diluted with ethanol, in order

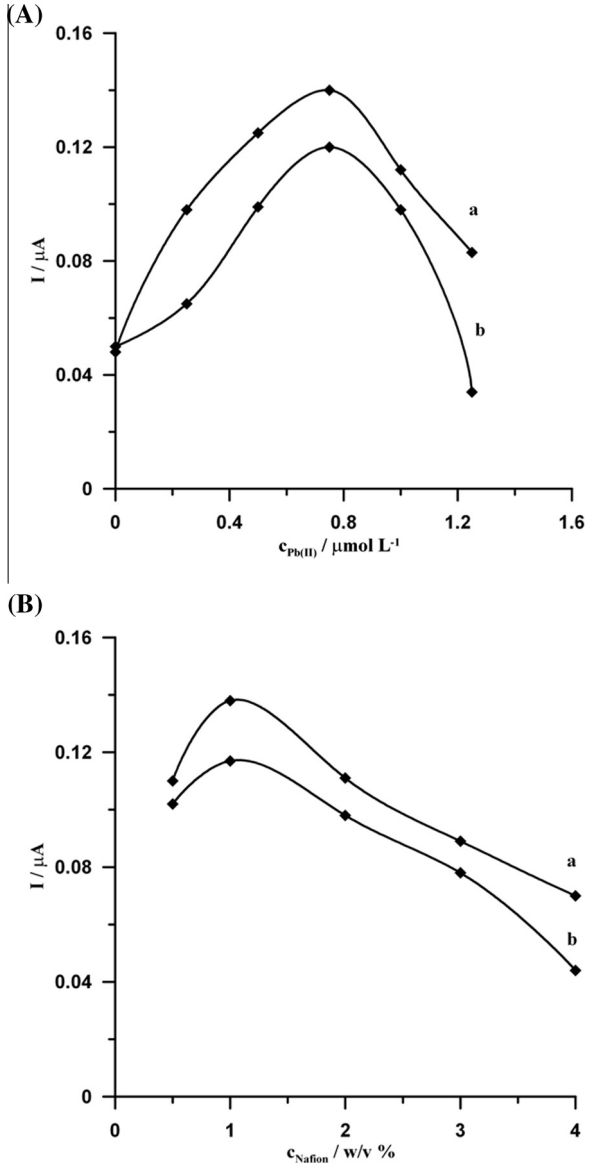

Fig. 3. Effect of the Pb(II) (A) and Nafion (B) concentration on the peaks current of 5×10^{-6} mol L^{-1} caffeine: (a) peak 1 and (b) peak 2. Other measurements parameters are the same as in Fig. 2.