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Use of boron-doped diamond electrode pre-treated cathodically for the determination of trace metals in honey by differential pulse voltammetry

Gláucio Gualtieri Honório, Gustavo Chevitarese Azevedo, Maria Auxiliadora Costa Matos, Marcone Augusto Leal de Oliveira, Renato Camargo Matos*

NUPIS (Núcleo de Pesquisa em Instrumentação e Separações Analíticas), Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Juiz de Fora, 36036-330 Juiz de Fora, MG, Brazil

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ABSTRACT

In this work, a methodology for the determination of Cu(II), Pb(II), Cd(II) and Zn(II) in honey by differential pulse anodic stripping voltammetry (DPASV) on a nano crystalline boron-doped diamond electrode (BDD) is proposed. A 3^3 Box-Behnken Design, 3^2 Factorial Design and Principal Components Analysis (PCA) were performed to optimise the electrochemical conditions. According to the response surfaces obtained, it was stipulated for Zn analysis a pH of 4, E_d of −1.50 V and t_d of 240 s. For simultaneous analysis of Cu, Pb and Cd a pH of 1, E_d of −0.95 V and t_d of 240 s was used. Detection limits of 0.37, 0.40, 1.28 and 0.16 μg L^{-1} were found for Cu, Pb, Cd and Zn, respectively. The analyte concentration ranged between 0.242 and 1.38 mg L^{-1} for Cu, 0.129 and 0.918 mg L^{-1} for Pb and 0.819 and 2.492 mg L^{-1} for Zn, while no significant concentrations were found during Cd analyses. The honey samples were also analysed by Hg-coated glassy carbon electrode and graphite furnace atomic absorption spectrometry (GF AAS) through non-parametric ANOVA and no evidence of significant differences among the results was observed within a 95% confidence interval.

1. Introduction

Honey is a sweet substance obtained from the nectar of different flowers (floral honey) and secretions of living parts of plants, or excretions of insects that suck living parts of plants (honeydew honey), which the bees collect and let ripen in the combs of the hive (Campos et al., 2003; Pohl, 2009). Honey plays an important role in traditional medicine because it has antioxidant and antibacterial properties among others (Lachman, Orsák, Hejtmánková, & Kovářová, 2010). Depending on the botanical origin and the chemical composition of the nectar or secretions, honeys contains a mixture of different carbohydrates, proteins, amino acids, minerals, enzymes, aromatic oils, pollen and wax, among others, which are added by bees or due to handling and honey maturation (Belitz, Grosch, & Schieberle, 2009; Franchini, Matos, Colombara, & Matos, 2008; Franchini, Matos, & Matos, 2011; Lachman et al., 2007). The contribution of minerals is generally low, about 0.1–0.2%. The final amount of water in honey generally does not exceed 20% (Alvarez-Suarez, Tulipani, Romandini, Bertoli, & Battino, 2010).

The main concentrations of metals in honey derive from the environment in which it is produced. They are absorbed from plants through the root and then pass to nectar, used for honey production. Thus, it can be used to collect information related to the environment in which they live (Anklam, 1998; Ioannidou, Zachariadis, Anthemidis, & Stratis, 2005; Pohl, 2009). Every day, from 1000 to 25,000 bees cover approximately 7 km^2, making contact with plants, air, water and soil of this region searching for nectar, pollen and water from flowers. During this process, various microorganisms, chemicals and airborne particles are intercepted by bees and retained in their body or inhaled, leading, to a certain extent, to contamination (Caroli, Forte, Iamiceli, & Galoppi, 1999; Rissato, Galhiane, Knoll, Andrade, & Almeida, 2006). Different regions can be studied for ensure environmental quality by means of the investigations of trace metals content in honey (Pohl, 2009). Besides the environmental monitoring, the determination of these elements is important to classify honey as a good source of these minerals (Miller-Ihli, 1996).

Several techniques were proposed to determinate metallic impurities in honey (Buldini, Cavalli, Mevoli, & Sharma, 2001; Caroli et al., 1999; Pohl, 2009; Sanna, Pilo, Piu, Tapparo, & Seeber, 2000; Wu, 1996). The largely preferred analytical approaches to the

* Corresponding author. Fax: +55 32 2102 3310.
E-mail addresses: renato.matos@ufjf.edu.br, renato.matos@live.com (R.C. Matos).

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determination are spectrometric techniques, including flame atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Caroli et al., 1999; Ioannidou et al., 2005; Pohl, 2009). For metals analysis, electrochemical techniques in general are cheaper and quicker for carrying out a determination, when compared with spectrometric techniques instruments. Recent papers show stripping techniques to determinate trace metals in honey, particularly anodic stripping methods. Depending upon the type of technique, they can be very specific and extremely sensitive (Buldini et al., 2001; Sanna et al., 2000; Wu, 1996).

In the past, mercury used as a dropping or a hanging electrode was the preferred working electrode because of the surface renewal of the drop and the low noise current. Associated with pulse techniques, the mercury electrode was one of the best for trace analysis (Wang, 2006). Nowadays, it is highly recommended to use other kinds of electrodes whose toxicity is low or nil. Some of the alternative electrodes that have been investigated are Ir (Nolan & Kounaves, 1999), Bi (Hutton et al., 2001), Au (Feeney & Kounaves, 2000), Ag (Bonfil & Kirowa-Eisner, 2002) and graphite (Brainina, Malakhova, & Ivanova, 1997). Recently, a diamond film carbon electrode has been developed. It consists of a thin film of sp^3 carbon deposited by chemical vapour deposition on an inert substrate such as silicon. This carbon is doped with boron, which has a high conductivity value (Granger, Xu, Strojek, & Swain, 1999). The boron-doped diamond electrodes (BDDs) have attracted much interest due to their superior properties, including low background currents, a wide working potential window, favourable electron-transfer kinetics, and surface inertness, which result in high resistance to deactivation. The BDD is resistant to fouling and can be reused many times (Langeloth, Chiku, & Einaga, 2010). Furthermore, the chemical and mechanical robustness of this electrode made it suitable for working in corrosive media and resistant to ultrasonic probes (Chen, Granger, Lister, & Swain, 1997; El Tall, Jaffrezic-Renault, Sigaud, & Vittori, 2007; McGaw & Swain, 2006). In addition, BDD can be a great alternative to mercury and Hg-film electrodes (El Tall et al., 2007).

The purpose of the present study was to optimise a method for determination of trace metals (Cu, Cd, Pb and Zn) in honey using chemometric approaching, BDD electrode and differential pulse anodic stripping voltammetry (DPASV). In general, works in the literature report univariate methods, where each variable of the system is investigated separately while the others are held constant. However, this procedure does not permit the study of the interaction effect among factors considering the different levels. The multivariate approach, in contrast to the univariate one, presents a more comprehensive understanding of the investigated system through simultaneous evaluation of variables combined with a reduced number of experiments, which results in lower spending on reagents, solvents and laboratory time.

2. Experimental

2.1. Reagents and chemicals

Cooper, cadmium, lead, gallium, mercury and zinc reference solutions were prepared from Titrisol standard solutions (1000 mg L^{-1}) obtained from Vetec (Rio de Janeiro, Brazil) and SpecSol (Jacareí, SP, Brazil). Solutions and samples were prepared with deionised water obtained from a Milli-Q water purification system. Supra pure hydrochloric acid (37%), analytical grade nitric acid (65%), glacial acetic acid, sodium acetate trihydrate and hydrogen peroxide (30%) were obtained from Vetec (Rio de Janeiro, RJ, Brazil) and were used without further purification.

Hydrochloric acid (0.1 mol L^{-1}) was used as the supporting electrolyte for Cu, Cd and Pb analysis, and 0.5 mol L^{-1} acetate buffer (pH 4.5) for Zn analysis.

2.2. Samples

This work was carried out on 10 honey samples obtained from local markets in Brazil. The samples were stored in the dark at room temperature (between 15 and 25 °C) prior to analysis. For metals determination, 2.5 g of honey was dissolved in 2.5 mL of deionised water and filtered through a 0.45 μm membrane. The digestion was performed in 10 mL closed glass vessels and then samples were stored in Falcon tubes at room temperature.

2.3. Electrodes, electrochemical cell and instrumentation

Electrochemical measurements were performed with a μAutoLab Type III potentiostat (EcoChemie, Ultrecht, Netherlands) coupled with a Faraday cage (Metrohm Autolab, Netherlands). An ultrasonic bath T28110 (Unique, Brazil) operating at 25 KHz and a heating plate was used for sample preparation. The agitation system was performed using a magnetic stirrer (IKA-lab Disc, Germany) with magnetic bars of 5 × 15 mm dimensions (Stirbar) and fixed around 1500 rpm for all analysis. A GF 95 model (GF 95, Thermo Scientific, China) graphite furnace atomic absorption spectrometer with Zeeman effect background correction was employed for the determination of Zn, Cd, Pb and Cu for comparison with the electroanalytical results. The spectrometer was operated with a single element hollow cathode lamp (Photron Lamps, Australian) of Zn, Cd, Pb and Cu using wavelengths of 213.9 nm, 228.8 nm, 217.0 nm and 324.8 nm, respectively.

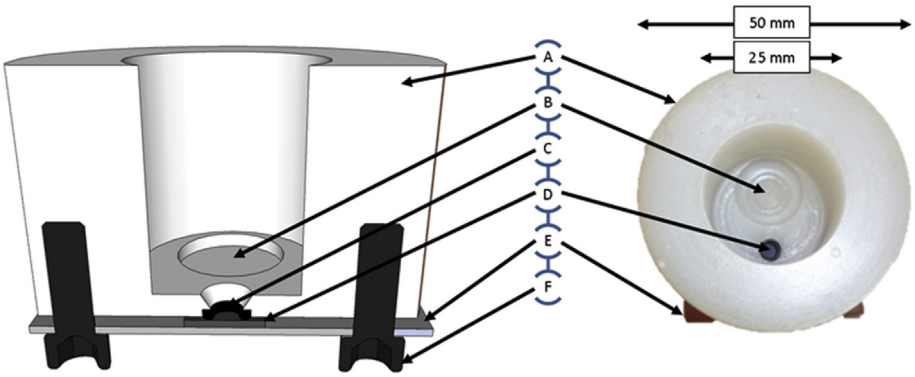

Fig. 1. Electrochemical cell. (A) Nylon, (B) stir bar, (C) rubber O-ring, (D) BDD electrode, (E) copper plate and (F) allen screw.