Microchemical Journal 133 (2017) 22–30

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Carbon paste electrode modified with ferrimagnetic nanoparticles for voltammetric detection of the hormone estriol

Jonas Pires da Silveira, Jamille Valéria Piovesan, Almir Spinelli *

Universidade Federal de Santa Catarina, Campus Reitor João David Ferreira Lima, Departamento de Química - CFM, 88040-900 Florianópolis, SC, Brazil

ARTICLE INFO

Article history:
Received 5 October 2016
Received in revised form 21 February 2017
Accepted 9 March 2017
Available online 10 March 2017

Keywords:
Ferrimagnetic nanoparticles
Modified electrode
Voltammetry
Estriol
Pharmaceuticals
Urine

ABSTRACT

A very simple, novel and environmentally-friendly electrochemical detector for estriol, based on a carbon paste electrode modified with ferrimagnetic nanoparticles, is proposed herein. The ferrimagnetic nanoparticles increase the surface area of the electrode and act as a catalyst for the electrochemical reaction of estriol. Estriol is an estrogen naturally produced by women during pregnancy. Its imbalance may engender disruption of the endocrine system, thereby impairing human growth and reproduction. Estriol is also considered to be an emergent pollutant. The proposed modified carbon paste electrode was used for the determination of estriol by anodic square-wave voltammetry. In 0.1 mol L^{-1} B-R buffer (pH 6.0), estriol presented a well-defined single oxidation peak at +0.68 V, indicating that under these conditions the electrochemical process is irreversible. The overall reaction rate is controlled by an adsorption step. Two protons and two electrons are involved in the estriol oxidation. The calibration curve for estriol showed good linearity in the concentration range of 0.86 to 32.0 ppm ($R^2 = 0.997$). The detection and quantification limits achieved were 0.79 and 2.41 ppm, respectively. The proposed modified electrode was successfully applied to the analysis of pharmaceutical and simulated urine samples; the results being comparable to those obtained using the UV–vis technique.

1. Introduction

Endocrine disrupting chemicals (EDCs) are substances capable of disturbing the animal endocrine system, affecting mainly human development and reproduction [1]. EDCs can be obtained from natural or synthetic sources. Estrone (E1), estradiol (E2) and estriol (E3 - Fig. 1), three major estrogens found in females, are among the naturally occurring EDCs. E3 is the main hormone produced during pregnancy [2,3]. It is produced by the placenta from 16-hydroxydehydroepiandrosterone sulfate (16-OH DHEAS), an androgen steroid made in the fetal liver and adrenal glands. Hence, E3 can be detected in maternal blood or urine and used as a marker of fetal health and wellbeing. Clinically, E3 is widely used for treating estrogen deficiency symptoms, such as sexual cycle disorders [4], but when in excess it has the capacity to disturb the endocrine system, causing growth and reproduction impairment [5–7]. Thus, the control of its level in both the human body and pharmaceuticals is of great important.

E3 is a hydrophobic organic compound of low volatility and low solubility in water. These properties hinder its permanence in the aqueous phase. In living organisms, the highest levels of E3 are found in fatty tissue [8], while in the environment it is found in soils, sediments and sludge [9,10]. Johnson and colleagues [11] claim that the amount of E3 excreted daily vary considerably and depends on the individual's conditions. It may range from 1.0 to 6000.0 mg by day for menopausal women or during gestation, respectively. If not adequately treated, the hormone can come into contact with the environment, causing serious damage to the health of living beings. As a consequence, due to the constant increase in E3 levels in the environment, mainly caused by the inefficient (or lack of) treatment of sewage to eliminate it, E3 is now considered as a potential pollutant, since it modifies the equilibrium of ecosystems [12]. Thus, it is necessary to develop analytical procedures capable of quantifying E3 in several matrices.

The quantification of E3 has been well reported in literature and several procedures have been used including chromatographic techniques [13–15], immunoassays [16–18], electrophoresis [19,20] and electrochemical methods [5,21,22]. Due to its operational simplicity, low cost, fast response, high sensitivity, and the possibility of miniaturization and automation, interest in electroanalytical methodologies has been growing, especially the use of modified electrodes. A non-exhaustive review on the subject is provided herein. Jin and Lin [23] used a graphite electrode modified with carbamylcholine embedded in paraffin for the simultaneous determination of E1, E2 and E3. The oxidation peaks of the three compounds were observed at a potential of +0.55 V (vs. SCE), allowing the total concentration of these estrogens to be determined. The individual concentration of the three hormones was estimated from the typical proportion of E1:E2:E3 (i.e., 2:2:1). The linear ranges were 0.3 to 30.0, 4.0 to 40.0 and 0.5 to 9.0 μmol L^{-1}, respectively.

* Corresponding author.
E-mail address: almir.spinelli@ufsc.br (A. Spinelli).

http://dx.doi.org/10.1016/j.microc.2017.03.010
0026-265X/

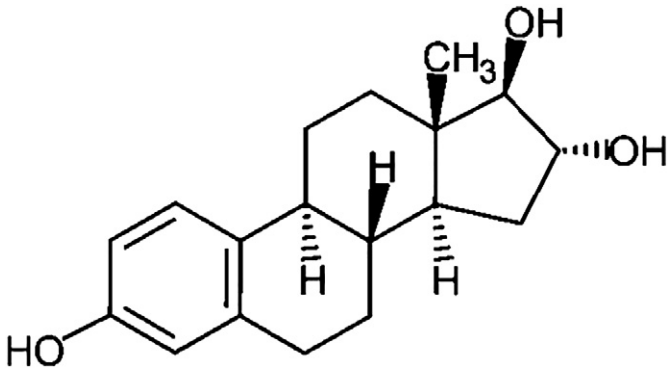

Fig. 1. Chemical structure of estriol (E3).

This method has been successfully applied in the analysis of blood serum samples collected from pregnant women. In 2010, Santos and colleagues, using boron-doped diamond electrodes, determined E3 levels in urine samples and pharmaceutical products electrochemically. The calibration curve for E3 obtained using the square-wave voltammetry technique was linear over the concentration range of 0.2 to 20.0 μmol L^{-1}, with detection and quantification limits of 0.172 μmol L^{-1} and 0.798 μmol L^{-1}, respectively [21]. Some years earlier, Lin and Li built a glassy carbon electrode modified with carbon nanotubes and platinum nanoparticles for the determination of E3 levels in blood serum. Making use of square-wave voltammetry as the analytical technique, the authors obtained a calibration curve with a linear range of 1.0 to 75.0 μmol L^{-1}. The detection limit was 0.62 μmol L^{-1} [22]. Recently, Cesarino and colleagues determined E3 in natural water samples (collected from a potable water reservoir in the city of São Carlos, São Paulo State, Brazil). In this study, the surface of a glassy carbon electrode was modified with reduced graphene oxide and antimony nanoparticles. The calibration curve for E3 obtained by differential pulse voltammetry was linear over the concentration range of 0.2 to 1.4 μmol L^{-1}, with a detection limit of 0.5 nmol L^{-1} [24].

The use of chemically modified electrodes for analysis of metals and organics is a well-established practice. A conductive substrate modified with electroactive thin films, monolayers, or thick coatings results in a chemically modified electrode. The modification of the conductive substrate has positive effects on the (i) electron transfer kinetics, (ii) electrocatalytic activity due to the use of materials with large surface area, (iii) sensitivity of measurement in electroanalytical applications, (iv) selectivity toward specific molecules due to immobilized functional groups, and (v) extraction and accumulation of an analyte at the electrode surface. Metal nanoparticles, which exhibit very interesting physico-chemical properties, are among the materials most commonly used for the modification of electrodes. In recent years, magnetic nanoparticles of iron oxide (Fe_3O_4) have attracted considerable interest due to their particular attributes, such as magnetic and optical properties, low toxicity, biocompatibility and easy preparation [25,26]. Many of the electrical and magnetic properties of metal nanoparticles are attributed to the electron transfer between Fe^{2+} and Fe^{3+} centers present in the oxide chemical structure [27].

In this context, we evaluated the performance of a very simple, novel and environmentally-friendly electrochemical detector for E3 based on a carbon paste electrode (CPE) modified with ferrimagnetic nanoparticles (Fe_3O_4NPs). As will be demonstrated, due to their physical and catalytic properties, Fe_3O_4NPs increase significantly the oxidation current of E3 compared to the unmodified CPE. The modified electrode (Fe_3O_4NPs/CPE) was successfully applied in studies on the electrochemical behavior of E3 and as a detector in an electroanalytical procedure employed for the quantification of this important hormone in urine and pharmaceutical samples. The use of the developed electrochemical device made possible analysis of pharmaceutical and biological samples at ppm level.

2. Material and methods

2.1. Reagents, solutions and samples

All reagents used in this study were of analytical grade and used without previous purification. The Fe_3O_4NPs, with an average diameter of 50 nm, were purchased from Sigma-Aldrich. The stock solution of E3 was prepared in ethanol (99.5%) in a concentration of 10.0 mmol L^{-1}. The buffer solutions used as the supporting electrolyte were McIlvaine ($Na_2HPO_4/C_6H_8O_7$), B-R ($C_2H_4O_2/H_3BO_3/H_3PO_4$), Sorensen ($Na_2HPO_4/KH_2PO_4$) and phosphate ($H_3PO_4/NaH_2PO_4$), all prepared at a concentration of 0.1 mol L^{-1} in ultrapure water, with a resistivity of 18.2 MΩ cm, obtained from a Milli-Q system (Millipore, USA). The pH of the buffer solutions was adjusted with 1.0 mol L^{-1} HCl or NaOH solutions. The pharmaceutical samples were prepared by macerating ten tablets of the drug Ovestrion®. The mass corresponding to three tablets was then dissolved in 100 mL of ethanol. The solution was stored under refrigeration. To carry out the experiments, an aliquot of 1000 μL was added to the electrochemical cell containing the buffer solution. Artificial urine was prepared according to the procedure described by Burns and Finlayson [28] with the following composition: sodium chloride 105.5 mmol L^{-1}, sodium phosphate 32.3 mmol L^{-1}, sodium citrate 3.21 mmol L^{-1}, magnesium sulfate 3.85 mmol L^{-1}, sodium sulfate

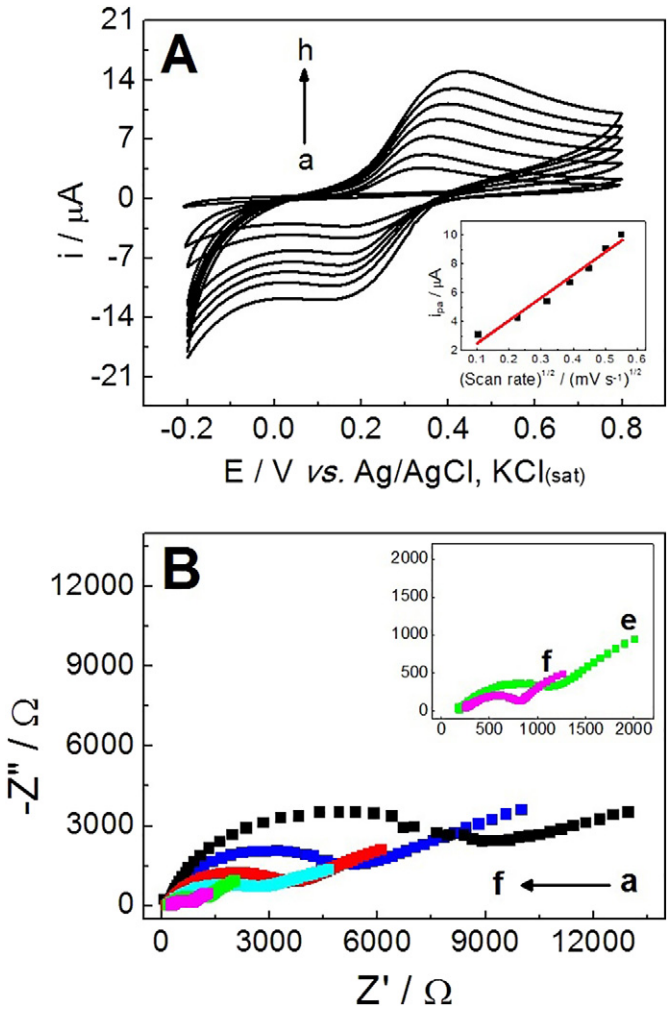

Fig. 2. (A) Cyclic voltammograms for the Fe_3O_4NPs/CPE in (a) 0.5 mol L^{-1} KCl (ν = 50 mV s^{-1}) in the presence of 1.0 mmol L^{-1} $K_3Fe(CN)_6$ ((b–g) ν = 10–300 mV s^{-1}). Insertion: plot i_{pa} vs. $\nu^{1/2}$. (B) Electrochemical impedance spectra for the (a) unmodified CPE and (b–f) CPEs modified with 5, 10, 20, 30 and 40% Fe_3O_4NPs, respectively, in 0.5 mol L^{-1} KCl solution containing 5.0 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1). Insertion: curves (e) and (f) expanded.