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A disposable electrochemical sensor for the rapid determination of levodopa

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Abstract

Levodopa (L-dopa), the biological precursor of catecholamines, is the most widely prescribed drug in the treatment of Parkinson's disease. The present work presents a proposal for the application of a gold screen-printed electrode an electrochemical sensor for monitoring L-dopa in stationary solution and a flow system. Using the electrooxidation of L-dopa at +0.63 V in acetate buffer pH 3.0 on a gold screen-printed electrode it is possible to obtain a linear calibration curve from 9.9×10^{-5} to 1.2×10^{-3} mol L^{-1} and a detection limit of 6.8×10^{-5} mol L^{-1}. Under amperometric conditions (E_{app} = 0.8 V; flow rate = 14.1 mL min^{-1}; pH 3.0), an analytical calibration graph for L-dopa was obtained from 1.0×10^{-6} mol L^{-1} 6.6×10^{-4} mol L^{-1} with a detection limit of 9.9×10^{-7} mol L^{-1}. The method was successfully applied to the determination of L-dopa in commercial dosage forms without any pre-treatment.

Keywords: L-Dopa; Screen-printed gold electrode; Amperometric determination; Flow system

1. Introduction

The development of screen-printing techniques for the fabrication of versatile, inexpensive and disposable electrodes has been a boon to electroanalytical chemistry for various applications [1–3]. Screen-printed electrodes are planar devices, based on different layers of inks printed on a plastic, glass or ceramic substrate. Many ink-type substrates have been used for sensor construction, where the most successful have included carbon and the noble metals as Au, Pt, Ag, etc. The main advantage of this kind of electrode system is associated with their modest cost, potential portability, simplicity of operation, reliable, and the small instrumental arrangement containing the working electrode, auxiliary and reference electrodes. In addition, its disposable characteristics permit the avoid one of electrode poisoning from repeated reuse of the same electrode surface for successive analyses. Therefore, screen- printing electrodes can be manufactured in bulk at relatively low cost, and their effective performance has gained consideration in environmental, biomedical, occupational hygiene monitoring and all the major fields of analytical chemistry [1–9].

Levodopa (L-dopa), 3 (3,4-dihydroxyphenyl)-L-alanine, the medication of choice for the treatment of Parkinson's disease, is principally metabolized by an enzymatic reaction (*dopa-descarboxilase*) to dopamine compensating for the deficiency of dopamine in the brain [10]. Parkinson's disease is a progressive neurological disorder that occurs when the brain fails to produce enough dopamine. This condition causes tremor, muscle stiffness or rigidity, slowness of movement (bradykinesia) and loss of balance. Dopamine cannot be administered directly because it cannot penetrate the blood–brain barrier. Therefore, L-dopa, which can be orally administered, is used to provide a source of dopamine, and is used in the treatment of Parkinson's disease to provide symptomatic relief to most patients at the initial stages of the disease.

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In order to support the evaluation of L-dopa in pharmaceutical formulations and biological fluids many methods have been developed for its determination. The literature has reported several techniques for their analysis in pharmaceutical formulations and biological fluids, especially spectrophotometry [11–13] and high-performance liquid chromatography [14–18].

Electrochemical methods are powerful techniques to follow the oxidation of catecholamines [19]. The two hydroxyl groups present in L-dopa can be electrochemically oxidized at a glassy carbon electrode and this is the basis for its determination. In agreement with the literature [20] L-dopa under very acidic conditions, is oxidized on glassy carbon electrodes by a quasi-reversible two-electron process to an open-chained quinone at potential of around +0.61 V (H_2SO_4 1 mol L^{-1}). In neutral solution the electrooxidation process is an irreversible electrochemical process (E_p = +0.31 V) followed by a chemical reaction, where dopaquinone cyclizes to cyclodopa, leading to the generation of new electroactive product assigned as dopachrome. In the reverse scan the voltammograms show two peaks attributed to reduction of the remaining dopaquinone and reduction of dopachrome to cyclodopa generated after a fast chemical reaction. Although the electrochemical behavior of L-dopa on glassy carbon electrodes is complex, its determination by voltammetric and amperometric methods are reported in the literature [21–27]. Nevertheless, may methods require the use of reagents clean up of the electrode surface and complicated steps involving modified electrode construction. The use of a simple and rapid method based on a screen-printed electrode could be a good strategy for L-dopa determination.

This paper reports on the application of a gold screen-printing electrode as an amperometric sensor for L-dopa determination. Taking into consideration that under flow analysis conditions, it is possible to add amplification of the amperometric signal, simplification of manifolds features and rapidity of analysis, a microflow cell system adapted to the screen-printed electrode was developed. The influence of several parameters (potential, pH and interference) besides the parameters of the flow system was studied and the method optimized for determining L-dopa in pharmaceutical formulations using a gold screen-printed electrode is described.

2. Experimental

2.1. Apparatus

Voltammetric and amperometric measurements were carried out with an AUTOLAB PGSTAT-30 (EcoChimie) connected to a microcomputer for data acquisition and experimental control. The measurements were performed in an conventional electrochemical cell and a microflow cell system (BVT Technologies, Czhec Republic) where the screen-printed gold electrode (BVT Technologies, Mod. AC1.W1.R1) has coupled.

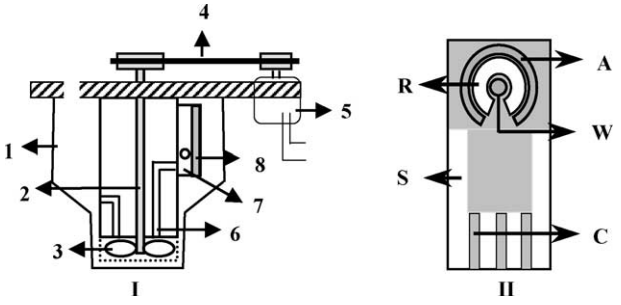

Fig. 1. Schematic diagram of the electrochemical microflow cell (I) and screen-printed gold electrode (II) used in the voltammetric and amperometric measurements.

The design of the gold screen-printed gold electrode used in all there electrochemical experiments is showed in Fig. 1II. The electrode is based on an alumina ceramic base(s) 26 mm long, 7 mm wide and 0.65 mm of thick. On to this surface the working (W), reference (R) and the auxiliary (A) electrodes were applied. The working and auxiliary electrodes were made of Au/Pd (98:2%) and the reference of Ag/AgCl (60:40%). At the end of the sensor was a contacting field, connected with the active part by the silver conducting parts that are covered by a dielectric protection layer. The sensor was connected with a cable to the potentiostat.

The arrangement of the microflow cell system is illustrated in Fig. 1I. A driving shaft (2) was located in the center of a conventional electrochemical vessel (1) carrying the body of the microflow insert (7). The driving shaft was connected to a pump rotor (3). The chamber located above the rotor (4) was connected to the electrode cell containing the three electrodes (8) via a capillary (6). The thin capillary was located in the bulk solution guided the fluid coming from the rotor to the electrode cell (7) where the screen-printed electrode was positioned. The capillary fulfilled the function of stabilizing the flow of liquid before it entered the electrode cell. Following its passage through the cell the liquid was mixed into the bulk content, repeating the cycle several times as necessary. The sensor placed in the cell responds to the sample liquid and this response was recorded as either amperometric or voltammetric mode on the suitable potentiostat.

Cyclic voltammograms under static conditions were recorded after immerging the gold screen-printed electrode directly into the conventional voltammetric cell containing 10 mL of supporting electrolyte and the analyte using a cable with banana plugs as termination. The potential was scanned from −0.2 to 1.2 V at a scan rate of 50 mV s^{-1}.

Under flow conditions, the amperometric and voltammetric measurements were performed recording the electrochemical signal obtained with the solution of L-dopa flowing through the gold screen-printed electrode using linear sweep voltammetry (ν = 3 mV s^{-1}, flow rate = 7.7 mL min^{-1}) and chronoamperometry (E = 0.8 V, t = 50 s and flow rate of 14.1 mL min^{-1}). The parameters were controlled by a GPES 4.9 software (EcoChimie).