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A sensitive nanocomposite-based electrochemical sensor for voltammetric simultaneous determination of isoproterenol, acetaminophen and tryptophan

Hassan Karimi-Maleh [a,*], Mahbobeh Moazampour [a], Hamid Ahmar [b], Hadi Beitollahi [c], Ali A. Ensafi [d]

[a] Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran
[b] Department of Chemistry, Faculty of Sciences, Shahid Beheshti University, G.C., P.O. Box 19396-4716, Tehran, Iran
[c] Environment Department, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran
[d] Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Iran

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ABSTRACT

The electrooxidation of isoproterenol (ISPT), acetaminophen (AC) and tryptophan (Trp) and their mixture has been studied using an 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one modified multiwall carbon nanotubes paste electrode (DMBQ-MCNTPE). The novel sensor exhibited potent and persistent electron mediating behavior followed by well separated oxidation peaks towards ISPT, AC and Trp with activation over-potential. The peak currents were linearly dependent on ISPT, AC and Trp concentrations using square wave voltammetry (SWV) method in the range of 0.04–400, 5.0–500, and 10.0–800 μmol L^{-1}, with detection limits of 0.009, 1.0, and 4.0 μmol L^{-1}, respectively. The modified electrode was used for the determination of ISPT, AC and Trp in biological and pharmaceutical samples.

1. Introduction

Electrochemical sensors satisfy many of the requirements for such tasks, particularly owing to their simplicity of preparation, high selectivity and sensitivity, and fast response [1–10]. Moreover, the limited number of electrode materials makes only a restricted number of analytes suitable for electrochemical detection with high sensitivity and selectivity [11–16]. Therefore, efforts have been made to modify the electrode surfaces for the purpose of lowering the overpotential, improving the mass transfer velocity for effective enrichment of the desired substance and/or restraining the effect of interferences [17–24].

Isoproterenol (ISPT) is usually used for the treatment of primary pulmonary hypertension and allergic emergencies, status asthmaticus, bronchial asthma, ventricular bradycardia, cardiac arrest, glaucoma. This drug also used to cardiac chock, bronchitis and heart attack. On the other hand, the excess of the drug may cause heart failure and arrhythmias [25]. Therefore, selective and sensitive determination of this drug is very important in pharmaceutical and biological samples. Various methods including chromatography [26], chemiluminescence [27], spectrophotometry [28,29], electrochemical methods [30–37] and flow injection analysis [38] have been used for the detection of ISPT.

Acetaminophen is an analgesic and antipyretic drug that widely used by people. It is an effective and safe analgesic agent used for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain [39]. On the other hand, AC causes liver necrosis in humans and experimental animals when high doses are administered [40]. So it is necessary to develop a precise, simple, rapid, and reliable method for the

* Corresponding author. Tel.: +98 911 2540112; fax: +98 151 2277733.
E-mail address: h.karimi.maleh@gmail.com (H. Karimi-Maleh).

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determination of AC. To date, various techniques including titrimetry [41], spectrophotometry [42], high performance liquid chromatography [43], fluorimetry [44] and electrochemical methods [45] have been reported for the determination of AC.

Selective and sensitive determination of amino acids is vital in different fields of research, particularly in medicine, food, biotechnology and wine industries [46]. Trp is a vital amino acid for humans and herbivores, they cannot live without consuming. It is sometimes added to dietary, food products, pharmaceutical formulas due to the scarcely presence in vegetables. Different electrochemical methods [46,47] have so far been available for the determination of TP. Result shows that acetaminophen inhibits liver tryptophan-2,3-dioxygenase activity with a concomitant rise in brain serotonin levels and a reduction in urinary 5-hydroxyindole acetic acid [48]. On the other hand, isoprenaline increases brain concentrations of L-tryptophan [49]. So, simultaneous determination of these compounds is very important in biological samples.

Carbon nanotubes are new type of inorganic material with nanostructure, which is promising as an immobilization substance for different electron transfer mediators [50,51]. The electronic properties of these nanomaterials have been exploited as a mean of promoting the electron transfer reaction for a wide range of molecules and biological species [52–54].

To the best of our knowledge, there are not any reports for simultaneous determination of ISPT, AC and Trp compounds using modified electrodes. The results show that the proposed method is highly selective and sensitive in the determination of ISPT, AC and Trp outperforming any method previously reported in literature.

2. Experimental

2.1. Reagents and apparatus

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. ISPT was used from Aldrich, acetaminophen and tryptophan from Fluka, all used as received.

8,9-Dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one was synthesized according to the previous report [55].

A 1.0×10^{-2} mol L^{-1} ISPT solution was prepared daily by dissolving 0.062 g ISPT in water in a 25-mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with buffer solution.

1.0×10^{-3} mol L^{-1} acetaminophen solution was prepared daily by dissolving 0.015 g acetaminophen in a buffer solution, pH 7.0, in a 100-mL volumetric flask, and under ultrasonication for several minutes. More dilute solutions were prepared by serial dilutions with buffer solution.

1.0×10^{-3} mol L^{-1} tryptophan solution was prepared daily by dissolving 0.024 g tryptophan in a buffer solution, pH 7.0, in a 100-mL volumetric flask, and under ultrasonication for several minutes. More dilute solutions were prepared by serial dilutions with buffer solution.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1} from Merck) solutions with different pH values were used.

Spectrally pure graphite powder (particle size <50 μm) from Merck and multiwall carbon nanotubes (>90%, MWCNTs, $d \times l$ = (90–60 nm) × (5–9 μm)) from Fluka were used as the substrate for the preparation of the carbon paste electrode. High viscosity paraffin (d = 0.88 kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the paste electrodes.

All the voltammetric measurements were performed using an Autolab PGSTAT 302 N, potentiostat/galvanostat (Utrecht, The Netherlands) connected to a three-electrode cell, Metrohm (Herisau, Switzerland) Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and with Autolab software. A platinum wire was used as the auxiliary electrode. DMBQ-MCNTPE or multiwall carbon nanotubes paste electrode (CNTPE) and Ag/AgCl/KCl_{sat} were used as the working and reference electrodes, respectively. The electrode prepared with carbon nanotubes was characterized by scanning electron microscopy (SEM) (Seron Tech. AIS 2100). A digital pH/mV-meter (Metrohm model 710) was applied for pH measurements.

2.2. Preparation of the electrode

50 mg of DMBQ was hand mixed with 850 mg of graphite powder and 100 mg of carbon nanotubes in a mortar and pestle. Using a syringe, 0.50 g of paraffin was added to the mixture and mixed well for 50 min until a uniformly wetted paste was obtained (67:33 (w/w)). The paste was then packed into a glass tube with diameter of 3.0 mm. The thickness of paste was 1.0 cm and electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The unmodified carbon paste electrode (CPE) was prepared in the same way without adding DMBQ and carbon nanotubes to the mixture.

2.3. Preparation of real samples

Ampoule (0.20 mg mL^{-1} ISPT, Galena Siena Srl, Italy) prepared and then 0.10 mL of the solution plus 10 mL of 0.1 mol L^{-1} buffer (pH 7.0) was used for the analysis.

Urine samples were obtained from the Sari Health Centre and were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 20 min at 2500 rpm. The supernatant was diluted 15 times with a phosphate buffer solution (PBS) (pH 7.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. The standard addition method was used for the determination of ISPT, AC and Trp in real samples.

Serum samples were obtained from the Sari Health Centre and were stored in a refrigerator immediately after collection. The serum sample was used without any pretreatment for real sample analysis.