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Graphene/polyvinylpyrrolidone/polyaniline nanocomposite-modified electrode for simultaneous determination of parabens by high performance liquid chromatography

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ABSTRACT

A nanocomposite of graphene (G), polyvinylpyrrolidone (PVP) and polyaniline (PANI) modified onto screen-printed carbon electrode (SPCE) using an electrospraying technique was developed for simultaneous determination of five parabens in beverages and cosmetic products by high performance liquid chromatography. PVP and PANI were used as the dispersing agents of graphene, and also for the enhancement of electrochemical conductivity of the electrode. The electrochemical behavior of each paraben was investigated using the G/PVP/PANI nanocomposite-modified SPCE, compared to the unmodified SPCE. Using HPLC along with amperometric detection at a controlled potential of +1.2 V *vs* Ag/AgCl, the chromatogram of five parabens obtained from the modified SPCE exhibits well defined peaks and higher current response than those of its unmodified counterpart. Under the optimal conditions, the calibration curves of five parabens similarly provide a linear range between 0.1 and 30 μg mL^{-1} with the detection limits of 0.01 μg $mL^{-1}$for methyl paraben (MP), ethyl paraben (EP) and propyl paraben (PP), 0.02 and 0.03 μg mL^{-1} for isobutyl paraben (IBP) and butyl paraben (BP), respectively. Furthermore, this proposed method was applied for the simultaneous determination of five parabens in real samples including a soft drink and a cosmetic product with satisfactory results, yielding the recovery in the range of 90.4–105.0%.

1. Introduction

Parabens (alkyl esters of p-hydroxybenzoic acid) have been widely used for a long time as antimicrobial preservatives in beverages, foods, pharmaceutical products and especially cosmetic products because of their biodegradability, stability, efficiency in wider pH range, non-volatility and other properties such as low cost and no color [1,2]. When the length of alkyl chain increases, the antimicrobial activities of the parabens increase while its water solubility decreases. Moreover, two or more parabens can often be used together to achieve synergistic effects [3,4]. However, high dose of these compounds are dangerous for customers because they can cause allergic contact dermatitis [5,6]. In addition, they can produce inhibitory effects on mitochondrial respiratory capacity, and eliminate the human reproductive potential [7–9], as well as promote breast cancer [10,11]. Therefore, the use of parabens has been limited by the European Economic Community (EEC), *i.e.* the maximum concentration allowed in cosmetics is 0.4% (w/w) for single paraben and up to 0.8% (w/w) for their mixtures, and the maximum thresholds of paraben concentration in foodstuffs and pharmaceutical products are 0.1% (w/w) and 1% (w/w), respectively [12,13].

Various analytical methods have been utilized for the determination of parabens, for instance, UV-spectroscopy coupled with high performance liquid chromatography (HPLC) [14–16], flame ionization detection in gas chromatography (GC) [17], and mass spectrometry (MS) [11,18]. Electrochemical detection (ECD) is an alternative and very attractive detection method for the determination of parabens because of its low cost, simplicity, fast analysis, portability and high sensitivity. A variety of working electrodes have been established for the detection of parabens, including molecularly imprinted polymers (MIPs) film on glassy carbon electrode [19], boron doped-diamond (BDD) electrode [20] and multi-wall carbon nanotubes (MWNTs) coupled with nafion

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modified glassy carbon electrode [21]. In this work, screen-printed carbon electrode (SPCE) was chosen as the working electrode due to its inexpensiveness and ease of preparation and modification. However, a bare SPCE may be limited by its inadequate sensitivity. To improve the sensitivity, nanomaterials such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) and carbon nanodots (CNDs) have been employed to modify the working electrodes and increase its surface area [22–24].

Graphene (G) is a monolayer, crystalline allotrope of carbon which is densely packed in a regular sp^2-bonded atom into a two dimensional honeycomb lattices. Graphene has been widely studied in different fields due to its excellent physical and chemical properties. Recently, graphene has been adopted as a popular nanomaterial in electrochemistry because it exhibits many desirable electrochemical properties such as large surface area, high electrical conductivity and rapid electron transfer [25–27]. Despite these numerous advantages, the uncontrolled agglomeration of graphene due to attractive Van der Waals forces can occur and result in inhomogeneity. Therefore, polyaniline (PANI) and polyvinyl pyrrolidone (PVP) were additionally used to increase the dispersion of graphene. PANI is an outstanding conducting polymer that is widely used for electrode modification in electrochemical biosensors because of its excellent electrochemical properties, ease of synthesis and functionalization, high environmental stability, and low toxicity [28,29]. Meanwhile, it has been reported that PVP can stabilize graphene at high concentration by dispersing it in any organic solvent [30].

Recently, there has been reported that G/PVP/PANI nanocomposite-modified, paper-based biosensor was successfully developed for the determination of cholesterol in a complex biological fluid [31]. In addition, G/PANI nanocomposite-modified SPCE was also effectively coupled with ultra-performance liquid chromatography (UPLC) system for determination of eight sulfonamides (SAs) in shrimp. The sensitivity of eight SAs was higher than the unmodified electrode including BDD electrode [32].

In this research, therefore, G/PVP/PANI nanocomposite-modified SPCE was fabricated and used as the working electrode of electrochemical detection coupled with HPLC. Electrospraying technique was chosen as the fabrication means because of its simplicity, homogeneity of droplets and cost efficiency. The coupled devices were utilized for simultaneous determination of five parabens with satisfactory results. This proposed method is simple and inexpensive hence it can be an alternative approach for sensitive determination of parabens in soft drinks and cosmetic products.

2. Experimental

2.1. Chemicals and materials

All solutions were prepared by dilution with ultra-purified deionized ($R \geq 18.2\ M\Omega\ cm^{-1}$), Milli-Q water (Merck Millipore, Germany). Stock standard solutions of five parabens ($1000\ \mu g\ mL^{-1}$), namely methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), butyl paraben (BP) (Sigma-Aldrich, USA) and isobutyl paraben (IBP) (Tokyo Chemical Industry, Japan), were prepared in Milli-Q water: acetonitrile (1:1, v/v). The standard working solutions were diluted from these stock solutions to the desired concentrations.

In HPLC, all solutions were filtered through 0.22 μm Nylon membrane filter paper (Vertical Chromatography Co., Ltd, Thailand). The mobile phase was a mixture of buffer solution and acetonitrile (60:40, %v/v). The buffer solution was 0.05 M phosphate buffer prepared from potassium dihydrogen phosphate (KH_2PO_4; Carlo Erba Reagenti-SDS, France) and di-sodium hydrogen phosphate (Na_2HPO_4; Merck, Germany), and then precisely adjusted to the desired pH with ortho-phosphoric acid (85%) and sodium hydroxide (NaOH) (Merck, Germany).

2.2. Instruments

Cyclic voltammetry was carried out by a potentiostat (CHI 1232A, CHI Instrument, USA) with three-electrode system; a G/PVP/PANI nanocomposite-modified screen-printed carbon electrode as working electrode, silver/silver chloride (Ag/AgCl) as reference electrode, and platinum wire as counter electrode. Electrochemical measurement was performed in a home-made cell at room temperature.

An HPLC system (Shimadzu LC-20AD XR UFLC Shimadzu, Japan) with a chromatographic column of Luna 5 μm C18 column (150 mm × 4.6 mm i.d.) from Phenomenex (CA, USA) was used. A thin-layer flow cell (GL Sciences, Inc., USA) was assembled to the HPLC as a detection unit which was comprised of three electrodes; a G/PVP/PANI-modified SPCE working electrode, a Ag/AgCl reference electrode (Bioanalytical System, Inc., USA) and a stainless steel tube counter electrode.

2.3. Fabrication of G/PVP/PANI nanocomposite-modified SPCE

SPCEs used in this research were produced in our laboratory by a screen-printing technique. First, Ag/AgCl ink (Gwent group, United Kingdom) was printed onto a PVC substrate as an electrical connector and then dried in an oven at 55 °C for 1 h. After that, carbon ink (Gwent group, United Kingdom) was printed as an active area of working electrode and dried in an oven under the same condition.

For the modification of SPCE, a G/PVP/PANI nanocomposite solution was sprayed onto the SPCE by the electrospraying technique. The conditions used including flow rate, the distance between the needle and the ground collector, and applying voltage were $1.0\ mL\ min^{-1}$, 5 cm, and 9 kV, respectively [31]. Twenty milligrams of graphene nanopowder (SkySpring Nanomaterials, Inc., USA) and 20 mg of PVP (Sigma-Aldrich, USA) were dispersed in 10 mL of dimethylformaminde (DMF) and sonicated for 6 h at room temperature. Next, PANI was doped with camphor-10-sulfonic acid (CSA) to make it conductive and subsequently dissolved in chloroform [28]. The G/PVP/PANI nanocomposite solution was then prepared by mixing of a dispersed graphene solution and a doped PANI solution with a ratio of 1:1 v/v.

2.4. Electrochemical measurement

The electrochemical characteristic of G/PVP/PANI nanocomposite-modified SPCE was investigated by cyclic voltammetry (CV) of ferri/ferrocyanideredox couple. CV was also used for the study of electrochemical behavior of each concerned paraben in 0.05 M phosphate buffer solution (pH 6) on the G/PVP/PANI modified SPCE. The potential range of CV was scanned from −0.6 V to +1.0 V for ferri/ferrocyanide and +0.4 V to +1.3 V for parabens with a scan rate of $100\ mV\ s^{-1}$.

A mixture of five parabens was separated by HPLC using 0.05 M phosphate buffer (pH 6):acetonitrile (60:40, %v/v) as mobile phase, flow rate of $1.5\ mL\ min^{-1}$, and injection volume of 50 μL. The resulting chromatograms were obtained with amperometry with an applied constant potential of +1.2 V *vs* Ag/AgCl at room temperature (~25 °C).

2.5. Analysis of real samples

The developed method was applied for the determination of five parabens in a soft drink sample and a cosmetic product