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Determination of butylparaben by adsorptive stripping voltammetry at glassy carbon electrodes modified with multi-wall carbon nanotubes☆,☆☆

María Ángeles Lorenzo [a], Alberto Sánchez Arribas [b], Mónica Moreno [b], Esperanza Bermejo [b], Manuel Chicharro [b], Antonio Zapardiel [a,*]

[a] Dpto. Ciencias Analíticas, Universidad Nacional de Educación a Distancia (UNED), Paseo Senda del Rey, 9, 28040 Madrid, Spain
[b] Capillary Electrophoresis Dual Detection Group, Dpto. Química Analítica y Análisis Instrumental, Universidad Autónoma de Madrid, C/Francisco Tomás y Valiente, 7, 28049 Madrid, Spain

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ABSTRACT

This work reports on the performance of glassy carbon electrodes (GCE) modified with a layer of multi-wall carbon nanotubes (MWCNTs) for the determination of butylparaben (BP) by adsorptive stripping voltammetry (AdSV). Several operating conditions and voltammetric parameters were examined. Under the chosen conditions, BP peak current obtained by differential pulse voltammetry increased linearly with BP concentration up to 100 μM with a limit of detection of 0.2 μM. A molecularly imprinted solid-phase extraction procedure (MISPE) was developed to improve the sensitivity and selectivity of BP electroanalysis when applied to real samples. The proposed methodology was successfully used for the quantification of BP in spiked water samples with recovery values between 82 and 85%. The MISPE procedure allowed the detection of BP at concentration levels of 0.02 μM in the presence of potential interfering substances such as 2,4,6-trichlorophenol (TPC), atrazine, paracetamol or diclofenac.

1. Introduction

Parabens, esters of 4-hydroxybenzoic acid, are an important group of chemicals used as preservatives in cosmetic and pharmaceutical products due to their antimicrobial activity and ideal physicochemical properties [1]. However, some studies have demonstrated that exposure to parabens may disrupt the endocrine system, exhibit weak estrogenic activity and may have harmful consequences on human and wildlife [2]. The European Union (EU) Directive [3] permits the use of parabens in cosmetics with a maximum concentration of 0.4% w/w for each one and 0.8% w/w as total concentration of parabens in mixtures, both expressed as 4-hydroxybenzoic acid. In pharmaceuticals their content seldom exceeds 1% w/w [4] whereas in foods their use is forbidden by European Directive 2006/52/CE [5]. Therefore, the development of analytical methodologies for monitoring the occurrence of parabens is demanded since these compounds are a concern for human health and environment.

Usual methodologies for the analysis of parabens include analytical separation techniques and a large number of methods have been reported in the last seven years. Among others, Gas Chromatography coupled to Mass (GC–MS) [6–12] and Tandem Mass Spectrometry (GC–MS/MS) [13,14] as well as High Performance Liquid Chromatography (HPLC) [15–17] and Liquid Chromatography–Mass Spectrometry (LC–MS) [18–20], have been extensively used for the separation and detection of these compounds. Other schemes including Capillary Electrophoresis modes such as Micellar Electrokinetic Capillary Chromatography (MEKC) [1,2,21–23], Non-Aqueous Capillary Electrophoresis (NACE) [4,24] and Capillary Zone Electrophoresis (CZE) [25,26] have been described elsewhere. Electrochemical detection has been employed in connection to HPLC and CZE [2,25,26] but scarce examples of simple electroanalysis of parabens have been reported to date [27,28].

In this contribution we report on the sensitive and reliable determination of butylparaben (butyl 4-hydroxybenzoate; BP) by adsorptive stripping voltammetry (AdSV) using glassy carbon electrodes (GCE) modified with multi-wall carbon nanotubes (MWCNTs) dispersed in Nafion. Carbon nanotubes represent a type of carbon nanomaterial whose unique electronic, mechanical and structural properties have produced a profound impact in electroanalysis. The incorporation of carbon nanotubes to transducers and (bio)sensors provides several advantages such as increased voltammetric currents, increased heterogeneous electron transfer rates and insignificant electrode fouling [29–31]. In the following sections it will be described the exploitation of these favorable qualities for the electroanalysis of BP in alliance with a molecularly imprinted solid-phase extraction (MISPE) procedure which provided improved selectivity and limit of detection when analyzing BP in real water

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☆☆ Dedicated to the memory of our dear colleague María Ángeles Lorenzo Vecino, may she rest in peace (1967–2013).
* Corresponding author. Tel.: +34 3987361; fax: +34 3986133.
E-mail address: azapardiel@ccia.uned.es (A. Zapardiel).

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samples by the molecular recognition properties of a molecularly imprinted polymer (MIP) [32].

2. Experimental

2.1. Reagents

Butylparaben, benzylparaben, methylparaben, ethylparaben, phenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, propylgallate, salicylic acid, paracetamol, diclofenac sodium, methacrylic acid (MAA), 2,2′-azobisobutyronitrile (AIBN), and divinylbenzene (DVB), were obtained from Sigma-Aldrich (Madrid, Spain) and HPLC grade organic solvents were from Scharlab S.L (Barcalona Spain). Atrazine and simazine were from Riedel-de-Häen (Madrid, Spain) whereas metamizol was from Fluka (Madrid, Spain). Stock solutions of butylparaben were prepared in acetonitrile and stored at 4 °C in the dark. Diluted standard was prepared daily by appropriate dilution with water from these stock solutions. Ultrapure water ($\rho > 18.2$ MΩ cm) from a Barnstead Nanopure system (Thermo Scientific) was used for preparing all solutions. Multi-wall carbon powder (MWCNT; 30 ± 15 nm diameter, 5–20 μm length, purity >95%, "hollow tube" type, prepared by chemical vapor deposition, nominal 1% Fe and 0.1% S residuals, Lot. PD30L520-60805) was obtained from NanoLab (Waltham, MA, USA). Nafion (NAF) 5% in alcoholic solution was purchased from Aldrich. A 0.020 M phosphate buffer solution of pH 7.0 was employed as supporting electrolyte and it was prepared from the corresponding 0.50 M phosphate acid solution and the desired pH was set by adding 1.0 M NaOH and made up to their final concentration.

2.2. Apparatus and electrodes

Electrochemical experiments were carried out with an Epsilon (BAS; Bioanalytical Systems Inc.; West Lafayette, IN, USA) electrochemical analyzer using a conventional three-electrode configuration. A Ag/AgCl/NaCl 3 M (BAS, model MF-2052) and a platinum wire were employed as reference electrode and counter electrode, respectively. All measured potentials were referred to this electrode system. A glassy carbon electrode (GCE) of 3-mm diameter (BAS, model MF-2012) was used as a working electrode.

2.3. Procedures

2.3.1. Preparation of the working electrodes

GCE were polished with 0.3- and 0.05-μm alumina slurries (Buehler; Spain) on polishing cloths (Buehler; Spain) and subjected to ultrasonic cleaning with water for 1 min before use. Modified GCE were prepared following the procedure reported by Sánchez et al. [26,33]. The MWCNT dispersions in NAF were prepared by dispersing 4.0 mg of the as-received MWCNT in 4.0 mL of ethanol/water (1:1 v/v) dispersant solution, containing 0.1% (w/v) NAF, by ultrasonic treatment for 60 min. Three dispersions were prepared at once and were employed during these studies. These dispersions remained homogeneous and stable for at least 6 months. A layer of MWCNT was obtained by dropping the MWCNT dispersion (15 μL) onto the clean GCE surface and leaving it to dry for at least 2 h.

2.3.2. Electrochemical measurements

All measurements were carried out using new electrode surfaces, namely a freshly polished GCE or a freshly-modified GCE. The electrodes were subjected to a pretreatment by applying 20 voltammetric cycles at 50 mV/s between 0 and +1.2 V in a 0.020 M phosphate buffer solution of pH 7.0 (BP-free) before electrochemical measurements. When the accumulation of BP was carried out for quantitative purposes, the analyzed solutions were placed in the electrochemical cell and were stirred (150 rpm) for 180 s under potentiostatic conditions (−100 mV). After that, the stirring was stopped and the differential pulse voltammetry (DPV) signal was recorded.

2.3.3. Polymer preparation and MISPE

Molecularly imprinted polymer (MIP) was prepared following the procedure described by Núñez et al. [32]. Polymer matrix was obtained by the reaction of MAA, DVB and AIBN in a mixture of acetonitrile and toluene (75:25 v/v) in the presence of the template molecule, benzylparaben. The polymerization reaction was allowed to proceed at 80 °C in a water bath for 12 h and the obtained solid was dried at 70 °C in heater. The template was removed by Soxhlet extraction with a methanol:acetic acid mixture (1:1 v/v) for 72 h and an amount (106 mg) of dry MIP was placed in an empty SPE cartridge. The MISPE procedure typically included the following steps: 1) conditioning with 3.0 mL of toluene; 2) washing with 1.0 mL of water; 3) loading of 100 mL of water sample; 4) washing with 1.0 mL of CCl_4; 5) elution with 4.0 mL of acetonitrile containing 2.5% (v/v) of acetic acid; 6) evaporation of the organic solvents to dryness under an argon stream; and 7) reconstitution in 10.0 mL of electrolyte by ultrasonic treatment (3 min) prior to AdSV analysis.

2.3.4. Sample preparation

Water samples were collected from different sites along the Tormes River (Ávila, Comunidad Autónoma de Castilla León, Spain) and were stored in the dark at 4 °C before analyzed. Addition of an appropriate amount of BP standard solution to the water samples was carried out to obtain the desired concentrations before being submitted to the MISPE process. In all cases, a blank sample was analyzed in the same way for comparison.

3. Results and discussion

3.1. Preliminary studies

The electrochemical response of BP was examined initially by cyclic voltammetry (CV) using a bare GCE as a working electrode. The effect of pH upon the voltammetric signal of BP was evaluated after CV experiments (scan rate, 50 mV/s) carried out in phosphate buffer solutions containing 0.50 mM concentration of analyte. A well-defined peak corresponding to BP electrochemical oxidation, exemplified in the voltammograms shown in Fig. 1, was observed in all cases within the pH interval (2–12) studied. This signal was observed only in the first scan, and no signal was noticed in subsequent scans as a consequence of the electrode fouling by BP oxidation products. The peak potential values (Fig. 1 inset) showed a negative shifting when pH was increased up to 8.0 and leveled off at higher pH. The fitting of peak potential (Ep) vs pH in these pH intervals resulted in the following equations: Ep = 1165 − 58.7 pH (r = 0.996; n = 7) and Ep = 713 − 3.0 pH (r = 0.67; n = 4) for pH values below and above 8, respectively. This Ep evolution at pH below 8 is quite similar to that reported previously [28] for methylparaben. The slope value (58.7 mV/pH) obtained at pH <8 indicates that the electrochemical process under these conditions implies the cleavage of equal number of protons and electrons in the rate determining step [34] whereas at pH >8 no proton exchange was evolved. The intersection point of these equations shows a pH value of 8.1 which is close to the pK_a values, ranging in the pH 8.2–8.4 interval, reported previously for BP [4,15,35]. These results allow proposing the following electrochemical reactions for the oxidation of BP, where the electrochemical process takes place at the hydroxyl substituent of the molecule.

$$C_4H_9-OOC-C_6H_4OH \rightarrow C_4H_9-OOC-C_6H_4O^{\bullet}+H^{+}+e^{-}\,\text{at pH}<8 \tag{1}$$

$$C_4H_9-OOC-C_6H_4O^{-} \rightarrow C_4H_9-OOC-C_6H_4O^{\bullet}+e^{-}\,\text{at pH}>8 \tag{2}$$

This process is common to other paraben derivatives [28]. After this initial electron transfer, the radical species can be further oxidized to quinone derivatives and/or alternatively form polymeric