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Electrochemical detection of benzo(a)pyrene in acetonitrile–water binary medium [☆]



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ABSTRACT

Electrochemical oxidation of adsorbed benzo(a)pyrene (BaP) on the glassy carbon electrode (GCE) was explored in acetonitrile–water. When the GCE was incubated in 100 nM BaP acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$) for 10 min at open circuit, and then transferred into blank acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$, pH = 0.70) for differential pulse voltammetry measurement, a distinct oxidation peak at 0.98 V (vs. Ag/AgCl) was observed. The peak potential was about 180 mV lower than that in acetonitrile. Importantly, the peak current was more than 22 times greater. The effects of water on BaP preconcentration on the electrode and electrochemical oxidation were revealed, respectively. Based on the results, an electrochemical assay for BaP detection was developed. The GCE was respectively incubated in acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$) with BaP concentration ranged from 0 nM to 1000 nM, and then transferred into the corresponding blank acetonitrile–water (pH = 0.70) for DPV measurements. When the BaP concentration was increased, an increased oxidative current at 0.98 V (vs. Ag/AgCl) was observed, and a detection limit of 0.67 nM was achieved. Because all other priority polycyclic aromatic hydrocarbons could not be electrochemically oxidized at 0.98 V, the electrochemical assay showed very high selectivity to BaP. Finally, the developed electrochemical assay was successfully applied to determination of BaP in a series of real world samples, such as drinking water, tap water, lake water and river water.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are well-known persistent organic pollutants owing to their high mutagenicity, teratogenicity and carcinogenicity [1–3]. They adversely affect the quality of human life through food chains or environmental cycles upon being released into the environments [3–5]. Among PAHs, benzo(a)pyrene (BaP) exhibits the greatest carcinogenic activity, and it always exists in PAHs contaminated environmental samples [6]. Therefore, BaP is frequently used as a marker for estimating the standard of PAH contamination [7,8].

Conventional identification and quantification techniques for BaP included high-performance liquid chromatography (HPLC), fluorescence spectrometry, gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS)

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[9–13]. Most of them involved the employment of expensive and huge instruments and required complex sample pretreatment steps, making these methods unsuitable for routine control analysis. Afterwards, quartz crystal microbalance and surface-enhanced Raman scattering had also been developed, but the selectivity of these techniques were needed to be addressed [6,14,15]. Recently, electrochemical immunoassay, photo-electrochemical immunoassay and electrochemiluminescence were also reported, which attempted to achieve the simplified, economized and miniaturized detection assays [16–19]. Electrochemical immunoassay and photo-electrochemical immunoassay involves the application of specific antibodies, but the limitation in acquiring proper antibodies restricts its extensive applications. For electrochemiluminescence, the design and synthesis of proper nanomaterials specific to BaP remain a great challenge (such as TiO₂ nanotubes adsorbing PAHs with more than four rings [19]), which still has a long way to go. In this context, the achievement of low cost, simple, selective and portable methods for the detection of BaP are not only meaningful but also necessary. BaP electrochemical oxidation was usually studied in organic solvents, such as acetonitrile [20,21]. Although acetonitrile was ready to solve BaP, the oxidation potential of BaP was relatively higher. Later, Zühre

et al. investigated the electrochemical behavior of BaP in aqueous medium and the detection limit of 27 nM was obtained [22,23]. BaP was more easily oxidized in water, but the solubility was greatly limited. Therefore, a facile electrochemical method for sensitive monitoring BaP is still highly desired. If acetonitrile–water binary mixture is introduced, water can reduce the oxidation potential of BaP, and acetonitrile can increase the solubility of BaP, which could overcome the disadvantages encountered in pure acetonitrile and pure water. To the best of our knowledge, the electrochemical behavior of BaP in acetonitrile–water has not been reported, and whether it can make a breakthrough in sensitivity and selectivity for electrochemical detection of BaP is not known.

In this paper, we reported the electrochemical oxidation of BaP in acetonitrile–water. BaP was adsorbed on the glassy carbon electrode (GCE) through preconcentrating 100 nM BaP in acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$) for 10 min at open circuit, and then transferred into the blank acetonitrile–water solutions ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$, pH= 0.70) for differential pulse voltammetry measurements. A distinct oxidation peak at 0.98 V was observed, which was about 180 mV lower than that in acetonitrile, and the peak current was more than 22 times greater. The peak current was more than 10 times greater than that in aqueous medium. Based on the results, a facile electrochemical assay for sensitive and selective detection of BaP was developed. The detection limit is 0.67 nM. Finally, the feasibility of the electrochemical assay for analysis of BaP in a series of real world samples, such as drinking water, tap water, lake water and river water, was also successfully demonstrated, respectively.

2. Experimental

2.1. Materials

Benzo(a)pyrene (BaP) was purchased from Fluka (Steinheim, Germany). Naphthalene, anthracene, phenanthrene, fluorene, acenaphthene, pyrene, 1, 2-benzanthracene, chrysene, and fluoranthene were purchased from Acros Organics (New Jersey, USA). Acenaphthylene, benzo(b)fluoranthene, and benzo(k)fluoranthene were purchased from Sigma-Aldrich Chemical (Sigma-Aldrich, USA). Dibenz(a, h)anthracene was achieved from Tci (Tokyo, Japan). Benzo(ghi)perylene was purchased from Accustandard (New Haven, CT). And indeno(1, 2, 3-cd)pyrene was received from Supelco (Bellefonte, PA). Sodium perchlorate (NaClO_4) was purchased from Sigma-Aldrich (St. Louis, MO). All reagents were used as received. Stock solutions of the PAHs (1 mM) were prepared in acetonitrile (HPLC Grade) and were stored at 4 °C in the dark. Deionized (DI) water (18.2 M Ω) from a Millipore Milli-Q system was used for washing, sonication, and preparing solutions. Glassy carbon electrodes (3.0 mm in diameter) and Ag/AgCl electrodes were obtained from Aida Instrument Inc. (Tianjin, China). Drinking water and tap water was from Beijing Normal University, Beijing. Lake water was collected from Baiyangdian in Hebei province. River water was collected from Guangxi province.

2.2. Electrochemical measurement

All electrochemical experiments were performed on a CHI650D electrochemical working station (CHI instruments, Shanghai Chenhua, China). A conventional three-electrode configuration was employed, consisting of a glassy carbon electrode as the working electrode, an Ag/AgCl electrode (saturated with KCl) as the reference electrode and a platinum wire (Shanghai Chenhua, 99.9% purity, 1 mm in diameter) as the auxiliary electrode. The measurements were carried out in a 10 mL electrochemical cell, at room temperature. Differential pulse voltammetry (DPV) measurement was applied

to detect the PAHs with the amplitude of 50 mV, pulse width of 0.2 s, potential increment of 10 mV, sampling width of 0.0167 s and pulse period of 0.5 s.

2.3. Electrochemical determination of PAHs

Glassy carbon electrode were thoroughly polished using 0.05 μm alumina powder in water to obtain a mirror finish. After sonicating in anhydrous ethanol and deionized water, respectively, the electrode was electrochemically cleaned in 1 M H_2SO_4 by cyclic voltammetry with the potential range from -0.5 to 0.8 V (vs. Ag/AgCl) at a scan rate of 500 mV/s until the reproducible cyclic voltammogram was obtained. The electrodes were then washed with copious amounts of water and dried under a nitrogen stream.

The electrochemical determination consisted of two consecutive steps: (1) preconcentration of analytes from the stirred solutions (520 rpm) to the electrode at open-circuit and (2) DPV measurement was performed to detect the adsorbed PAHs in a blank solution (with 0.2 M NaClO_4 as electrolyte) after having rinsed the electrode thoroughly with the blank solution. For the analysis of spiked real water samples, water was changed from deionized water to drinking water, tap water, lake water or river water, and other conditions and procedures were the same as that of standard solution.

3. Results and discussion

3.1. Electrochemical oxidation of BaP

100 nM BaP in acetonitrile (with 0.2 M NaClO_4 as electrolyte) did not virtually produce corresponding electrochemical response (Fig. S1 in the Supporting information). However, upon the glassy carbon electrode (GCE) being incubated in 100 nM BaP acetonitrile for 10 min at open circuit, and then transferred into the blank acetonitrile (with 0.2 M NaClO_4 as electrolyte) for DPV measurement, a weak and broad oxidation peak at 1.16 V (vs. Ag/AgCl) was observed as shown in Fig. 1A, which was due to the oxidation of adsorbed BaP on the GCE. The result demonstrated that BaP preconcentration was an essential step for achieving BaP oxidation at low concentrations. Alternatively, when the GCE was incubated in 100 nM BaP acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$) for 10 min at open circuit (Figs. S2 and S3 in the Supporting information), followed by being measured in blank acetonitrile–water ($V_{\text{water}}:V_{\text{acetonitrile}}=1:1$, pH= 0.70, Fig. S4 in the Supporting information), a distinct oxidation peak at 0.98 V (vs. Ag/AgCl) was observed as shown in Fig. 1B. The BaP oxidation potential was about 180 mV lower than that in acetonitrile. Importantly, the oxidation current was more than 22 times greater. If GCE was incubated in 100 nM BaP aqueous solution ($V_{\text{water}}:V_{\text{acetonitrile}}=4995:5$, which could be referred to as aqueous solution) for 10 min at open circuit, then transferred to the corresponding blank solution (pH= 0.70) for DPV measurements, a small oxidation peak at 0.90 V was obtained as shown in Fig. 1C. From the shift of the oxidation potential to the enhancement of the oxidation current, the effect of water on BaP electrochemical oxidation is evident. These results demonstrated that acetonitrile–water binary mixtures were more facile for the electrochemical oxidation of BaP compared to both acetonitrile and water.

Firstly, the effect of water on BaP oxidation potential was analyzed. GCE was incubated in 100 nM BaP acetonitrile for 10 min at open circuit, and then transferred into a series of blank acetonitrile–water solutions with different volume ratios for DPV measurements. The BaP oxidation potential was gradually decreased from 1.16 V to 0.90 V (vs. Ag/AgCl) when the water volume ratio was increased (Fig. S4 in the Supporting information). The oxidation potential shift demonstrated that the presence of water in measurement system facilitated the electrochemical oxidation of adsorbed

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