Talanta 130 (2014) 207–212

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Simultaneous determination of endocrine disrupting compounds bisphenol F and bisphenol AF using carboxyl functionalized multi-walled carbon nanotubes modified electrode

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ARTICLE INFO

Article history:
Received 22 February 2014
Received in revised form
22 June 2014
Accepted 25 June 2014
Available online 4 July 2014

Keywords:
Bisphenol AF
Bisphenol F
Carboxyl functionalized multi-walled carbon nanotubes
Differential pulse voltammetry

ABSTRACT

A novel, simple and selective electrochemical method was developed for simultaneous determination of bisphenol F (BPF) and bisphenol AF (BPAF) in aqueous media (phosphate buffer solution, pH 6.0) on carboxyl functionalized multi-walled carbon nanotubes modified glassy carbon electrode (MWCNT-COOH/GCE) using differential pulse voltammetry (DPV). In DPV, MWCNT-COOH/GCE could separate the oxidation peak potentials of BPF and BPAF present in the same solution though, at the bare GCE, the peak potentials were indistinguishable. The results showed that the electrochemical sensor exhibited excellent electrocatalytic activity towards the oxidation of the two analytes. The peak current in DPV of BPF and BPAF increased linearly with their concentration in the ranges of 0.6–1.6 mmol/L BPF and 0.6–1.6 mmol/L BPAF. The detection limits were 0.1243 mmol/L and 0.1742 mmol/L ($S/N=3$) correspondingly. The modified electrode was successfully used to simultaneously determine BPF and BPAF in real samples.

1. Introduction

Bisphenol AF [1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxyphenyl)propane] (BPAF) and bisphenol F [4,4′-dihydroxydiphenyl-methane] (BPF) have been confirmed to be the endocrine disrupting compounds (EDCs) by the Environmental Protection Agency (EPA) of the United States. The adverse health effects of exposure to EDCs have been reported, such as decreased sperm count, reduced fertility, increased incidences of breast, ovarian and testicular cancers [1–6]. BPAF and BPF have broad applications in the areas such as electronic devices and optical fibers (as a monomer in a multitude of polymers), food processing equipment and agricultural purposes [7,8]. Especially within the plastic compounds, the uses of BPF and BPAF in diverse domestic materials and products have led to its presence in greater or lesser concentrations in food, drinking water and wastewater. However, they used indiscriminately can accumulate in food and water sources with subsequent bioconcentration through the food chain [9–11]. These organic toxins enter human bodies through the food chain or drinking water and threaten human health. Considering the serious adverse impacts of bisphenol derivatives on the human health and environment, thus, sensitive, accurate, and rapid detection of these bisphenol-type endocrine disrupting compounds is important to protect the environment and human health.

In practice, a mixture of two or more components is generally present in real wastewater systems. Since these substances are chemically similar, the analysis becomes difficult at traced levels without previous separation. Generally, detection of endocrine disrupting compounds like BPF and BPAF was generally carried out by capillary electrophoresis (CE) with different detectors, high performance liquid chromatography (HPLC), liquid chromatography coupled with mass spectrometry (LC–MS), gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC–MS) [12–24]. However, some of these techniques are time consuming and often require expensive instrumentation (the apparatuses are normally located far away from the possibly polluted sites) and toxic organic reagents, making them complicated and thus unsuitable for field routine operation. In recent years, electrochemical techniques have drawn the interest of researchers. Electrochemistry offers the possibility of direct, on-line and real-time measurements of important biological species, which has become a sensitive and convenient method for chemical analysis [25]. Especially, voltammetric techniques offer the possibility of determining the analyte concentration directly in the sample without any special pre-treatment or chemical separation, as well as analyzing colored materials and samples with dispersed solid particles [26]. According to our knowledge, little literature about electrochemical methods for the simultaneous determination of BPF and BPAF had been reported.

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http://dx.doi.org/10.1016/j.talanta.2014.06.056
0039-9140/

In the present study, the main target is to develop a simple and fast but sensitive and selective electrochemical sensor for the simultaneous determination of BPF and BPAF. The conditions of simultaneous determination of BPF and BPAF by DPV were optimized; the interference experiment was carried out. Furthermore, the practical application was investigated using standard addition method and satisfactory results were obtained.

2. Materials and methods

2.1. Apparatus and chemicals

Cyclic voltammetry (CV) and DPV were performed using a CHI660D electrochemical workstation (Chenhua Instrument Company of Shanghai, China) coupled with a conventional three-electrode cell. The working electrode was the MWCNT-COOH/GCE (3 mm diameter), the auxiliary electrode was platinum wire, and the reference electrode was saturated calomel electrode (SCE). A S-3C Model pH meter (Shanghai Precision Scientific Instrument Co., China) was used for measuring the pH of solutions.

MWCNT-COOH (length 0.5–2 μm; specific surface area $>500\ m^2\ g^{-1}$; outer diameter <8 nm; –COOH content 3.86%; 95% purity) was purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences.

The analytical standard BPAF and BPF (Chemical reference substance, 99.0% purity) was purchased from HEOWNS Biochemical technology Co., Ltd. (Tianjin, China). The analytical reagent grade N,N-dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were of analytical reagent grade and purchased from Shenyang Chemical Company, China. Ultrapure water used throughout experiments was purified using a Sartorius Arium 611 system (Sartorius, Göttingen, Germany).

A 1×10^{-2} mol/L stock standard solution of BPAF was prepared by dissolving 168.1 mg of BPAF in 10.00 mL ethanol, and diluted by adding ethanol up to a 50.00 mL brown volumetric flask. The standard stock solutions of BPAF were diluted successively to the required concentration with ethanol in the experiment, and kept in dark below 4 °C. To prepare the 1×10^{-2} mol/L stock standard solution of BPF the same method was used with BPAF. A 3.0 mg mL^{-1} [MWCNT-COOH]–DMF dispersion was prepared by dissolving 15.0 mg of MWCNT-COOH in 5 mL DMF by ultrasonication for 30 min.

2.2. Construction of the MWCNT-COOH/GCE

Before modification, the bare glassy carbon electrode (GCE, 3 mm in diameter) was polished with three grades of a-Al_2O_3 slurries (1.0, 0.3 and 0.05 mm), rinsed thoroughly with redistilled deionized water between each polishing step, followed by sonication in anhydrous ethanol and ultrapure water after each stage of polishing successively and dried in air before use. A 7.0 μL (the optimum concentration of MWCNT-COOH 3.0 mg/mL) DMF dispersion was coated on the surface of GCE, and then the solvent was evaporated under the infrared lamp to obtain the MWCNT-COOH/GCE.

2.3. Procedure for simultaneous determination of BPF and BPAF analysis

The electrochemical behavior and the determination of BPF and BPAF were performed by CV and DPV. All the experiments were carried out in a conventional electrochemical cell holding 5.00 mL 0.2 mol/L PBS (pH 6.0) and 10^{-3} mol/L BPF and BPAF at room temperature (25 ± 1 °C). Before analysis, the experimental solution was deaerated by highly pure nitrogen for 10 min.

2.4. Real samples

The real samples were collected from rubber gloves. The rubber gloves were cut into small pieces (2.00 g). Ultrasonicated for 30 min in 20 mL ethanol to extract BPF and BPAF in rubber gloves and then immersed in ethanol for 24 h. The extracting solution was filtered and the volume was set to 50.00 mL volumetric flask. The extraction process was repeated twice.

The wastewater used in this study was taken from a municipal wastewater treatment plant (Shenyang, China); upon reception, sample was filtered through 0.45 μm nylon. Above samples were kept in dark below 4 °C.

If the samples were verified to be free of BPF or BPAF, then they were spiked with BPF and BPAF at different concentration levels – 0.8 and 1.5 mmol/L.

3. Results and discussion

3.1. Electrochemical behavior of BPF/BPAF at MWCNT-COOH/GCE

The effectiveness of MWCNT-COOH/GCE for the oxidation of BPF/BPAF was assessed by cyclic voltammetry in the elected

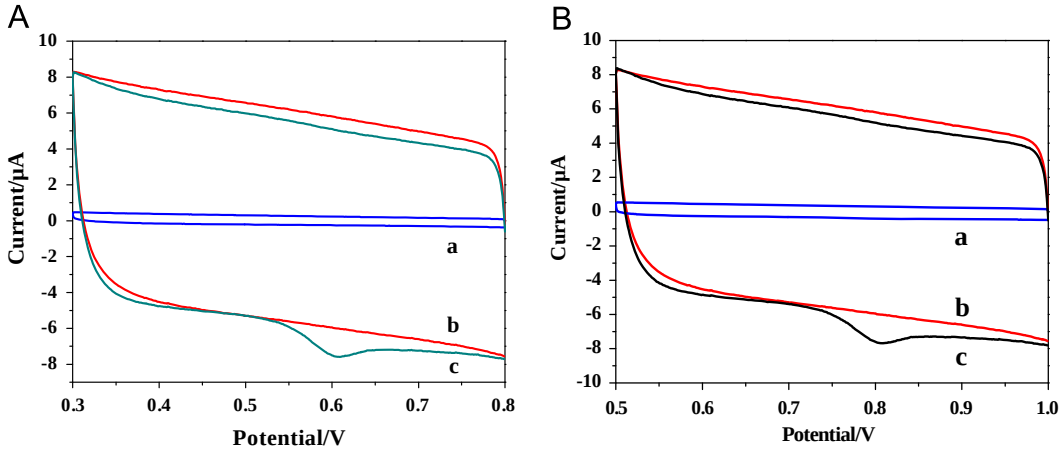


Fig. 1. CVs of BPF (A)/BPAF (B) in 0.2 mol/L PBS (pH 6.0) solution ((a) bare GCE; (b) MWCNT-COOH/GCE in the absence of BPF or BPAF and (c) MWCNT-COOH/GCE containing 10^{-3} mol/L of BPF/BPAF).

electrolyte (0.2 M pH 6.0 PBS, N_2 saturated). Fig. 1A and B displays the CVs of 10^{-3} mol/L BPF and BPAF at bare GCE and MWCNT-COOH/GCE respectively. Compared with bare GCE (curve a), sharp and well-resolved oxidation peak of BPF/BPAF was found on the MWCNT-COOH/GCE (curve c), suggesting that the MWCNT-COOH has a strong enhancement ability for the electric signal of BPF/BPAF. The electrochemical reaction of BPF/BPAF on the MWCNT-COOH/GCE was a totally irreversible process. MWCNT-COOH/GCE can be used for the simultaneous determination of BPF and BPAF due to which the two determinants have different peak potential, and MWCNT-COOH has the ability to enhance the peak current of BPF/BPAF.

3.2. Electrocatalytic oxidation of BPF and BPAF in a mixture

The electrochemical behaviors of BPF and BPAF in a mixture were studied using CV and DPV to establish a sensitive and selective method for simultaneous determination of BPF and BPAF. The electrocatalytic behavior of BPF and BPAF was 1.0 mmol/L in 0.2 M PBS (pH = 6.0) solution. Fig. 2A and B shows the CV and DPV responses of BPF and BPAF in a mixed solution with MWCNT-COOH/GCE as compared with bare GCE respectively.

The electrochemical response of BPF and BPAF was resolved into two separate CV peaks at approximately 0.6 and 0.8 V with MWCNT-COOH/GCE and no visible signal was found on the bare GCE (Fig. 2A). However, better-resolved peaks were obtained by DPV, two peaks at 0.50 and 0.71 V for the oxidation of BPF and BPAF, respectively (Fig. 2B). The 0.21 V peak separation between BPF and BPAF was large enough to determine BPF and BPAF individually and simultaneously.

Carbon nanotubes (CNTs) can act as a promoter to enhance the electrochemical reaction, increasing the rate of the heterogeneous electron transfer. It is also believed that the increased surface area provided by CNTs plays an important role in the current enhancement [27]. CNTs with carboxylic acid group (MWCNT-COOH) possess high dispersion quality, binding activity for molecular recognition and π–π conjugated bond, which lead to the conjugation effect of BPF and BPAF with the electrode interface. The π–π interaction between phenyl structure of BPF or BPAF and MWCNT-COOH makes the electron transfer more feasible [28]. Based on the above reasons, MWCNT-COOH/GCE showed the ability to enhance current responses of BPF and BPAF. The observed oxidation peak of BPAF could be attributed to the anodic oxidation of the aromatic ring and the formation of resonance via a two-electron and two-proton process, and the possible product of oxidation is found to be 4,4′-(perfluoropropane-2,2-diyl) bis(cyclohexa-2,5-dienone). The electro-oxidation mechanisms of BPF were similar to that of BPAF. Both the electro-oxidation mechanisms of BPF and BPAF are illustrated in detail in Scheme 1.

3.3. Optimization studies

3.3.1. Effect of pH

It is well known that the pH value has a profound effect on the amperometric responses. Fig. 3 shows the effect of pH value on the peak potential and peak current for 10^{-3} mol/L BPF and 10^{-3} mol/L BPAF in the solution. Fig. 3A displays that the DPV peak potential of BPF and BPAF oxidation shifted with change in pH value, which suggested that protons have taken part in their electrode reaction processes. As shown in Fig. 3B, the current responses of BPF increased from pH 4.5 to 6.0, while the current responses of BPAF reached the maximum at pH 5.0. Furthermore, at pH 6.0, BPF and BPAF can be completely separated, which makes it possible to simultaneously detect them in the mixture. Thus, solution with pH 6.0 was taken for the following experiments. The pH 6.0 was lower than the pK_a of BPF and BPAF (pK_a of BPF is about 10 and pK_a of BPAF is about 8.3) which indicated that in this way the non-dissociated BPF and BPAF can be adsorbed better than the dissociated BPF and BPAF on MWCNT-COOH/GCE surface.

3.3.2. Effect of preconcentration time

Accumulation time can improve the amount of determinant absorbed on the electrode surface, and then improve determination sensitivity and decrease detection limit. Therefore, the effect of accumulation time was investigated. With potential shifting from 0 to 1.0 V at a fixed accumulation time of 240 s, the oxidation peak current of BPF increased remarkably. That is to say, more BPF could be adsorbed on the electrode surface with extending accumulation time. Further increasing the accumulation time, there is no significant increase in the current response. This phenomenon could be attributed to the saturated adsorption of BPF at the electrode surface. The same experiments were also taken to deliberate the accumulation time of BPAF; we have obtained similar phenomenon. Thus, the optimal accumulation time of BPAF was 30 s. Considering both sensitivity and work efficiency, the optimal accumulation time of 240 s for BPF and 30 s for BPAF was employed in the further experiments for the simultaneous determination of BPF and BPAF.

3.3.3. Simultaneous determination of BPF and BPAF using MWCNT-COOH/GCE

The determination of BPF and BPAF in their mixtures was performed at the MWCNT-COOH/GCE by using the DPV mode.

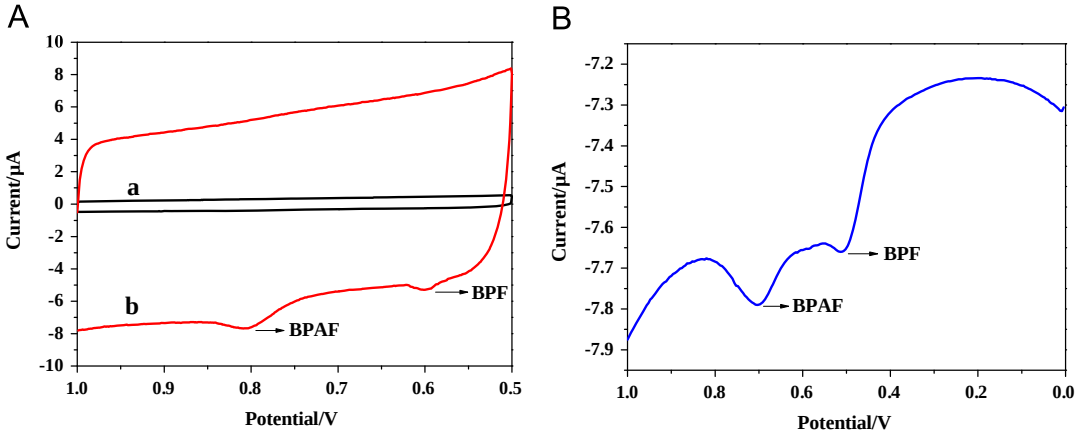
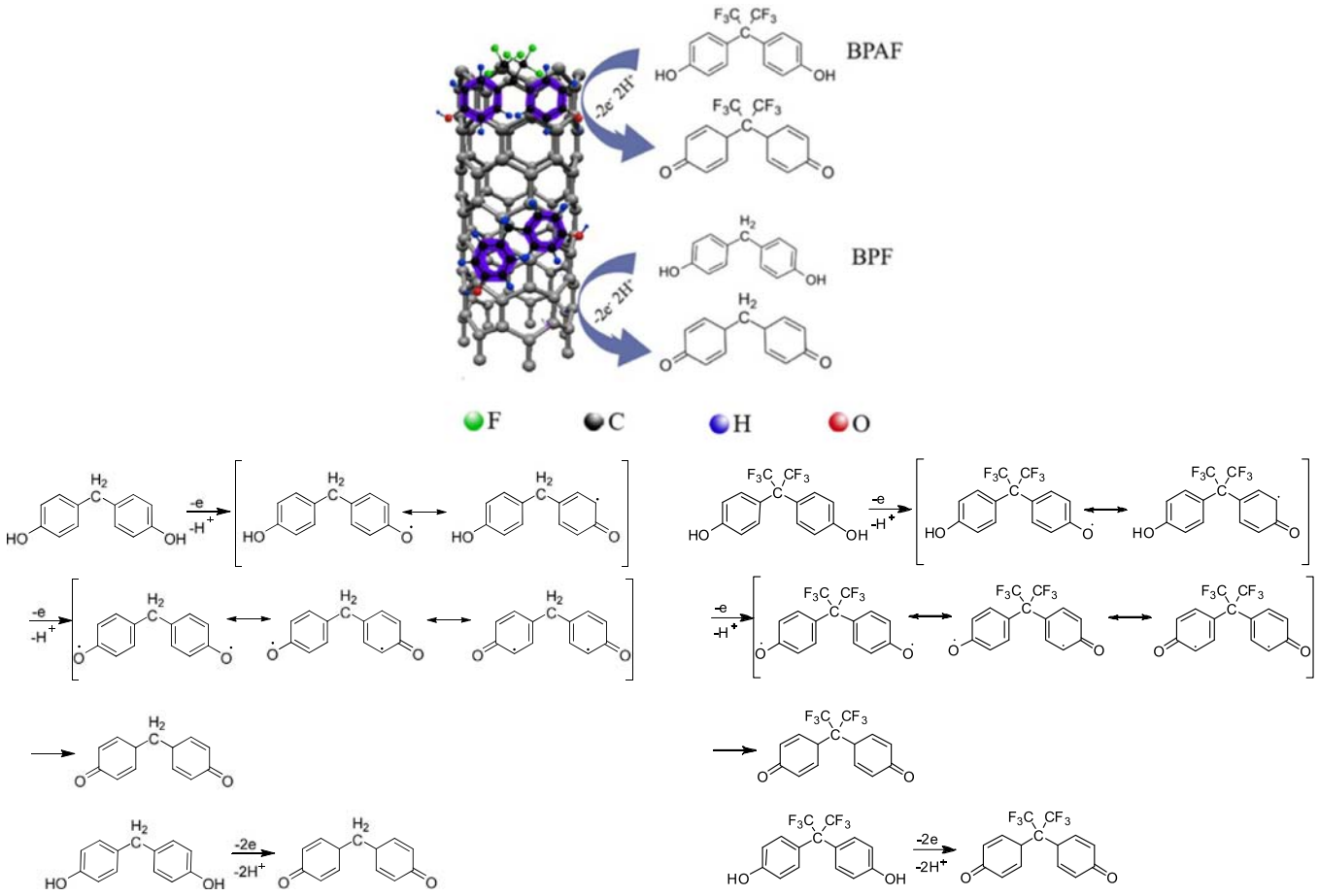


Fig. 2. (A) CVs of 1.0 mmol/L BPF and BPAF in a mixture solution with MWCNT-COOH/GCE in 0.2 M PBS (pH 6.0) solution ((a) EDCs on the bare GCE; and (b) EDCs on the MWCNT-COOH/GCE). (B) DPV of 1.0 mmol/L BPF and BPAF in a mixture solution with MWCNT-COOH/GCE in 0.2 M PBS (pH 6.0) solution.



Scheme 1. The possible electro-oxidation of BPF and BPAF at MWCNT-COOH/GCE.

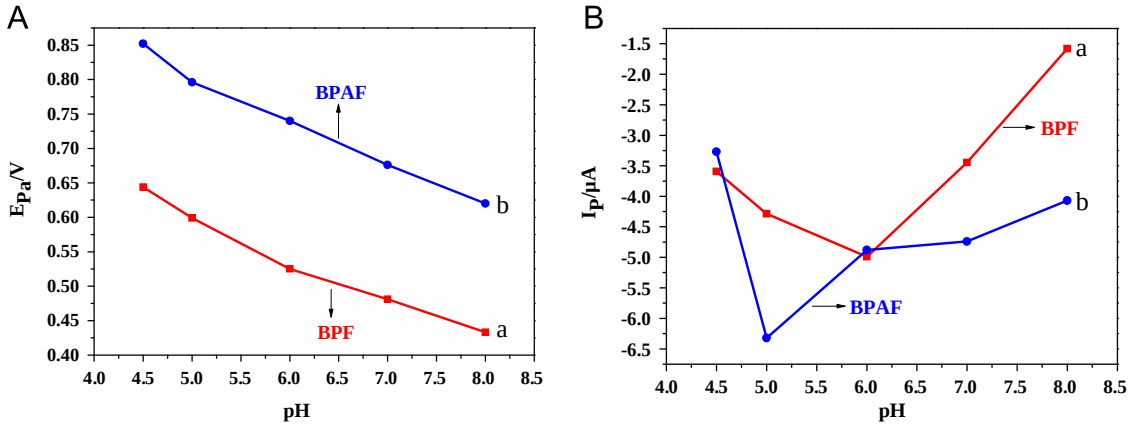


Fig. 3. Influence of pH on the peak potential (A) and peak current (B) for the oxidation of 1.0 mmol/L BPF and BPAF on the MWCNT-COOH/GCE ((a) BPF; (b) BPAF).

When the concentration of one species changed, the concentrations of the others were constant. The results are shown in Fig. 4. As shown in Fig. 4A, the peak current of BPAF was increased linearly within the concentration range of 0.6–1.6 mmol/L. However, the change in BPAF concentration has no significant influence on the peak currents and peak potentials of BPF. Similarly, as shown in Fig. 4B, when the concentration of BPAF was constant, the oxidation peak currents of BPF increased linearly with the increase of its concentration from 0.6 to 1.6 mmol/L. The above results confirmed that the oxidation peaks for BPF and BPAF at MWCNT-COOH/GCE were well separated with each other when they co-existed at pH 6.0 PBS. The corresponding regression equation can be expressed as $y=-0.2561x+0.1036$ ($r=0.9951$) for BPAF and as $y=-0.3194x-0.2446$ ($r=0.9905$) for BPF. The detection limit was calculated as 0.1243 mmol/L for BPAF and 0.1742 mmol/L for BPF. Therefore, it is possible to simultaneously determine BPF and BPAF in mixture samples at the MWCNT-COOH/GCE.

3.4. Interference study

The influence of various foreign species on the determination of 10^{-3} mol/L BPF and BPAF was investigated by DPV under the above optimized conditions; the tolerance limit was defined as the maximum concentration of foreign substances. Some common phenolic complexes and inorganic ions were tested to check their

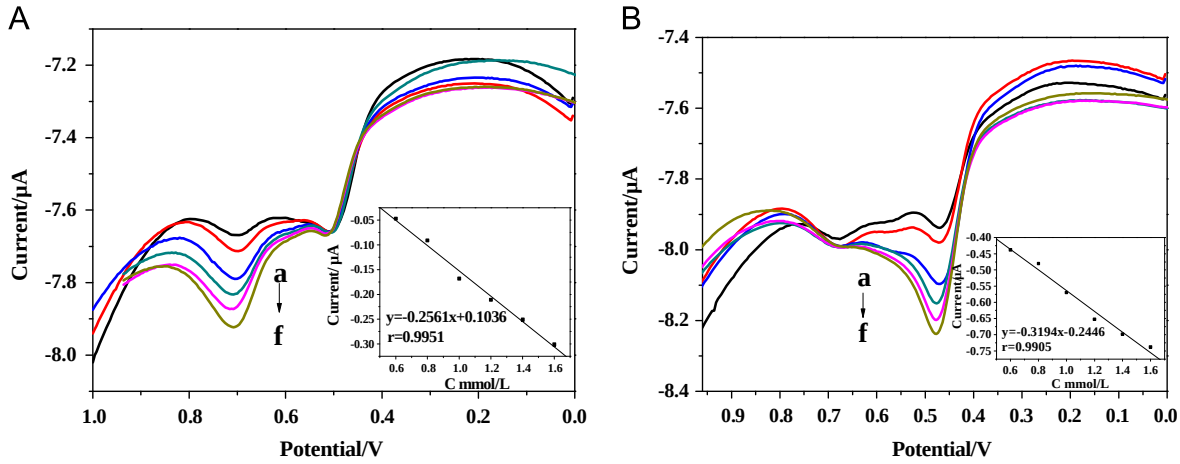


Fig. 4. Simultaneous determination of BPF and BPAF using MWCNT-COOH/GCE ((A) keeping the concentration of BPF constant and BPAF changed; and (B) keeping the concentration of BPAF constant and BPF changed; inset: the related calibration curve).

Table 1
Influence of common substances on the determination of BPF and BPAF.

Influences	Tolerance limits ($C_{influences}/C_{BPF}$)
Hydroquinone, hydroxyphenol, pyrocatechol	1000
Bisphenol AP	500
Bisphenol A	50
K^+, Mg^{2+}, Na^+, Cl^-, NO_3^-	1000
SO_4^{2-}	500
Zn^{2+}, Cu^{2+}	200

Table 2
Simultaneous determination of BPF and BPAF in real samples.

Samples	BPF added (mmol/L)	BPAF added (mmol/L)	BPF		BPAF	
			Found[a] (mmol/L)	Recovery (%)	Found[a] (mmol/L)	Recovery (%)
Rubber gloves	0	0	0	–	0	–
	0.80	0.80	0.83 ± 0.20	103.75	0.78 ± 0.15	97.50
	1.50	1.50	1.48 ± 0.70	98.70	1.52 ± 0.40	101.30
Wastewater	0	0	0	–	0	–
	0.80	0.80	0.79 ± 0.10	98.75	0.82 ± 0.23	102.50
	1.50	1.50	1.51 ± 0.40	100.60	1.53 ± 0.17	102.00

[a] Mean of three measurements.

levels of interference on simultaneous determination of BPF and BPAF by DPV. The results (Table 1) suggested that 1000-fold concentration of hydroquinone, hydroxyphenol, pyrocatechol, 500-fold of bisphenol AP and 50-fold of bisphenol A have no influence on the signals of simultaneous determination of BPF and BPAF. Otherwise, some inorganic ions such as 1000-fold concentration of K^+, Mg^{2+}, Na^+, Cl^-, NO_3^-, 500-fold of SO_4^{2-} and 200-fold of Zn^{2+}, Cu^{2+} have no influence on simultaneous determination of BPF and BPAF.

3.5. Stability and reproducibility

When the MWCNT-COOH/GCE electrode was not in use, it was stored in a refrigerator at 4 °C for 10 days; no obvious decrease in the current response of MWCNT-COOH/GCE was observed. The MWCNT-COOH/GCE showed a well reproducibility and the relative standard deviation (R.S.D.) was 3.5%, which was evaluated by nine repetitive measurements of 1×10^{-3} mol/L BPF and BPAF.

3.6. Sample analysis

The developed DPV method for simultaneous determination of BPF and BPAF was applied to real samples. The recoveries from the samples were measured by spiking with different amounts of standard BPF and BPAF into the detection system of samples. The detection results of the samples obtained were listed in Table 2. The accuracy of the method was evaluated by recovery. The recoveries of BPF and BPAF were studied by spiking the standard at different concentrations (0.8, 1.5 mmol/L) into the samples before the determination by the proposed method. The recoveries determined were in the range from 97.5% to 103.8%. Good recoveries indicated that little interference was observed which could be neglected. Therefore, the proposed method has the

potential for applicability for simultaneous determination of BPF and BPAF in real samples.

4. Conclusion

The results obtained in this work demonstrated the potentiality of the MWCNT-COOH modified electrode for simultaneous determination of BPF and BPAF. The MWCNT-COOH modified electrode exhibited high electrocatalytic activity and high sensitivity for the oxidation of BPF and BPAF in mixtures, and was successfully applied for the simultaneous detection of BPF and BPAF in real samples with satisfactory results. The simple fabrication procedure, rapid measuring speed, good precision, wide linear range, low detection limit, and high stability present this sensor as an attractive candidate for practical application.

Acknowledgment

This project was supported by the National Natural Science Foundation of China (NSFC51178212), Liaoning Provincial Department of education innovation team projects (LT2012001), the Shenyang Science and Technology Plan (F12-277-1-69) and the Foundation of 211 project for Innovative Talent Training, Liaoning University. The authors also thank their colleagues and other students who participated in this work.

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