Journal of Electroanalytical Chemistry 770 (2016) 39–43

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Signal enhancement of cetyltrimethylammonium bromide as a highly-sensitive sensing strategy for tetrabromobisphenol A

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ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 24 March 2016
Accepted 24 March 2016
Available online 25 March 2016

Keywords:
Signal enhancement
Cetyltrimethylammonium bromide
Tetrabromobisphenol A
Electrochemical determination

ABSTRACT

It is quite important to monitor tetrabromobisphenol A (TBBPA) in environmental samples due to its wide existence and high toxicity. Herein, a highly-sensitive electrochemical method was developed for the determination of TBBPA based on the strong signal enhancement effects of cetyltrimethylammonium bromide (CTAB). In pH 7.5 phosphate buffer, an irreversible oxidation peak with low height is observed for TBBPA on the surface of a carbon paste electrode (CPE), and the oxidation wave is improved greatly after addition of a low concentration of CTAB. The great peak current enlargements indicate that CTAB exhibits remarkable enhancement effects toward TBBPA oxidation. The enhancement mechanism of CTAB was investigated using electrochemical impedance spectroscopy and chronocoulometry. It is found that the existence of CTAB obviously increases the accumulation efficiency of TBBPA and facilitates its electron transfer. The linear range of this new sensing system is from 2.5 to 800 nM, and the detection limit is 0.99 nM. It was used in water sample analysis, and the recovery value was over the range from 95.74% to 102.6%.

1. Introduction

Tetrabromobisphenol A (TBBPA) is the highest-volume brominated flame retardant (BFR) in the world representing about 60% of the total BFR market [1]. The global consumption of TBBPA has increased from 64,000 t in 1994 to 119,700 t in 2001 [2]. In China, the TBBPA production capacity is about 18,000 t in 2007 [3]. Currently, TBBPA has attracted much attention due to the adverse health effects such as endocrine disrupting behaviors [4–6], immunotoxicity [7,8] and neurotoxicity [9,10]. Therefore, it is quite important to develop sensitive, simple and accurate determination methods for TBBPA.

Electrochemical determination has obtained increasing attention in environmental monitoring because it is superior in terms of speediness, handling convenience, low cost, in situ monitoring and miniaturization. However, the electrochemical studies about direct determination of TBBPA are very limited. Surfactants with amphiphilic structure have been extensively used in the field of electrochemistry for various purposes. It has been proved that the assembly of surfactants on the electrode surface has big impacts on the structure of the electrode interface, and then heavily affects the electrochemical processes of species [11–13]. Until now, cetyltrimethylammonium bromide (CTAB), a typical cationic surfactant, has been successfully employed to improve the response signals of estrogens [14], nitrophenol isomers [15], bisphenol A [16] and ciprofloxacin [17].

The main objective of this work is to develop a simple, sensitive and accurate method for the determination of TBBPA utilizing the excellent enhancement effects of CTAB. On the surface of a carbon paste electrode (CPE), the oxidation activity of TBPPA is very low, and the resulting oxidation signals are also weak. However, the oxidation wave of TBBPA on the CPE surface is improved significantly after addition of CTAB. The existence of CTAB enhances the electron transfer ability and the surface accumulation efficiency of TBBPA, showing strong signal amplification ability. As a result, the oxidation signals and detection sensitivity of TBBPA are improved greatly.

2. Experimental section

2.1. Reagents

All chemicals were of analytical grade and used as received. 0.01 M stock solution of TBBPA (Laboratories of Dr. Ehrenstorfer, German) was prepared using ethanol, and stored at 4 °C. Cetyltrimethylammonium bromide (CTAB), graphite powder (spectral reagent) and paraffin oil were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Ultrapure water was obtained from a Milli-Q water purification system and used throughout.

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http://dx.doi.org/10.1016/j.jelechem.2016.03.039
1572-6657/

2.2. Instruments

Electrochemical measurements were carried out on a CHI 660C electrochemical workstation (Chenhua Instrument, Shanghai, China). A conventional three-electrode system, consisting of a carbon paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed.

2.3. Preparation of CPE

The carbon paste electrode (CPE) was prepared using 1.0 g graphite powder and 0.2 mL paraffin oil. The mixture was mixed homogeneously in a carnelian mortar, and the resulting carbon paste was then tightly pressed into the end cavity of the working electrode body. Finally, the electrode surface was polished on a smooth paper.

2.4. Analytical procedure

0.1 M, pH 7.5 phosphate buffer containing 6.0 μM CTAB was used as the supporting electrolyte for the detection of TBBPA. After 4-min accumulation, the differential pulse voltammograms were recorded from 0.20 to 0.60 V, and the oxidation peak currents at 0.47 V were measured. The pulse amplitude was 50 mV, the pulse width was 40 ms, and the scan rate was 40 mV s^{-1}. After each measurement, the used paste was carefully removed from the end cavity and a new carbon paste was prepared to guarantee good reproducibility.

3. Results and discussion

3.1. Electrochemical behaviors of TBBPA

The electrochemical behaviors of TBBPA in 0.1 M phosphate buffer solutions with different pH values were studied using cyclic voltammetry (CV). As shown in Fig. 1A, a pH-dependent oxidation wave is observed for TBBPA, and it moves negatively when improving the pH value from 6.0 to 8.0, indicating that protons are involved in the oxidation process. Moreover, a good linear relationship is observed for the oxidation peak potential (E_p) of TBBPA and the pH values, as confirmed from Fig. 1B. The slope value of the E_p–pH plot is −63.8 mV/pH, suggesting that the number of protons and electrons that transferred in the oxidation process of TBBPA is equal. From Fig. 1C, we also find that the oxidation peak currents of TBBPA are controlled by pH values. The oxidation peak currents of TBBPA gradually increase with the pH value from 6.0 to 7.5, and then gradually decrease with further improving the pH value to 8.0, revealing that the oxidation activity of TBBPA is pH-dependent. To achieve higher oxidation signals for TBBPA, 0.1 M phosphate buffer with pH of 7.5 is used as the supporting electrolyte. Additionally, the successive cyclic voltammograms of TBBPA were recorded in Fig. 1D to further discuss the oxidation process of TBBPA. Only an oxidation wave is observed, and the oxidation peak decreases greatly during the second cyclic sweep. No observation of the corresponding reduction wave suggests that the oxidation of TBBPA is totally irreversible, and the signal decline after the first anodic sweep may be attributed to the surface adsorption of oxidative products.

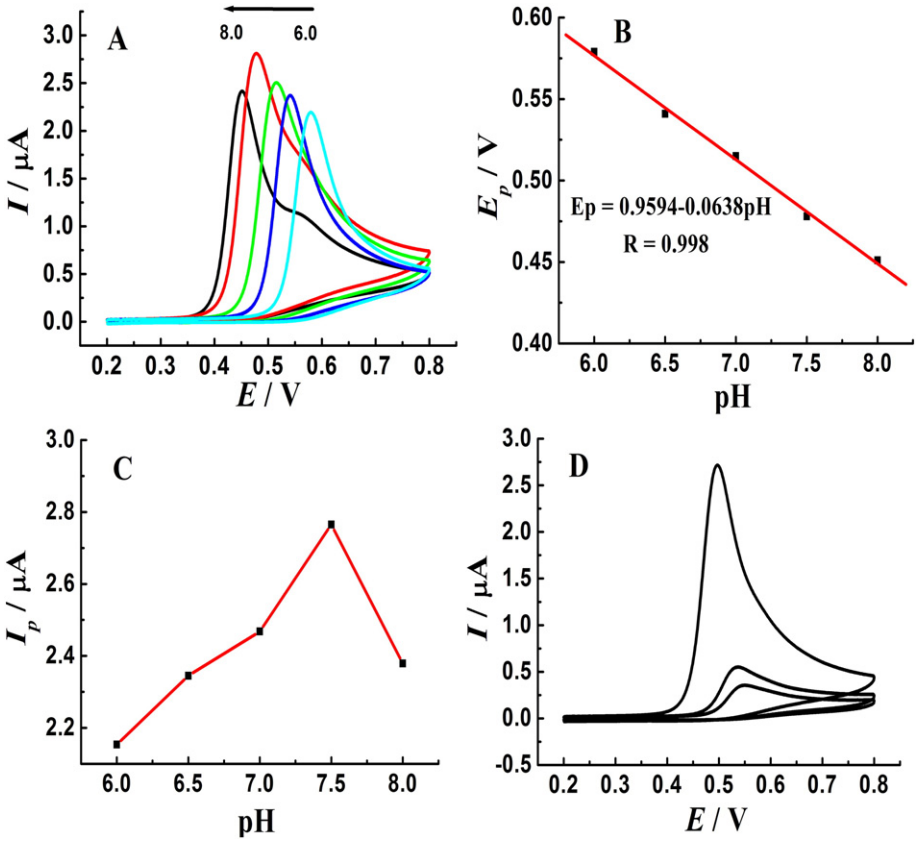

Fig. 1. (A) CV curves of 10 μM TBBPA on CPE in 0.1 M phosphate buffer solutions with different pH values in the presence of 6.0 μM CTAB; (B) linear relationship between oxidation peak potential and pH values; (C) effects of pH value on the oxidation peak currents of TBBPA; (D) successive CV curves of 10 μM TBBPA in pH 7.5 phosphate buffer containing 6.0 μM CTAB. Scan rate: 100 mV s^{-1}.