

Effective Improving the Detection Limit of Tris(2,3-dibromopropyl) Isocyanurate by Bis-amino in *O*-phenylenediamine

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Abstract. A facile approach for ultrasensitively sensing tris(2,3-dibromopropyl) isocyanurate (TBC) was reported. Based on coupling molecularly imprinting with electropolymerization of *o*-phenylenediamine (OPD), which is electro-active monomers, the poly-OPD film was deposited in an OPD solution by potentiodynamic cycling of potential (scan rate is 50mV/s) on a glassy carbon electrode. Using K₃[Fe(CN)₆] as an electro-active marker, the properties of the TBC imprinting electrode were investigated by differential pulse voltammetry and amperometric *i-t* curve and exhibited an excellent imprinting effect. The results showed that a linear relationship between the value of peak current and the TBC concentration was found in the range of 1.4×10⁻¹²~6.7×10⁻¹² mol/L and a low detection limit of 6.26×10⁻¹³ mol/L for TBC determination.

1. Introduction

Tris-(2,3-dibromopropyl) isocyanurate (TBC), which is a "novel" brominated flame retardant (BFR), has been widely applied in polymer products for fire safety due to its excellent capability to reduce flammability. Numerous studies showed that these chemicals are persistent, have long distance transport and bioaccumulative abilities, and may potentially harm ecosystems and human health [1]. Several methods to detect TBC in environment were established including gas chromatography (GC) and liquid chromatography coupled with mass spectrometry (LC-MS) [2]. Zhao [3] and Feng [4] et al developed electrochemiluminescence (ECL) and photoelectrochemical immunosensor (PCI) techniques on the basis of a series of inorganic nanoparticles with good sensitivity and low detect limit. However, these protocols are either much complicated, or need relatively expensive equipments. Due to the low concentration in the environment and absence of recognizable sites for TBC, it is still an important but challenging task to develop a sensitive, rapid, convenient, and selective method for on-site determination of TBC.

In this paper, a strategy to incorporate molecule imprinting with electropolymerization of *o*-phenylenediamine (OPD) is proposed to sense one of emerging bromine substituted

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pollutants—TBC, which is insoluble in water. Considering that TBC is electro-inactive over the studied potential range, an electro-active substance, hexacyanoferrate ($K_3[Fe(CN)_6]$), is chosen as the redox probe of the film coated electrodes in solutions. The experiments show that the current of MIP electrode showed the linear proportional to the TBC concentration within the measured range from amperometric $i-t$ curve. In comparison with *o*-aminophenol (OAP) containing an amino&hydroxyl group and aniline containing a hydroxyl group, limit of detection for poly-OPD film-coated electrode is ca. 100 times smaller than that for poly OAP-coated one, and 1000 times smaller than that for poly aniline-coated one [5].

2. Experimental

2.1 Instruments and Reagents

A CHI660E electrochemical workstation (CHI Instrument, Shanghai Chenhua Apparatus Company, China) was used for electrochemical measurements. A conventional three-electrode system was employed with a modified glassy carbon electrode (GCE, 3.0mm in diameter) as the working electrode, a platinum electrode as the counter electrode, and a Ag/AgCl electrode with saturated KCl as the reference electrode. All potentials reported in this article were referenced to the Ag/AgCl electrode. All measurements were carried out at room temperature.

Tris(2,3-dibromopropyl) isocyanurate (TBC, purity > 97%) was purchased from TCI (Tokyo, Japan). *o*-phenylenediamine (OPD, chemically pure) was obtained from Sinopharm Chemical Reagent Co., Ltd. All the other chemicals were analytical reagent grade or better.

2.2 Preparation of MIP Sensor

Prior to modification, the GCE was polished with emery paper and chamois leather containing 0.3 and 0.05 μ m Al_2O_3 slurry, respectively, and then thoroughly rinsed ultrasonically with HNO_3 , ethanol, and doubly distilled water for 5 min in turn. Then the electrode was cycled between -0.3 and 1.5 V in 0.5 mol/L H_2SO_4 at 100 mV/s scan rate that reproducible voltammogram was obtained.

As shown in Fig. 1, TBC imprinting Poly-OPD-modified GCE (MIP sensor) was fabricated by the following descriptions: The electro-polymerization solution was obtained by 20mL OPD solution and 10mL 1.0×10^{-4} mol L^{-1} TBC acetonitrile solution, in which, the OPD solution was prepared with dissolving 0.0108g OPD in 20mL acetate buffer with pH=5.8. Potentiodynamic cycling of potential for 20 scans in the range from 0~0.8 V was conducted at a scan rate of 50 mV/s. The sensor was rinsed with H_2SO_4 for several times to remove TBC from the polymer matrix after electro-polymerization. The non-imprinted polymer sensor (NIP sensor) was also prepared in the same manner but without adding the template.

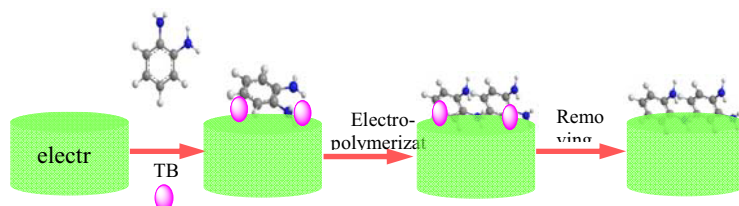


Fig. 1 Schematic diagram for the fabrication process of MIP sensor

2.3 Measurements

A standard three-electrode cell connected to the CHI660E was used for electrochemical measurements. Due to TBC is electro-inactive over the studied potential range, $K_3[Fe(CN)_6]$ was chosen as the redox probe of the MIP/NIP sensors in solutions. The differential pulse voltammetry (DPV) experiments were performed in the 5 ml 5 mmol L⁻¹ background solution $K_3[Fe(CN)_6]$ containing 0.1 mol L⁻¹ KCL as support electrolyte. The detection limit of the MIP sensor was obtained from the change of oxidation current of $K_3[Fe(CN)_6]$ by amperometric *i-t* curve.

3. Results and Discussion

3.1 Electropolymerization

To satisfy the different detection purposes, imprinted sensor with well controlled physical forms have been developed through various fabrication methods [6,7]. Among these methods, electropolymerization provides some advantages, for example, thickness control of the polymer layer that is crucial to the sensing of the analyte; ability to attach the sensor film to electrode surfaces of any shape and size, and compatibility with combinatorial and high-throughput approaches critical for the commercial development of molecular imprinting [8]. In this work, the electropolymerization was employed to prepare the sensitive film of MIP sensor with uniform and controlled thickness. As shown in Fig. 2, there appeared two oxidation peaks current at ~ 0.65 V and ~ 0.4 V by changing the potential from 0 V to 0.8 V, while there didn't appear any reduction peaks by changing the potential from 0.8 V to 0 V. It indicated that the electrochemical polymerization of OPD on the GCE was a completely irreversible process. In addition, with the increase of scanning times, the peak current decreased obviously (arrow direction) and even disappeared. It is due to the non-conducting dense poly-OPD film generated on the surface of GCE.

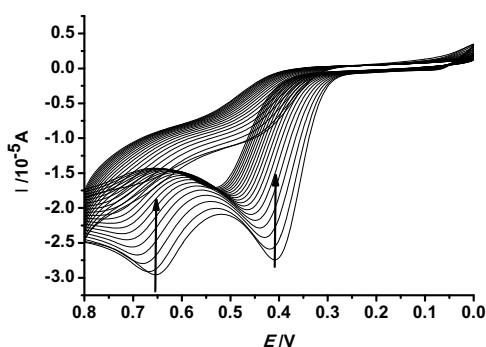


Fig. 2 CV for the electro-polymerization of OPD

3.2 Effect of Imprinting

In this study, DPV was employed for the quantitative determination of TBC, which is relatively sensitive compared to the conventional CV method. DPV was performed after the MIP sensor was immersed in solutions containing TBC of different concentration (1.0×10^{-10} , 1.0×10^{-9} , 1.0×10^{-8} mol L⁻¹) and the background solution (5 mmol L⁻¹ $K_3[Fe(CN)_6]$ solution). When the MIP sensor was immersed in the solution containing TBC, the cavities in the film

were partially occupied by TBC, which led to the decrease of current signal produced by $[\text{Fe}(\text{CN})_6]^{3-}$. As shown in Fig. 3, the higher the concentration of TBC, the lower the current would be, which suggests that more and more binding sites in the film are occupied by TBC molecules.

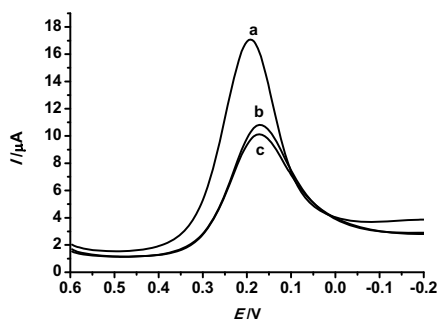


Fig. 3 DPV responses of MIP sensor to the different concentration of TBC

(a: 1.0×10^{-11} , b: 1.0×10^{-10} , c: 1.0×10^{-9} mol L⁻¹)

3.3 The Detection Limit of the Sensors

In order to evaluate the detection limit of sensors which was obtained from the change of reduction current of $\text{K}_3[\text{Fe}(\text{CN})_6]$, measurements of amperometric *i-t* curve were performed in the 7 mL 5 mmol L⁻¹ $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution, and 0.1 mL 1.0×10^{-10} mol L⁻¹ TBC was added in it every the same time. The reduction peak current of $\text{K}_3[\text{Fe}(\text{CN})_6]$ gradually decreased with increasing TBC concentrations, shown in Fig. 4. It appeared a platform at every concentration stage (curve a) and stability in 30s, which indicated that the MIP sensor has short response time. The result showed that the recognition sites of TBC were formed in the MIP sensor, which played an important role in the process of recognition. The relative change of the peak current is linearly proportional to the TBC concentration in the range of 1.4×10^{-12} mol L⁻¹ to 6.7×10^{-12} mol L⁻¹ (shown in Fig. 4 inset), with a correlation coefficient of 0.9884. The results showed that the sensor with a low detection limit of 6.26×10^{-13} mol L⁻¹ ($S/N=3$) for TBC determination was significantly different from the non-imprinted electrode.

Selecting OAP with a amino&hydroxyl group and aniline with a hydroxyl group as a reference for controlled trials by using the same method⁵, limit of detection for poly-OPD film-coated electrode is ca. 100 times smaller than that for poly OAP -coated one (6.64×10^{-11} mol L⁻¹), and 1000 times smaller than that for poly aniline-coated one (5.22×10^{-10} mol L⁻¹). This may be due to poly-OPD film easily protonated and deprotonated in redox process [9]. That is, the utilization of bio-amino groups on the OPD could improve the detection limit of MIP sensor. Due to the amino groups of the film and carbonyl groups of TBC molecule, OPD can bind to TBC probably via N-H...O hydrogen bonds, which facilitates the recognition for the analyte. When MIP electrode was immersed into the mixture solution of TBC and $\text{K}_3[\text{Fe}(\text{CN})_6]$, TBC molecules could be absorbed because of the imprinting spatial similarity. Therefore, it causes the variation of the $\text{K}_3[\text{Fe}(\text{CN})_6]$ peak current response. The MIP sensor we proposed is desirable for the detection of trace amounts TBC in environmental samples.

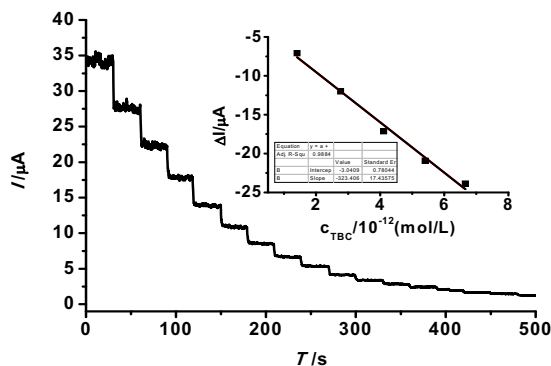


Fig. 4 Amperometric $i-t$ curve of the sensor, inset shows the linear relation of $\Delta I \sim C_{\text{TBC}}$

4. Conclusions

To determine ultra-trace TBC, another functional monomer with bis-amino for the fabrication of the TBC-MIP sensor was presented. The fabrication procedure is very simple, rapid, and inexpensive. The limit of detection (LOD, $S/N=3$) of the modified electrode was $6.26 \times 10^{-13} \text{ mol L}^{-1}$, which was more significantly outperformed than the imprinted sensors constructed by *o*-aminophenol and polyaniline. We believe that our strategy is instructive to the determination of other bromine substituted pollutants, which is insoluble in water.

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