



Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: [www.elsevier.com/locate/cclet](http://www.elsevier.com/locate/cclet)



Communication

## Rapid detection of organophosphorus pesticide residue on Prussian blue modified dual-channel screen-printed electrodes combing with portable potentiostat

Qianwei Shi, Yuanjie Teng\*, Yuchao Zhang, Wenhan Liu\*

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

### ARTICLE INFO

#### Article history:

Received 6 September 2017  
Received in revised form 14 November 2017  
Accepted 16 November 2017  
Available online xxx

#### Keywords:

Pesticide residue  
Rapid detection  
Electrochemical method  
Screen-printed carbon electrodes  
Portable potentiostat

### ABSTRACT

A novel electrochemical method for the rapid detection of organophosphorus pesticide residues was realized on a dual-channel screen-printed electrode (DSPE) that was integrated with a portable smartphone-controlled potentiostat. The two carbon working channels of DSPE were first modified by electrodeposition of Prussian blue. The channels were then modified with acetylcholinesterase (AChE) via Nafion. The inhibition ratio of AChE was detected by comparing the electrical current of acetylthiocholine (ATCh) that was catalyzed by the enzyme electrodes with (channel 1) and without (channel 2) organophosphorus pesticide. Inhibition ratios were related with the negative logarithm of the organophosphorus pesticide (trichlorfon, oxamyl, and isocarbophos) concentrations at optimum experimental conditions (pH 6.9 of electrolyte, 0.2V working potential, 2.5  $\mu$ L AChE modification amount, and 15 min inhibition time). The linear equations were  $I\% = 32.30\lg C + 253.3$  ( $R = 0.9750$ ) for isocarbophos,  $I\% = 35.99\lg C + 270.1$  ( $R = 0.9668$ ) for chlorpyrifos, and  $I\% = 33.70\lg C + 250.5$  ( $R = 0.9606$ ) for trichlorfon. The detection limits were calculated as  $10^{-7}$  g/mL. Given that the inhibition ratios were only related with pesticide concentration and not with pesticide species, the proposed electrodes and electrometer can rapidly detect universal organophosphorus pesticides and assess pesticide pollution.

© 2017 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

Organophosphorus pesticides are the most commonly used pesticide in China since the prohibition of organochlorine pesticides. To date, more than 70% of the pesticides used in China are organophosphates and carbamates [1]. The excessive use of these highly toxic organophosphate pesticides has numerous harmful effects [2–4]. Poisoning from pesticide residues directly threatens human health and survival [5]. Thus, the detection and treatment of organophosphorus pesticide residues have received wide spread attention.

Pesticide residues are detected with numerous instrument-based quantitative and qualitative methods, such as gas chromatography [6], high-performance liquid chromatography [7,8], and gas chromatography-mass spectrometry [9,10]. Although these methods are highly accurate, they are expensive with lengthy and time-consuming pre-treatment processes. Fast and continuous pre-process technologies, such as solid phase extraction [11,12],

microwave extraction [13,14], and liquid-liquid extraction [15], have been developed to adapt to market demand. However, these methods are also limited to laboratory experiments and cannot provide real-time analytical results quickly and easily. Some recently developed methods for field analysis use enzyme inhibition [16–18], which is based on the inhibitory and attenuative effects of organophosphophate pesticides on acetylcholinesterase (AChE) activity. The electrochemical method and enzyme-specific color reaction [19,20] are the two commonly used detection methods that are based on enzyme inhibition. However, the degree of color change usually need to be performed by UV–vis spectrometry, while some existed testing strips identified by eyes usually has high false-positive ratios.

The electrochemical method utilizes the difference in current signals to determine the degree of enzyme inhibition and concentration of organophosphophate pesticides. Some papers [21–25] have reported to improve the sensitivity using different modified methods for electrodes. These methods can satisfy the requirement of detection limit and has high sensitivity, however, the complex modification process of electrodes and extraction of organophosphophate pesticides from samples prior to detection

\* Corresponding authors.

E-mail addresses: [yuanjieteng@zjut.edu.cn](mailto:yuanjieteng@zjut.edu.cn) (Y. Teng), [liuwh@zjut.edu.cn](mailto:liuwh@zjut.edu.cn) (W. Liu).

<https://doi.org/10.1016/j.cclet.2017.11.023>

1001-8417/© 2017 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

are required or the large size of the electrochemical workstation is used which is not conducive for field analysis. Also, these modification and detection processes are hard to be integrated.

Screen-printed electrode (SPE) is an electrochemical electrode that is fabricated by thick film-integrated circuit technology [26] and has the advantages of cheap price, ease of use, and high detection sensitivity [27]. It can be modified with different printing materials, such as ink proportions [28], metals [29–31], enzymes [32–35], polymers [36–38], or composites [39–41]. Moreover, SPE can be modified *via* different electrodeposition methods [42,43]. Prussian blue (PB) is a kind of blue dye with good properties of chemical stability, reversibility and catalytic performance [44,45]. Also, the costless PB film can be obtained by simple electrodeposition method [46,47].

In this paper, a novel double-channel SPE (DSPE) modified by PB was designed to simultaneously measure the rates of enzyme catalysis and inhibition to reduce the detection error from two different modification electrodes and shorten the time of measurement. The proposed method realizes the quantitative detection of pesticide residues and shows good detection sensitivity. Also, the limit of detection agreed with the requirements of Chinese standard [48]. Therefore, it can be used for rapid analysis and has potential market applications combined with a portable electrochemical analyzer.

The fabrication steps of DSPE were similar with the single channel of screen-printed three electrodes which we have reported [49] (as shown in Supporting information). The electrochemical deposition of PB on DSPE was performed *via* chronoamperometry (CA) in a mixed solution that contained 2 mmol/L  $K_3[Fe(CN)_6]$ , 2 mmol/L  $FeCl_3$ , 0.1 mol/L KCl, and 10 mmol/L HCl at a fixed potential of 0.4 V for 200 s. Then, DSPE was deposited *via* CV in a mixed solution that contained 2 mmol/L  $K_3[Fe(CN)_6]$ , 2 mmol/L  $FeCl_3$ , 0.1 mol/L KCl, and 10 mmol/L HCl solution at a potential range of  $-0.5$  V to 1 V for 12 cycles at a scan rate of 50 mV/s. The electrode was designated as PB-DSPE. Then, 2.5  $\mu$ L of 1 mg/mL AChE was dipped on the surface of the electrode and dried in air. Finally, 2.5  $\mu$ L of 0.05% Nafion solution was dipped on the surface of the electrode, which was dried in air and maintained at 4 °C for 24 h. This electrode was designated as Nafion-AChE/PB-DSPE.

After that, the samples of cowpea, kalimeris and cabbage were first milled into a paste. 0.5 g of these samples were weighed following by adding 3 mL of methanol/ethyl acetate/acetone (1:2:3, v/v/v). The mixture was fully oscillated under ultrasonic for 10 min. Then, it was transferred to the centrifuge for 10 min at 3000 r/min to obtain the supernatant.

At last, an appropriate concentration of pesticide prepared above was deposited on the surface of the working electrode in channel 2. No pesticide was deposited on channel 1. Then, the Nafion-AChE/PB-DSPE was placed in 0.05 mol/L pH 6.9 PBS after inhibition using CA. Electrode signals from channels 1 and 2 were simultaneously measured on a portable smartphone-controlled potentiostat (Xenstat, Ningbo Yuangan Biological Technology Co., Ltd.) or an electrochemical workstation (CS350, Wuhan CorrTest Instruments Co., Ltd.).

The schematic diagram of organophosphate pesticides detection by Nafion-AChE/PB-DSPE was showed in Fig. 1. Both channels were deposited AChE. AChE catalyzes the hydrolysis of ATCh, which produces an electroactive thiocholine (TCh) product (Scheme 1, Eq. (1)). TCh reduces  $PB_{ox}$  to  $PB_{red}$  *via* electron exchange (Scheme 1, Eqs. (2) and (3)). A response current is produced when  $PB_{red}$  is oxidized on the electrode surface (Scheme 1, Eq. (4)). Given that organophosphate pesticides inhibit AChE, as well as decrease catalytic efficiency and the response current, the inhibition ratio *via* response current reduction (Inhibition rate (%) =  $(i_1 - i_2)/i_1$ ) can be obtained.

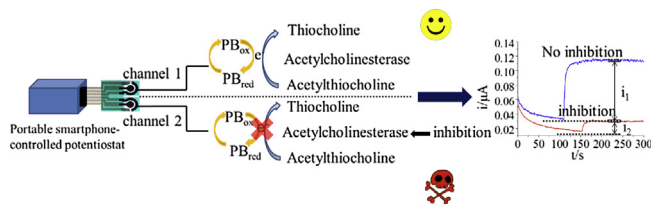


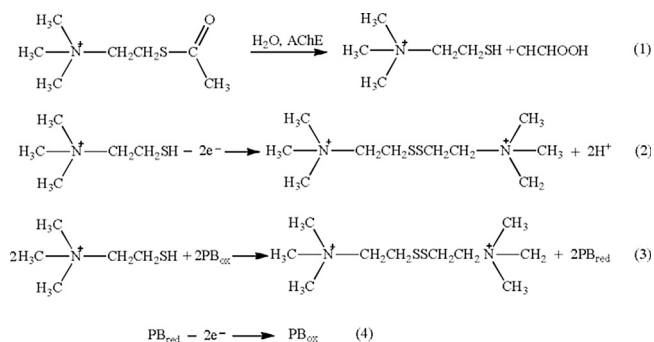
Fig. 1. Schematic diagram of the measurement mechanism.

The morphology of bare SPE and PB-DSPE electrodes were characterized by SEM. Comparing with the bare SPE (as shown in Fig. S1a in Supporting information), the SEM image of the PB-DSPE electrode (as shown in Fig. S1b) showed PB film was deposited on the surface of working electrode with average PB particle size around 5  $\mu$ m. Also, the PB film was identified by cyclic voltammerty (as shown in Fig. S2 in Supporting information). With the increasing of electrodeposition time, the response current increased successively. And it is almost stable after 12 cycles scan.

Nafion-AChE/PB-DSPE was obviously catalyzed by 0.01 mol/L ATCh (black curve) (as shown in Fig. S3 in Supporting information). Therefore, the response currents of the Nafion-AChE/PB-DSPE in a series of PBS solutions (0.05 mol/L, containing 0.5 mmol/L ATCh) with various pH (6.0 to 8.0) were investigated. The maximum value of the response current was found at pH 8.0 (as shown in Fig. S4 in Supporting information). Although the larger response current was obtained at alkaline condition, PB is easily buffered in alkaline conditions and organophosphate pesticides were easily hydrolyzed when the solution pH exceeded 8.0 which caused a relatively large error. Thus, PBS with a pH of 6.9 was used in subsequent experiments.

Then, the response currents of the PB-DSPE at various operating voltages (from 0.1 V to 0.7 V) in 0.05 mol/L PBS (pH 6.9) that contained 0.25 mmol/L ATCh were investigated. Current intensity first increased and then decreased as voltage increased from 0.1 V to 0.4 V (as shown in Fig. S5 in Supporting information). Moreover, current intensity increased with voltage when the current exceeded 0.4 V. Therefore, we used 0.2 V as the operating voltage in subsequent experiments because of the interference from high voltage.

Furthermore, the response currents of the Nafion-AChE/PB-DSPE that were coated with various amounts of AChE (0.5  $\mu$ L to 2.5  $\mu$ L) were measured. Measurements were taken in 0.05 mol/L PBS (pH 6.9) that contained 0.25 mmol/L ATCh. Current intensity gradually increased as AChE increased (as shown in Fig. S6 in Supporting information). The maximum value for current intensity was found with 2.5  $\mu$ L AChE. Thus, subsequent experiments were performed with 2.5  $\mu$ L AChE load.



Scheme 1. Equations of the measurement mechanism.

Download English Version:

<https://daneshyari.com/en/article/8942765>

Download Persian Version:

<https://daneshyari.com/article/8942765>

[Daneshyari.com](https://daneshyari.com)