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Exploring pralidoxime chloride as a universal electrochemical probe for organophosphorus pesticides detection



Qiqi Zheng ^{a, b}, Yuan Chen ^{a, b}, Kai Fan ^c, Jian Wu ^{a, b, *}, Yibin Ying ^{a, b, d}

^a College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, China

^b Key Laboratory of on Site Processing Equipment for Agricultural Products, Ministry of Agriculture, China

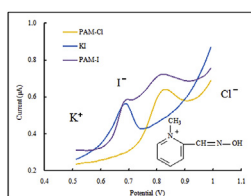
^c College of Life Information Science & Instrument Engineering, Hangzhou Dianzi University, Hangzhou 310018, China

^d Faculty of Agricultural and Food Science, Zhejiang A & F University, Hangzhou, 311300, China

HIGHLIGHTS

- A novel electrochemical detection for different types of organophosphorus pesticides.
- Pralidoxime chloride as a universal electrochemical probe for the detection of organophosphorus pesticides.
- Study of the influence of anions and the optimization of testing conditions.
- The non-enzymatic electrochemical detection of organophosphorus pesticides in real samples.

GRAPHICAL ABSTRACT



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ABSTRACT

An electrochemical method based on non-enzymatic inhibition for the determination of organophosphorus pesticide (OPPs) using pralidoxime chloride (PAM-Cl) as a universal electrochemical probe was reported. Cyclic voltammetry was performed to characterize the redox properties of pralidoxime and OPPs. Differential pulse voltammetry (DPV) was carried out to analyze the influence of anion (chloride and iodide ions), to optimize the pH of testing condition, and to explore the relationship between pralidoxime and OPPs. The results showed that iodide ion generated an anodic peak close to the peak of pralidoxime, which would interfere in the detection of OPPs. Phosphate buffer solution (pH 7.0) was chosen because of its high peak current and low peak potential when testing PAM-Cl by DPV. Chlorpyrifos, fenthion, and methyl parathion were examples of three existing OPPs detection methods. The peak current of PAM-Cl decreased along with the increase of concentration of OPPs in the solution. The limit of detection was 0.018 μM , 0.100 μM , and 0.215 μM , respectively. It was the first time for PAM-Cl to be used as a universal electrochemical probe to develop a simple, cheap and stable method for OPPs detection.

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1. Introduction

Organophosphorus pesticides (OPPs) are widely used for protecting crops from pests [1]. However, extensive utilization of OPPs has caused serious public concern considering environment pollution and hurt of the central nervous system of

* Corresponding author. College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, China.

E-mail address: wujian69@zju.edu.cn (J. Wu).

humans [2]. Therefore, it is important to develop an effective method for the determination of OPPs in crops to ensure the food safety.

Traditional methods including liquid chromatography [3], ultrahigh performance liquid chromatography-tandem mass spectrometry [4] and gas chromatography [5] are highly sensitive and accurate for OPPs detection [6]. But they still suffer from some disadvantages such as expensive instruments, requirement of well-trained operators, and complicated pretreatments of samples [7]. Electrochemical detection is a kind of simpler, faster, and more cost-effective method. The electrochemical detection of OPPs usually includes three aspects: directly oxidative method [8], hydrolase-based method [9] and acetylcholinesterase inhibited method [10]. Among them, directly oxidative method is the simplest method but only suitable for a handful of pesticides that can generate self-oxidation-reduction reaction [11]. We have fabricated an ionic liquid-carbon nanotube composite electrode for solid-phase extraction to improve the limit of detection of methyl parathion [12]. Hydrolase-based method is using organophosphorus hydrolase to decompose pesticides, which is appropriate for most types of OPPs [13]. However, it is complicated to synthesize organophosphorus hydrolase. Acetylcholinesterase (AChE) inhibited method is widely used for OPPs detection [14]. Thiocholine is hydrolyzed from acetylthiocholine chloride with the catalyst of AChE [15]. OPPs are detected by monitoring the oxidation current of thiocholine, because the activity of AChE is inhibited by OPPs [16]. However, the stability of enzymes including AChE is always a problem. Besides, some low-toxic OPPs do not inhibit AChE directly but after metabolic activation. According to the former research in our lab [17], Tang et al. discovered that chlorpyrifos, a kind of moderate toxic OPPs, which containing the chemical bond “P=S” need to be oxidized into “P=O” to improve the toxicity to AChE so that chlorpyrifos can be effectively detected with AChE inhibited method. Therefore, developing a simple, stable, cheap and universal method for OPPs detection is of great importance.

In this work, we proposed the electrochemical method based on non-enzymatic inhibition for the determination of OPPs using pralidoxime chloride (PAM-Cl) as a universal electrochemical probe. The structural formula of PAM-Cl is shown in Fig. 1. Pralidoxime is the antidote of OPPs for its ability to reactivate inhibited AChE [18,19]. Pralidoxime can be detected by ultraviolet spectrophotometry [20], fluorimetric determination [21], and also can be detected by electrochemical method according to its oxidized current [22,23]. In our work, we chose chlorpyrifos as an example because it is not able to generate self-oxidation-reduction reaction, and also hard to inhibit AChE directly but after oxidation. It was the first time for PAM-Cl to be used as an electrochemical probe in order to develop a simple, cheap, stable and universal method for OPPs detection. We explored the relationship between pralidoxime and OPPs (chlorpyrifos, fenthion, methyl parathion), analyzed the influence of anion, optimized the testing condition, and detected pesticides in real samples in the following sections.

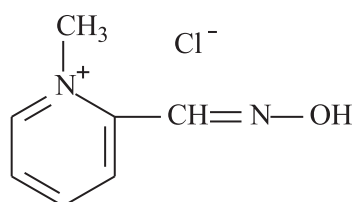


Fig. 1. Structural formula of pralidoxime chloride.

2. Materials and methods

2.1. Reagents and apparatus

Pralidoxime chloride (PAM-Cl) injection was purchased from Haipu Pharmaceutical Co. Ltd (Shanghai, China). Pralidoxime iodide (PAM-I) was purchased from Sigma-Aldrich (St. Louis, Mo, USA). Sodium phosphate dibasic dodecahydrate, sodium dihydrogen phosphate dihydrate, acetic acid, sodium acetate, potassium iodide, and pesticides (chlorpyrifos, fenthion, and methyl parathion) were obtained from Aladdin (Shanghai, China). They were of analytical grade and used without further purification. Samples (Chinese cabbage, pakchoi, and corn) were bought from a local supermarket (Hangzhou, China). Ultrapure water ($18.2 \text{ M}\Omega\text{cm}^{-1}$, Millipore Co. Ltd. USA) was used in all experiments.

Electrochemical measurements were carried out by a CHI440 electrochemical working station (CH Instruments, Austin, TX, USA). A three-electrode system was employed with a glass carbon electrode as working electrode, an Ag/AgCl electrode as reference electrode and a platinum wire electrode as counter electrode (CH Instruments, Austin, TX, USA).

2.2. Electrochemical detection of OPPs using PAM-Cl as a probe

Pralidoximes with different anions (I⁻ and Cl⁻) and chlorpyrifos were diluted to $100 \mu\text{M}$ in 10 mL buffer solution (0.1 M phosphate buffer, pH 7.0), respectively. Cyclic voltammetry (CV) was performed between 0.5 V and 1 V at a scan rate of 0.1 V^{-1} to characterize the response of electrode to pralidoxime and chlorpyrifos. Differential pulse voltammetry (DPV) was carried out from 0.5 V to 1 V with 4 mV incremental potential, 50 mV amplitude, 0.05 s pulse width, 0.0167 sample width and 0.2 s pulse period to compare the response of electrode to PAM-Cl and PAM-I using KI solution as a contrast ($100 \mu\text{M}$ in pH 7.0 phosphate buffer; $25 \mu\text{M}$ in pH 5.6 acetate buffer). Chlorpyrifos ($5.09 \mu\text{M}$) was added into PAM-Cl ($100 \mu\text{M}$) and PAM-I ($100 \mu\text{M}$) respectively to explore the feasibility of being a probe for OPPs detection. Prepare a series of buffer solutions with different pH (acetate buffer: pH 4.6, pH 5.6; phosphate buffer: pH 6.6, pH 7.0) for optimizing the testing condition of PAM-Cl. At this time, the potential range of DPV was from 0.6 V to 1.05 V while other parameters were not changed.

Differential pulse voltammetry was carried out from 0.5 V to 1 V in 10 mL buffer solution (0.1 M phosphate buffer, pH 7.0) for OPPs detection. Pralidoxime chloride ($100 \mu\text{M}$) was added in buffer solution as an electrochemical probe. Pesticides were added in the above-mentioned solution to analyze the relationship between the degree of inhibited peak current and the concentration of OPPs. The concentration gradient of chlorpyrifos was 0.025, 0.28, 0.79, 3.33, and $13.5 \mu\text{M}$, and the gradient of fenthion was 0.18, 0.45, 1.168, 8.35, and $15.5 \mu\text{M}$. As for methyl parathion was 0.38, 2.28, 6.078, 11.777, and $19.37 \mu\text{M}$. Every data point used to obtain calibration curve was calculated from 3 parallel tests.

2.3. Sample analysis

Chinese cabbage (3 g), pakchoi (3 g) and corn (6 g) were used to evaluate the performance of the proposed method. Samples were chopped into small pieces and dipped into 30 mL 0.1 M phosphate buffer (pH 7.0) for 2 min. DPV was performed with a drop of pralidoxime chloride ($100 \mu\text{M}$) into 10 mL extracted solution to detect OPPs. As for the recovery test, samples were mixed with the known amount of OPPs [16]. Remainder procedures were the same as above. The recovery of standard addition was the average value calculated from 3 parallel tests according to the inhibition ratio.

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