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Mini Review

Electroanalytical Methods for Detecting Pesticides in Agricultural Products: a Review and Recent Developments

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In modern agricultural production, the extensive use of pesticides plays an irreplaceable and important role in agricultural production because it effectively improves crop yield. As the most widely used and most toxic pesticides, organophosphorus pesticides can irreversibly inhibit the activity of cholinesterase, causing acetylcholine to accumulate in synapses in large quantities, thus interfering with the normal conduction of nerve impulses and even leading to the death of animals. At present, the main pesticide detection methods are traditional large-scale instrument detection methods. Although these methods have the advantages of high sensitivity and high accuracy, it is difficult to realize real-time and rapid field detection due to the expensive instruments and equipment, long time consumption and professional operation requirements. In recent years, electrochemical biosensors have been widely used in pesticide detection because of their simple operation, low cost and fast in situ detection. This review summarizes the research progress in the direct quantitative determination of organophosphorus pesticides using basic electrochemical sensors. The main performances of different types of carriers in terms of enzyme immobilization, as well as their advantages and disadvantages, are reviewed in detail.

Keywords: Pesticide determination; Electrochemical sensor; Organophosphorus hydrolase; Analytical method;

1. INTRODUCTION

It is well known that pesticides play a vital role in agricultural production because they can effectively increase the yield of crops. Pesticides are widely used to prevent, control or eliminate harmful diseases, insects, grasses and other pests in the production of agricultural products [1–3]. Pesticides are a group of compounds including herbicides, insecticides, fungicides, nematodes and rodenticides [4–6]. According to their chemical structure, pesticides can be classified into organophosphorus pesticides,

carbamate pesticides, organochlorine pesticides, and pyrethroid pesticides. Organophosphorus pesticides and carbamate pesticides account for the majority of the market share. At present, the use of pesticides guarantees a high quality and high yield of crops in most agricultural areas. In view of the fact that pesticides have promoted crop production, alleviated the huge population pressure and brought huge economic benefits to mankind, it is foreseeable that the development, production and widespread use of pesticides will continue to be sustainable in the coming decades [7–9].

The extensive use of pesticides not only increases crop yield but also has a huge negative impact on the ecological environment and human survival. A series of serious ecological, environmental and food safety problems caused by undegraded pesticide residues in soil, air and water environments have become the focus of global concern. In terms of the ecological environment, the use of pesticides can break the balance of ecological communities, and many pesticides (such as organochlorine pesticides) are difficult to degrade in the environment and can even be stored in aquatic animals for decades [10–14]. Around the world, millions of people suffer acute poisoning from pesticide-contaminated agricultural products every year, and food safety is a serious threat to the health of consumers. Therefore, the research and development of rapid, sensitive, accurate, reliable and low-cost methods for pesticide residue analysis and detection have been a focus of great concern [15–18].

In agricultural production, organophosphorus pesticides (organophosphorus pesticides, OPs) have become some of the most widely used pesticides because of their prevention and control of target pests, low cost, wide application range and efficient characteristics. At present, more than 50 organophosphorus pesticides are widely used in the world, such as parathion, methylparathion, malathion, dichlorvos, dichlorvos, dimethoxylates, dimethoxylates, dimethoxylates, etc. OPs are mainly used as agricultural pesticides and are also the most important pesticide variety in China, and their sales volume has led to all kinds of pesticides. However, due to the widespread use of organophosphorus pesticides and long-term unreasonable application methods, a large number of crops retain organophosphorus pesticides in the surface and environment, posing a serious potential threat to human survival and the ecological environment [19–21]. OPs with high biological activity and toxicity mainly enter the body through the food chain, respiratory system, or skin and can rapidly combine with cholinesterase in the body; the phosphorus acylation of cholinesterase inhibits the cholinesterase catalytic ability of acetylcholine, causing the neurotransmitter acetylcholine to produce nervous system disorders (poisoning), influencing the normal activity of the nervous system and causing headache, nausea, vomiting, respiratory paralysis and even death [22,23].

2. ANALYTICAL METHODS FOR OP DETECTION

In view of the widespread use of organophosphorus pesticides and the environmental pollution and food safety problems caused by their residues, the rapid and accurate detection of OPs has been a research focus of great importance in recent decades. At present, there are many methods of OP residue detection, including chromatographic detection/spectral detection technology, enzyme-linked immunoassay, the enzyme inhibition method, and biosensor detection technology [24–27].

Chromatography is the most commonly used and mature pesticide residue detection technology at present. It mainly uses the selective distribution of different substances in different phase states for

separation. The response signal of the detector (such as the peak height or peak area of the chromatograph) is directly proportional to the amount of pesticide in the detected substance being quantified [28–33]. Gas chromatography, high-performance liquid chromatography, mass spectrometry, liquid-mass chromatography, capillary electrophoresis and supercritical fluid chromatography are widely used in the detection of pesticide residues. In particular, gas chromatography is the standard method for detecting pesticide residues in agricultural products in most countries of the world, and the detection limit can reach 1 pM. This method has the advantages of high sensitivity, high separation efficiency, strong selectivity, a low detection limit, good stability and repeatability, and accurate qualitative and quantitative analysis [34–37]. Recently, Albanis and co-workers used SDME combined with GC–MS for the determination of organophosphorus pesticides in water samples [38]. In the present work, we developed SDME by using a modified 1.00 μl microsyringe for the determination of organophosphorus pesticides in water samples combined with a gas chromatography-flame photometric detector (GC-FPD). By using a 1.00 μl microsyringe, the repeatability of the drop volume and injection were improved because the maximum volume of the microsyringe and no dead volume were used. However, because this kind of analysis mostly involves large instruments, the equipment is expensive, professional operators are needed, the detection steps are complicated and time-consuming, and it is difficult to achieve rapid in situ detection.

Spectral detection technology is also a common pesticide residue detection technology. This analysis method is mainly based on the emission and absorption of electromagnetic radiation by the material and their interactions. At present, the main spectral technologies commonly used in organophosphorus pesticide residue detection are spectrophotometry, fluorescence spectrometry, chemiluminescence, Raman spectroscopy and near-infrared spectroscopy [39–45]. Spectrophotometry is widely used in pesticide residue detection and analysis. Its main principle is that the functional groups or reduction products of pesticides react with special colour reagents or under specific conditions such as oxidation, esterification and coordination; this process is used to qualitatively or quantitatively determine the change in absorbance of the solution at a particular wavelength. The advantages of this method are rapid detection, simple operation and easy modification, but its disadvantages are that there are many interference factors and its sensitivity and accuracy are low. Generally, this method is only used for qualitative analysis of pesticide residues.

Immunoassay is an analytical method based on antigen- and antibody-specific recognition and binding reactions. The main methods are enzyme-linked immunosorbent assay, fluorescence immunoassay and radioimmunoassay. The most developed and widely used method is enzyme-linked immunosorbent assay [46,47]. The principle of ELISA is the specific binding of an antigen or antibody with small molecules, enzymes or proteins to achieve qualitative and quantitative detection [48,49]. However, organophosphorus pesticides are small molecular compounds, so OPs must be coupled with large molecular proteins to prepare antigenic substances and then used in the form of artificial antigens to immunize animals so that they produce specific antibodies. Hua et al. [50] successfully detected the residues of eight organophosphorus pesticides, including methylparathion, imidacloprid and parathion, by an ELISA sensor constructed based on BsMcAb, a bispecific monoclonal antibody. Xu et al. [51] reported a simple, rapid and high-throughput fluorescent polarization immunoassay (FPIA) for the simultaneous determination of organophosphorus pesticides using a broad-specificity monoclonal

antibody. The effects of tracer structure, tracer concentration, antibody dilution, methanol content and matrix effect on FPIA performance were studied. The FPIA method can detect 5 OPs simultaneously with a limit of detection below 10 ng/mL. The time required to reach antibody–antigen interaction equilibrium was less than 10 min. The recovery from spiked vegetable and environmental samples ranged from 71.3% to 126.8%, with the coefficient of variation ranging from 3.5% to 14.5%. The developed FPIA method was applied to analyse samples, followed by confirmation with high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) analysis. The developed FPIA method demonstrated good accuracy and reproducibility and is suitable for rapid and high-throughput screening for organophosphorus pesticide contamination with high efficiency and low cost. ELISA technology, which combines immunotechnology with modern detection methods, has the advantages of strong specificity, high sensitivity, high accuracy, a large analytical capacity and simple operation steps. However, the influence mechanism of antibody specificity and stability on the test results is still unclear, so it is difficult to control the uncertainties in the test, making it difficult to produce a standardized test.

The enzyme inhibition technique (EI) is a pesticide residue detection technique based on the inhibition mechanism of organophosphorus and carbamate pesticides on AChE activity [52–54]. In the enzyme inhibition test, an enzyme reaction substrate and corresponding colour reagent are added. However, since both organophosphorus and carbamate pesticides can inhibit the activity of AChE, if the samples of crops, fruits and vegetables to be tested contain organophosphorus or carbamate pesticides, the activity of AChE will be inhibited so that the substrate cannot be hydrolysed, resulting in colour changes [55–57]. The colour changes can be used to determine whether the agricultural products contain organophosphorus or carbamate pesticide residues. In addition, the products obtained after the reaction of the enzyme with a specific compound can also be measured, and the presence of OPs or carbamate pesticides in the tested samples can be judged by the changes in the physical or chemical signals of the products [58–61]. In most cases, the changes in the signals generated by enzyme inhibition correspond to the concentration of the pesticide within a certain range, so the pesticide content in the measured substance can be calculated [62]. This kind of detection method has the advantages of quick response, no need for large instruments and simple operation, which are suitable for the quick detection of pesticide residues in the field. However, its selectivity is poor, and its enzyme activity is easily disturbed by external environmental conditions.

Although the traditional large-scale instrument detection methods for pesticide residues have high sensitivity, accuracy and reliability, these methods still have many disadvantages, such as the high cost of instruments and equipment, complicated steps, time-consuming detection, and the operational need for professional and technical personnel [63]. Biosensors have attracted extensive attention at home and abroad due to their advantages, such as simple operation, high sensitivity, quick response, low cost and easy miniaturization [64–66]. At present, the construction of enzymatic electrochemical sensors for organophosphorus pesticide residue detection mainly depends on the use of inhibitory enzymes such as acetylcholinesterase, butyrylcholinesterase and plant esterase, as well as catalytic enzymes such as organophosphorus hydrolase that can directly catalyse the hydrolysis of OPs.

Enzyme-inhibiting electrochemical sensors are generally constructed based on the irreversible inhibition of enzyme activity by the target compound to be measured [67]. As shown in Figure 1, when

the enzyme reacts with the corresponding substrate, products with electrical activity are produced, which are converted into detectable electrical signals through the signal converter. After the addition of the substance to be measured into the system, the reaction of the enzyme and substrate is inhibited, and the corresponding electroactive products are reduced, resulting in the reduction of the electrical signal.

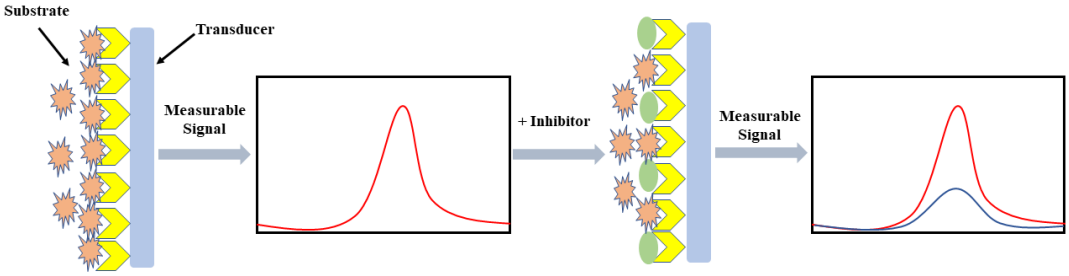

Figure 1. Schematic diagram of the enzyme-inhibited electrochemistry biosensor.

Enzyme electrochemical sensors can be divided into potential enzyme sensors and current enzyme sensors according to different detection modes. Potentiometric enzyme sensors convert the mass change caused by an enzymatic reaction into a potential signal output. However, the high impedance of potential-type electrochemical enzyme sensors and the noise components that affect the measurement accuracy and are often included in the output signal must be suppressed in order to effectively detect the target compounds. In current-type enzyme sensors, at a given potential value, the enzymatic or electroactive substances undergo oxidation or reduction on the surface of the working electrode, and the concentration of the measured substance is determined by detecting the current signal. Current-type enzyme sensors have the advantages of good stability, a low background current, a wide linear range and fast detection speed.

Enzyme-inhibited agroresidue electrochemical sensors are biosensors based on the catalytic action of enzymes on Ops [68]. As shown in Figure 2, the enzyme acts directly on the object to be detected to catalyse the production of electrically active products, which are converted into an electrical signal output by a signal converter. When the concentration of the substance to be detected increases, the enzyme-catalysed products increase, and the measured electrical signals are enhanced. At present, enzyme-catalysed electrochemical sensors for detecting pesticide residues are mainly designed based on the catalysis of OPs by organophosphorus hydrolase.

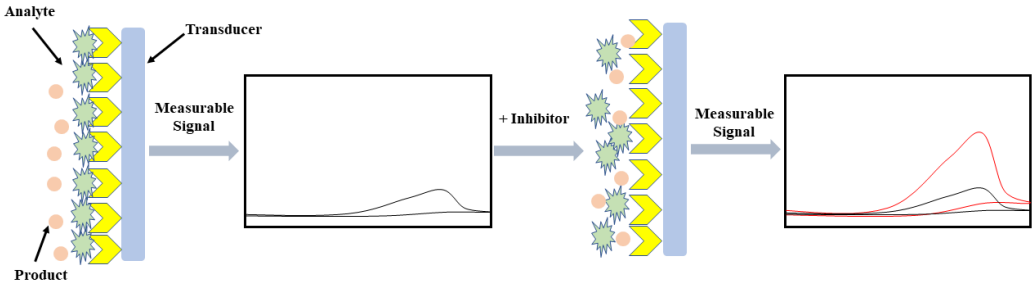

Figure 2. Schematic diagram of an enzyme-catalysed electrochemical biosensor

The use of pesticides plays an irreplaceable role in modern agricultural production, but pesticide residues in the environment, water resources and crops pose a serious threat to the ecological environment, animals and human survival. Organophosphorus pesticides are among the most widely used pesticides and are the main objects of pesticide residue detection. Therefore, the rapid, sensitive, efficient and accurate detection of OP residues is of great significance. Although the traditional method of detecting pesticide residues with large-scale instruments is accurate and reliable, it still has some disadvantages, such as expensive equipment, complicated steps, long detection cycles and the need for professional operators, which limit its large-scale use. Because of its advantages of simple operation, rapid operation and low cost, electrochemical enzyme sensors have been developed rapidly in recent decades and have been widely used in pesticide residue detection and research.

3. RECENT DEVELOPMENTS IN ELECTROCHEMICAL SENSORS FOR DETECTING PESTICIDES

In membrane-based pesticide biosensors, an enzyme is immobilized on a suitable substrate. The membrane used as a support can be natural or artificial. The enzyme is bound to a semipermeable membrane, which will allow the substrate to pass through it. The biocompatibility of artificial membranes can improve the sensitivity and selectivity of membrane-based biosensors. Table 1 summarizes the different membrane-based electrochemical sensors. As can be seen from the table, artificial membranes are selective for different biomolecules, and due to their high flexibility, they can enhance the response. Such membranes are durable and stable and suitable for a variety of pH values. However, such biosensors suffer from membrane fouling. The pores of semi-permeable membranes become blocked, causing the passage of solutes to be blocked.

Table 1. Electrochemical sensors for pesticide detection using membranes as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Trichlorfon	2.5-30 μM	0.038 μM	[69]
DZN-oxon	1.0×10^{-3}–0.3 μM	1.2×10^{-3} μM	[70]
Paraoxon	3.6×10^{-8}–3.6×10^{-5} μM	5.0×10^{-9} μM	[71]
Paraoxon	3.6×10^{-7}–3.6×10^{-4} μM	0.026×10^{-5} μM	[72]
Aldicarb	0.05–2.62 μM	0.119 μM	[73]
Paraoxon	-	7.2 × 10−5, 0.049 μM	[74]
Dichlorvos	-	3.62×10^{3} μM	[75]

Polymer substrates can generate various functional groups on the carrier through chemical treatment. Depending on the specific enzyme, functional groups of interest can be synthesized on such supports. The life of the enzyme can also be improved by this method because it provides a

microenvironment for the enzyme [76], which can be stored for a long time. However, due to the poor conductivity of the polymer, it will become a barrier between the electronics and the sensor, which will affect the sensitivity and detection range of the sensor. Table 2 summarizes recent developments in polymer-based electrochemical pesticide sensors.

Table 2. Electrochemical sensors for pesticide detection using polymers as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Paraoxon	3.6×10^{-8}–3.6×10^{-5} μM	5.0×10^{-9} μM	[70]
Monocrotophos	0.2×10^{-3}–44.8×10^{-3} μM	0.2×10^{-3} μM	[77]
Paraoxon	-	1.91×10^{-2} μM	[78]
Carbofuran	4.8×10^{-3}–9.0×10^{-2} μM	4.0×10^{-3} μM	[79]
Paraoxon	1.3–3.9 ppb	-	[80]
Chlorpyrifos	25 ppb–1.5 ppm	-	[81]
Dichlorvos	-	1.0×10^{-4} μM	[82]
Dichlorvos	-	1.0 μM	[83]
Methyl parathion	$1.0 \times 10^{-5}$and 1.0 μM	1.0×10^{-6} μM	[84]
Methyl parathion	0.018–0.45 and 1.89–17.0 μM	7.5×10^{-3} μM	[85]
Methyl parathion	$3.5 \times 10^{-6}$to 2.0×10^{-3} M	5.0×10^{-7} M	[86]

The sol-gel method can also be used for enzyme immobilization. The primary property of sol-gels is that the pore size can be adjusted as needed. Sol-gels are chemically inert, do not show swelling in aqueous media, and have photochemical and thermal stability. Du *et al.* [87] proposed a simple method to immobilize acetylcholinesterase (AChE) on a silica sol–gel (SiSG)-AuNP assembly for the sensitive, fast and stable amperometric determination of monocrotophos, an OP pesticide. They observed that the large quantities of hydroxyl groups in the sol–gel composite provided a biocompatible microenvironment around the immobilized AChE and thus stabilized its biological activity to a large extent through hydrogen bond formation. A significant change in voltammetric signal occurred at the AChE-AuNPs-SiSG/GCE after 10 min incubation in a standard solution of monocrotophos. The increase in monocrotophos concentration led to the irreversible inhibition of AChE, which was obvious from the considerable decrease in peak current. Therefore, sol-gels provide a good substrate for antibodies and enzymes for immobilization. However, this method also has some problems, such as the denaturation of biomolecules under highly acidic conditions and/or high alcohol concentrations. Sol-gels are not suitable for substrates with curved surfaces, such as optical fibres. Furthermore, proteins are insoluble or aggregate in alkoxysilane solution. Table 3 summarizes recent developments in sol-gel-based electrochemical pesticide sensors.

Table 3. Electrochemical sensors for pesticide detection using sol-gel generated films as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Paraoxon	0.01–0.001 μM	0.012 μM	[88]
Dichlorvos	1.0 and 3.0 × 10^{-3} μM	1.0 × 10^{-3} μM	[89]
Oxydemeton methyl	0.008–0.81 μM	0.008 μM	[90]
Dichlorvos	0.1–80 μM	0.01 μM	[91]
Carbaryl	2 × 10^{-2} μM	-	[92]
Monocrotophos	-	0.44 μM	[93]
Chlorpyriphosethyl oxon	2.5 × 10^{-4} μM	0.5 μM	[94]
Parathion	0.1–1.0 ppb	0.04 ppb	[95]

Quantum dots are highly luminescent fluorophores. Quantum dots are semiconductor particles whose size is limited to the nanometre scale. They are because of their large size dependence and are similar in size to the biomolecules used for immobilization. Therefore, quantum dots have been used in biosensors. Quantum dots can even bind to a variety of biological molecules, so they are very important in the sensing and development of sensitive sensors. They have some disadvantages, such as a large size (10-30 nm); furthermore, if they do not emit interfering fluorescence for a long time, flickering will occur. Cadmium sulphide quantum dots (QCdS) have also been effectively employed in sensing OP pesticides such as trichlorfon. Poly(*N*-vinyl-2-pyrrolidone) (PVP)-capped CdS quantum dots (QCdS-PVP) were synthesized by Li *et al.* [96] using $CdCl_2$ and Na_2S in the presence of PVP. Table 4 summarizes recent developments in quantum dot-based electrochemical pesticide sensors.

Table 4. Electrochemical sensors for pesticide detection using quantum dots as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Monocrotophos	0.44 μM	-	[93]
Monocrotophos	1.34 μM	4.4 × 10^{-3}–4.48 μM	[97]
Carbyl	2.98 × 10^{-3} μM	4.96 × 10^{-3}–2.48 μM	[98]

Modifying nanomaterials on an electrode surface can improve the reliability of electrochemical technology. Nanoparticles have valuable properties, such as a large surface area, high electrical conductivity, and good catalytic performance, and have broad application prospects in the field of biosensing. Nanomaterials can greatly increase the electron transfer rate. Carbon nanomaterials are commonly used electrochemical modification materials. MWCNT-modified electrodes have also been successfully used in triazophos determination. Du *et al.* [99] reported a sensitive, fast and stable amperometric sensor for the quantitative determination of triazophos. They used MWCNTs and chitosan

(Chi) as an AChE immobilization matrix. They carried out a covalent immobilization technique to immobilize AChE on MWCNT-Chi-modified electrodes. Table 5 summarizes recent developments in nanomaterial-based electrochemical pesticide sensors.

Table 5. Electrochemical sensors for pesticide detection using nanomaterials as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Monocrotophos	4.48×10^{-3}–4.48×10^{-2} μM	3.5×10^{-9} μM	[100]
Malathion	3.0×10^{-3}–3.027 μM	1.81×10^{-3} μM	[101]
Phoxin	6.6–440 μM	1.3 μM	[102]
Paraoxon	50×10^{-4} μM	50–200 $\times 10^{-3}$ μM	[103]
Methamidophos	1.0×10^{-3} μM	0.1×10^{-3} μM	[104]
Carbyl	1.4×10^{-3} μM	4.9–74.5 and 74.5–9.9×10^{3} μM	[105]
Chloropyrifos	1.58×10^{-4} μM	1×10^{-4}–1.0 μM	[106]
Monocrotophos	0.01 μM	0.1–10 μM	[107]

In addition to animal cholinesterases, researchers have also reported on plant esterases with similar inhibitory mechanisms (PLaE). PLaE belongs to the carboxylate hydrolases, which can catalyse the decomposition of carboxylate compounds with the participation of water. PLaE is widely found in wheat, soybean, and other agricultural products with abundant sources and low cost. It has a similar mechanism of action to AChE, whose enzyme activity can also be inhibited by organophosphorus pesticides, and can also be applied to the detection of OPs. Bacterial electro-chemical sensors, such as those including genetically engineered *Moraxella sp.*, *Pseudomonas putida* or *Escherichia coli*, have become attractive for direct OP determination. Table 6 summarizes recent developments in bacterial-based electrochemical pesticide sensors.

Table 6. Bacterial electrochemical sensors for pesticide detection using quantum dots as matrices.

Analyte	Linear detection range	Detection of limit	Reference
Paraoxon	-	2.0 μM	[108]
Methyl parathion	-	1.0 μM	[109]
Paraoxon	-	0.1 μM	[110]
Paraoxon	-	55 ppb	[111]
Fenitrothion	-	553 ppb	[112]

4. CONCLUSION

This review summarizes the recent studies of electrochemical sensors for OP detection. The direct measurement of OPs as enzyme substrates can easily and quickly detect the amount of pesticide. Although chromatographic technology is still the main detection technology in this field, research in recent years has shown that electrochemical sensors are more sensitive and thus have an advantage. Electrochemical biosensing is currently considered a screening method that is very suitable for in situ expression determination.

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