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THE PERFORMANCE OF ORGANOPHOSPHATE PESTICIDES DETERMINATION USING BIOSENSOR BASED A SMALL DEVICE POTENTIOMETER AS A TRANSDUCER

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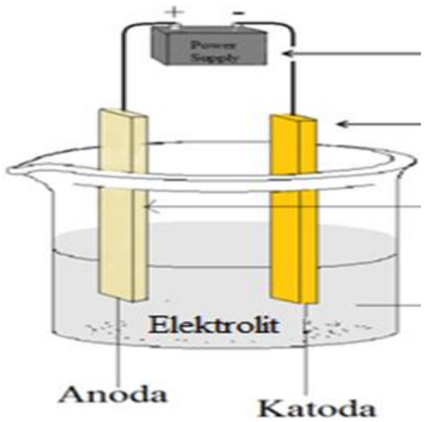

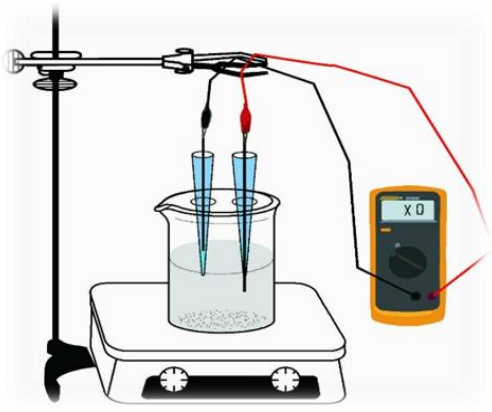

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ABSTRACT

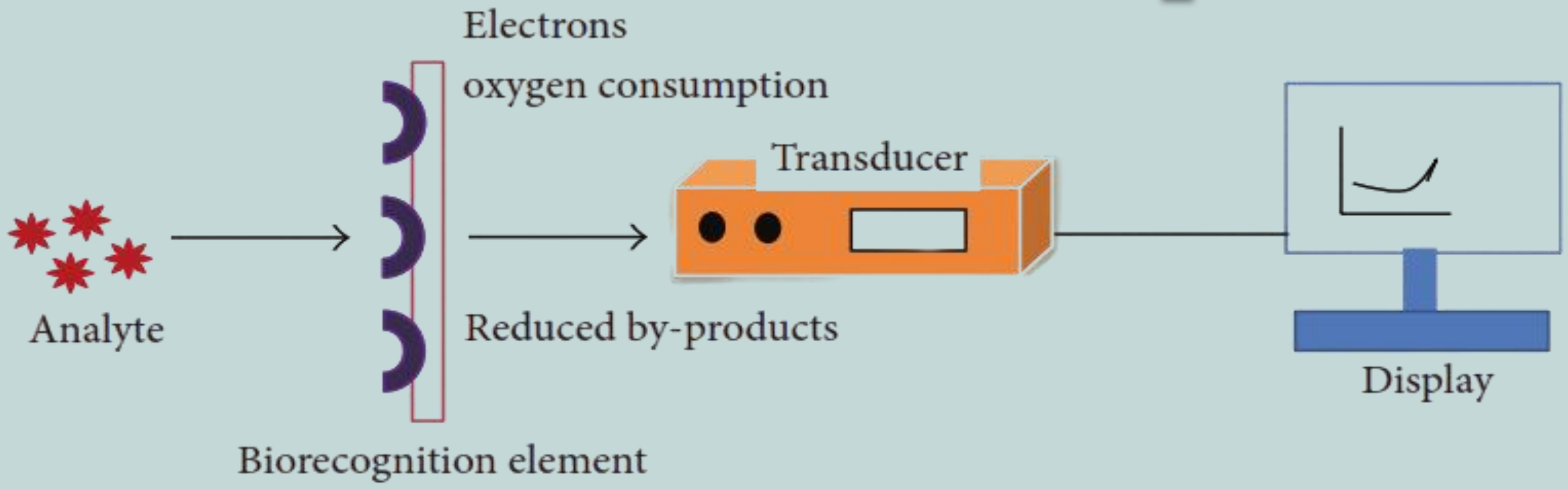
The need to control pesticide residues in foodstuffs in a fast and straightforward analysis for the field scale is required. Therefore, this research develops a transducer-based biosensor with a small device potentiometer (SDP) to produce a fast and accurate pesticide detection tool. The biosensor based on Pt/Au electrodes by immobilizing the acetylcholinesterase (AChE) enzyme coated membrane cellulose acetate (CA) 15% (w/v) cross-linked glutaraldehyde (GA) 25% (v/v) and SDP as a transducer that produces a potential value. The biosensor testing results on the organophosphate pesticide class, namely diazinon and profenofos, in which they showed the sensitivity of 21.204 and 21.035 $mV.decade^{-1}$, Limit of Detection (LoD) 10^{-8} $mg.L^{-1}$, selectivity coefficient $K_{i,j} < 1$ and accuracy of 99.497 and 94.765 %, respectively. The results showed that the biosensor connected to an SDP transducer had an excellent performance in determining the presence of organophosphate pesticides.

Keywords: small device potentiometer; biosensor; organophosphate; pesticide; sensitivity; limit of detection; selectivity; accuracy

INTRODUCTION

Biosensors are “self-standing devices”, devices that record physical, chemical, or biological changes and convert them into measurable signals from the sample and monitor the analyte of interest [1,2]

Electrochemical biosensors are a subclass of chemical sensors that combine sensitivity, such as low detection limit, electrochemical transducers with the high specificity of biological recognition processes [4]



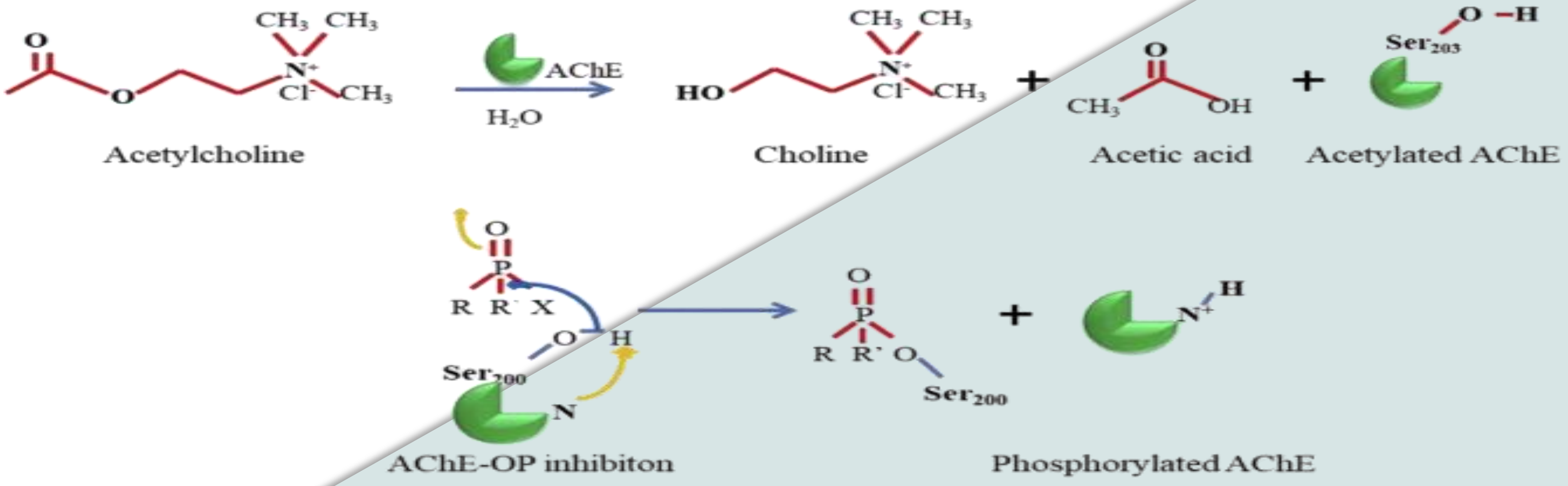
The sensor contains a recognition element that allows a selective response to a specific analyte or group of analytes, minimizing interference from other sample components. Another significant component of a sensor is a transducer or detection device that produces a signal [3]

ELECTROCHEMICAL BIOSENSOR [5]

- Low cost
- Rapic response
- Simple operation
- Excellent selectivity
- In-place inspections

INTRODUCTION

The electrochemical method using measurement tools is based on potentiometric [6], amperometric [7] or conductometric [8]. Potentiometric biosensors are suitable for measuring the response value of pesticide detection measurements [9].



Potentiometric are efficient when used in field analysis because they are more straightforward and ideal for real-time analysis.

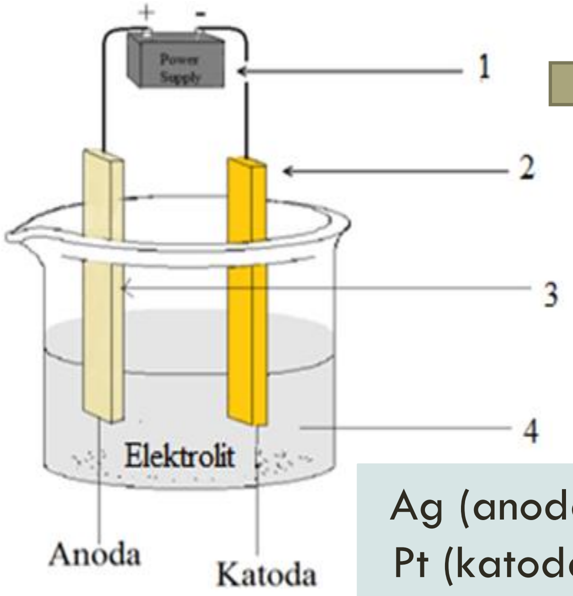
The detection system using potentiometric developed by Timur, S., & Telefoncu, A., 2004 [10], *has the underlying principle of inhibition of AChE activity due to its properties in identifying organophosphate compounds.*

Pesticides were effectively detected in the range of 0.1-100 mM for parathion-methyl and methamidophos and 0.6-600 mM for Malathion. However, in the presence of higher pesticide concentrations, only partial regeneration of the enzymatic activity was regenerated [9,10].

The combination of potentiometric-based AChE enzyme biosensors as transducers with analytical techniques has been widely reported in the literature as a suitable method.

EXPERIMENTAL

The electrolysis process of Ag/AgCl (Mashuni *et al*, 2016)



Ag (anoda)
Pt (katoda)

Ag/AgCl electrode

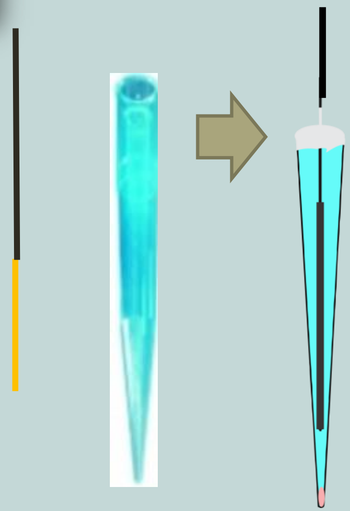
Mashuni et al. 2016

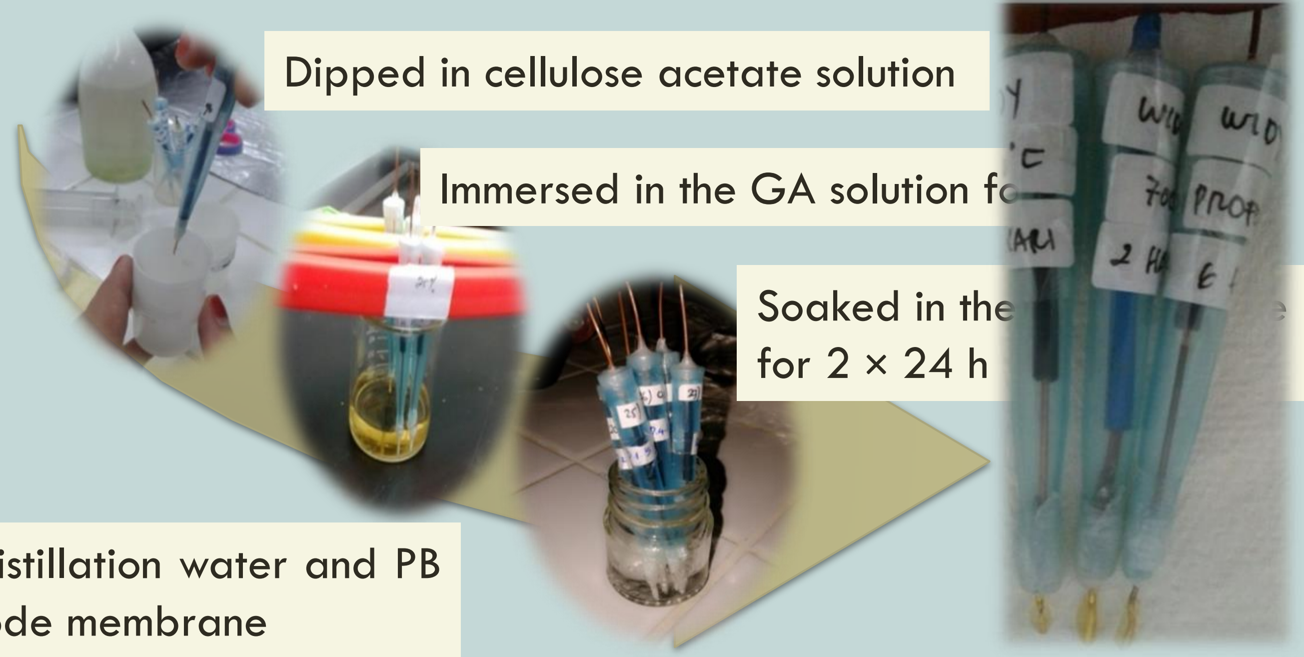
1. Battery
2. Platina (Pt) wire
3. Silver (Ag) wire
4. 0.1 M KCl solution

Biosensor membrane (Mashuni *et al*, 2016)

Comparison of membrane composition (%)	
Cellulose Acetate (CA)	Glutaraldehyde (GA)
15	25

Working Electrode Design (Mashuni *et al*, 2016)





Dipped in cellulose acetate solution

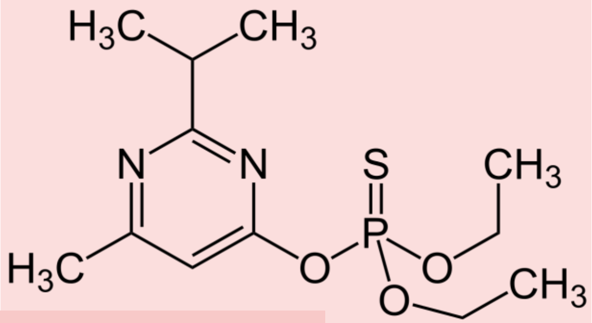
Immersed in the GA solution fo

Soaked in the
for 2 × 24 h

The electrode is washed with distillation water and PB Solutions pH 8 is formed electrode membrane

EXPERIMENTAL

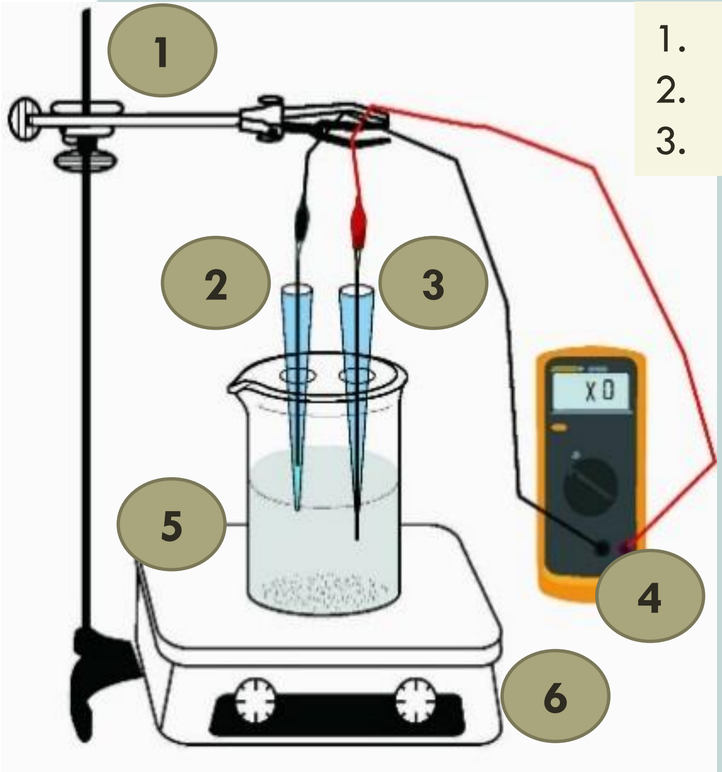
Profenofos



Diazinon

Biosensor Performance Test

Potentiometric biosensor equipment design



1. Stative
2. Standard electrode Ag/AgCl
3. Working Electrode
4. Potentiometer
5. ATCI Substrate 10^{-3} M
6. *Hot plate*

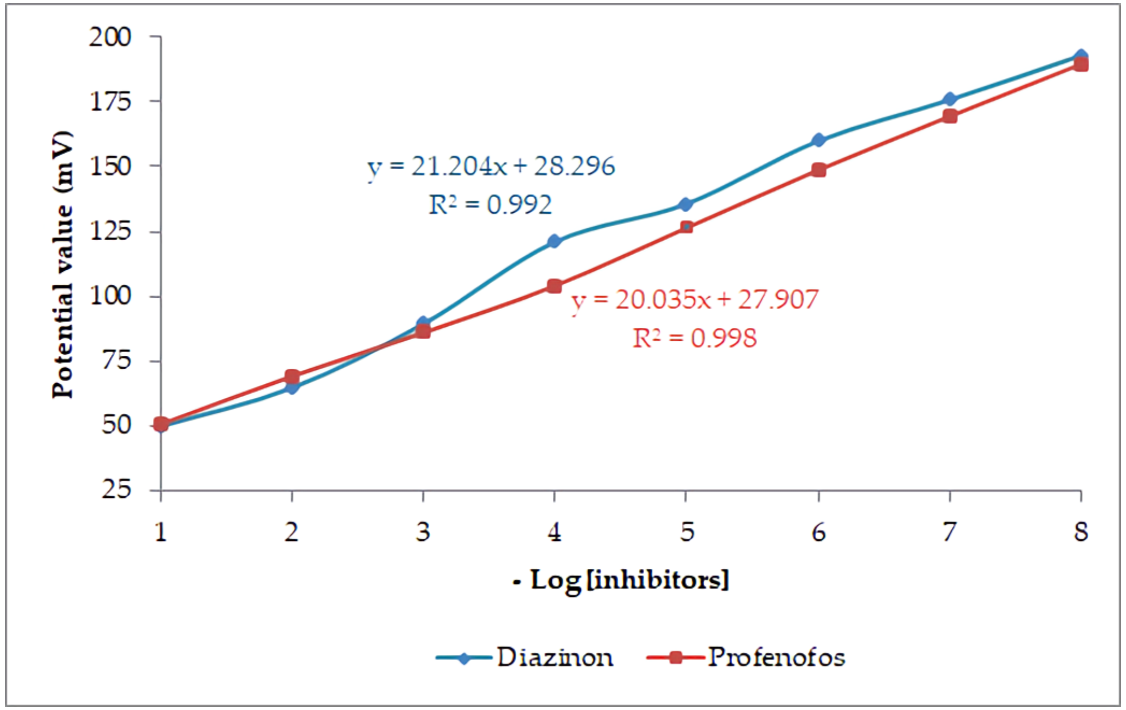
- *Sensitivity*
- *Limit of detection (LoD)*
- *Selectivity*
- *Accuracy*

Pesticide concetrations are 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mg.L^{-1}

RESULT & DISCUSSION

Measurement of potential value, sensitivity value and LoD of biosensor

Substrate Concentration (M)	Inhibitor Concentration ($mg.L^{-1}$)	Potential Value	
		Diazinon	Profenofos
10^{-3}	10^{-1}	50	50.7
	10^{-2}	64.8	69.3
	10^{-3}	89.5	86.1
	10^{-4}	121.1	104.2
	10^{-5}	135.7	126.5
	10^{-6}	159.9	148.7
	10^{-7}	175.8	169.4
	10^{-8}	192.9	189.6
Potential value of substrate (mV)		199.8	195.7
The reference solution (mV)		199.1	196,3
Inhibitor Concentration, 10^{-8} $mg.L^{-1}$ (mV)		195.5	194.6
Sensitivity ($mV.decade^{-1}$)		21.204	21.035
Linear regression equation (R^2)		0.992	0.998
LoD ($mg.L^{-1}$)		10^{-8}	10^{-8}



The sensitivity of the performance of SDP-based biosensors to the detection of pesticide diazinon and profenofos of 21.204 and 21.035 $mV.decade^{-1}$, respectively.
The LoD value of the SDP-based biosensor as a transducer, which is 10^{-8} $mg.L^{-1}$.

RESULT & DISCUSSION

Selectivity of biosensor based small device potentiometric (SDP)

a_i (mg.L^{-1})	a_j (mg.L $^{-1}$)	Potential Value (mV)				$K_{i,j}$, Selectivity	
		a_i		a_j			
		[diazinon]	[profenofos]	[profenofos]	[diazinon]	[diazinon]	[profenofos]
10^{-5}	0	160	126.5	0	0	0	0
	10^{-9}			159.5	127.9	-0.24	0.64
	10^{-8}			158.9	126.1	-0.53	-0.19
	10^{-7}			158.6	125.9	-0.67	-0.29
	10^{-6}			158.1	124.7	-0.91	-0.87
	10^{-5}			157.4	124.5	-1.26	-0.96
10^{-4}	0	131.1	104.2	0	0	0	0
	10^{-9}			130.5	106.3	-0.29	0.96
	10^{-8}			130.1	105.7	-0.48	0.68
	10^{-7}			129.8	104.8	-0.63	0.27
	10^{-6}			129.5	103.3	-0.77	-0.43
	10^{-5}			129.1	102.2	-0.97	-0.97
10^{-3}	0	90	80.1	0	0	0	0
	10^{-9}			89.8	82.2	-0.1	0.95
	10^{-8}			89	81.9	-0.49	0.81
	10^{-7}			88.7	80.5	-0.63	0.17
	10^{-6}			88.2	79.6	-0.88	-0.25
	10^{-5}			88	78.1	-0.98	-0.98

*a_i is the concentration of the analyte/main compound, a_j is the concentration of the analyte/interference compound, $K_{i,j}$ is the selectivity coefficient

Variations in the value of $K_{i,j}$ depend on the electrode's response and the environment of the elements in the solution. **The selectivity coefficient value obtained is smaller than +1.**

The overall values obtained for the range of concentrations of the low nuisance components are still within tolerance. The average selectivity coefficient value received still meets **the specified selectivity value standard, more excellent than -1 and more minor than +1, so $K_{i,j}$ < 1, is a very selective electrode for pesticide detection compared to interfering compounds.**

RESULT & DISCUSSION

Accuracy of biosensor based ***small device potentiometric (SDP)***

$[C'_A]$	$[C_A]$	$[C_F]$	Potential Value (mV)						Accuracy, % Recovery	
			Diazinon			Profenofos			Diazinon	Profenofos
			$[C'_A]$	$[C_A]$	$[C_F]$	$[C'_A]$	$[C_A]$	$[C_F]$		
10^{-2}	10^{-3}	10^{-2}	64.8	131.1	79.1	80.4	118.6	76.9	79.123	76.899
10^{-3}		10^{-3}	90		84.8	118.6		99.2	84.79	99.232
10^{-4}		10^{-4}	131.1		107.7	130.8		108.2	107.69	108.165
Mean of % Recovery									99.497	94.765

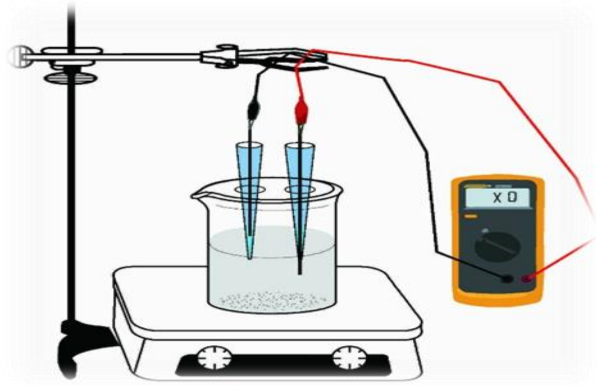
*C'_A is the concentration of analyte/compound added, CA is the concentration of the sample, CF is the total concentration of the sample obtained from the measurement

The average % recovery of the SDP-based biosensor as a transducer has an accuracy rate of 99.497 and 94.765% for diazinon and profenofos pesticide detection, respectively.

Accuracy is expressed as the % recovery of the added analyte. In general, the acceptance criteria for accuracy (% recovery) are 80-110%

Based on the results and data obtained from the study of SDP-based biosensors as transducers in the detection of organophosphate pesticides, **the sensitivity was 21,204 and 21,035 mV/decade, LoD 10-8 mg L-1, selectivity coefficient Ki,j < 1 and accuracy of 99,497 and 94.765%.** *Thus, potentiometric biosensors with CA and GA membranes immobilized by AChE enzymes have good sensitivity, selectivity and accuracy in detecting the presence of organophosphate pesticides in a sample and LoD from tiny biosensors is effective for detecting at low scale and concentration.*

CONCLUSION



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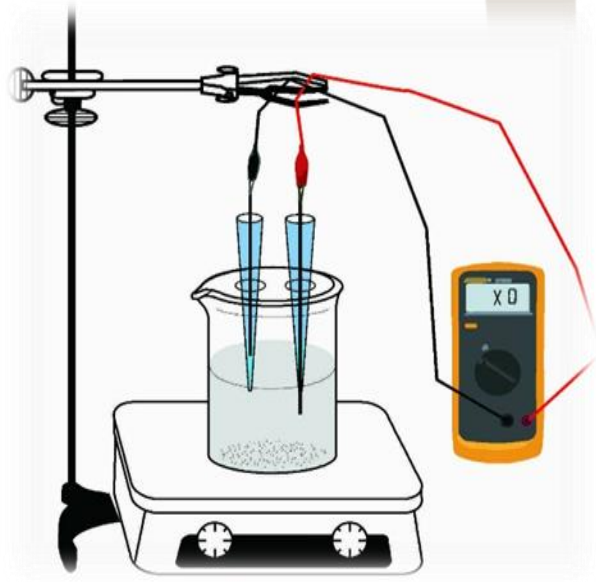
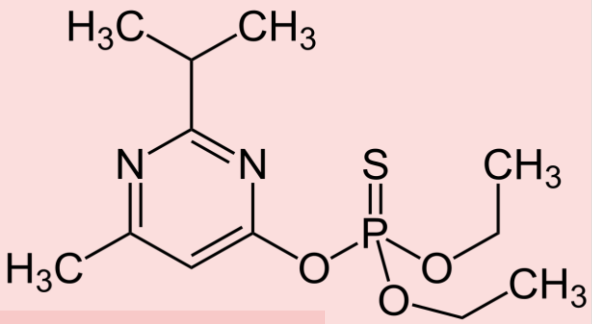
Thank you



Profenofos



Diazinon