Science of the Total Environment 426 (2012) 346–350

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Screen-printed acetylcholinesterase-based biosensors for inhibitive determination of permethrin

Olga Domínguez-Renedo *, M. Asunción Alonso-Lomillo, Pedro Recio-Cebrián, M. Julia Arcos-Martínez

Analytical Chemistry Department, Faculty of Sciences, University of Burgos, Pza, Misael Bañuelos s/n, 09001 Burgos, Spain

ARTICLE INFO

Article history:
Received 15 November 2011
Received in revised form 14 March 2012
Accepted 15 March 2012
Available online 13 April 2012

Keywords:
Permethrin
Acetylcholinesterase
Biosensor
Screen-printed electrodes

ABSTRACT

An amperometric assay based on acetylcholinesterase (AChE) inactivation has been developed for the monitoring of permethrin using a screen-printed three-electrode system. The enzyme AChE catalyzes the hydrolysis of acetylthiocholine to thiocholine, which can be electrochemically oxidized. The presence of permethrin inhibits the AChE activity, resulting in a lower thiocholine production and thus, a decrease in the amperometric oxidation current. Immobilization of AChE was performed by cross-linking giving a capability of detection of 8.1 ± 0.4 μM. Repeatability and reproducibility of the developed AChE biosensor were also calculated, yielding values of 9.6% ($n = 4$) and 5.4% ($n = 5$), respectively related to the slopes of the calibration curves performed in the range from 6.2 up to 41 μM. The method was successfully applied to the determination of permethrin content in a commercial lice gel.

1. Introduction

Permethrin [3-phenoxibenzyl-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxilate] is a broad spectrum synthetic pyrethroid insecticide used in the elimination of a great diversity of insects on different kinds of vegetables. It can also be used as a good repellent against different insect species. In this way, permethrin has been widely used as a moth-proofing agent in the textile industry and it is often used in agriculture, forestry, horticulture, public health centers and households (Thriveni and Sreedhar, 2004). Its residues in fruits, vegetables and other agricultural products represent a serious risk to human health causing cancer, infertility, nerve disorders, and immunological disorders (Du et al., 2010). Therefore, it is essential to monitor the concentration of this molecule to determine its fate in the environment and its effects on human health.

Many analytical methods have been described in the literature for the determination of permethrin, most of them related to chromatographic (Chocholous et al., 2008; de Souza Pinheiro and de Andrade, 2009; Du et al., 2010; Vazquez et al., 2008; Vonderheide et al., 2009) and spectrophotometric techniques (Butte and Kemper, 1999; Kazemipour et al., 2002). The analysis of similar insecticide species has also been performed by electroanalytical methods (Coomber et al., 1998a, 1998b; Manisankar et al., 2009, 2008, 2005; Oudou et al., 2001) but, to the authors' knowledge, few of them describe the successful determination of permethrin using this kind of method. In the work described by Thriveni and Sreedhar (2004), the determination of the insecticide was carried out using a hanging mercury drop electrode (HDME). Kaushik et al. (2009) have also described an electrochemical method for the determination of permethrin based on the immobilization of single standard *calf tymus* deoxyribose nucleic acid onto chitosan (CH)–iron oxide (Fe_3O_4) nanoparticles hybrid nanobiocomposite film deposited onto an indium–tin-oxide glass plate. The unfriendly environmental effects of HDME can be reduced by using disposable screen-printed electrodes (SPEs). In addition, SPEs present many other advantages, such as ease-of-use and in situ analysis, emphasizing the great variety of possible modifications including the immobilization of enzymes for biosensor construction (Domínguez-Renedo et al., 2007; Starowicz et al., 2006).

Enzymatic sensors constructed with SPEs present a great number of applications in the determination of pollutants, such as pesticides. The analysis of this kind of molecule is generally based on enzymatic inhibition processes (Marty et al., 1993; Mionetto et al., 1994; Periasamy et al., 2009). Among the most common enzymatic disposable biosensors used in pesticide determination we should highlight those based on enzymatic inhibition of AChE (Marty et al., 1993; Mionetto et al., 1994; Andreescu et al., 2002a, 2002b; Domínguez-Renedo and Arcos-Martínez, 2006; Domínguez-Renedo et al., 2007; Ovalle et al., 2009; Periasamy et al., 2009; Istamboulie et al., 2010).

AChE is an important enzyme present in the synaptic clefts of the central nervous system of living organisms which promotes the following reaction (Stoytcheva et al., 1998),

$$\underset{\text{acetylthiocholine}}{(CH_3)_3\,N^+(CH_2)_2SCOCH_3} + H_2O + \text{AChE} \rightarrow \underset{\text{thiocholine}}{(CH_3)_3\,N^+(CH_2)_2SH} + CH_3COOH.$$

* Corresponding author. Tel.: +34 947258818.
E-mail addresses: olgado@ubu.es (O. Domínguez-Renedo), malomillo@ubu.es (M.A. Alonso-Lomillo), jarcos@ubu.es (M.J. Arcos-Martínez).

0048-9697/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2012.03.042

It has been proven that thiocholine ($(CH_3)_3\,N^+(CH_2)_2SH$), which is the product of this enzymatic process, is electroactive and suffers an anodic oxidation, according to the following diagram,

$$2(CH_3)_3N^+(CH_2)_2SH \rightarrow \begin{matrix} S-CH_2-N^+-(CH_3)_3 \\ | \\ S-CH_2-N^+-(CH_3)_3 \end{matrix} + 2H^+ + 2e^-.$$

This oxidation signal can then be used for the monitoring of the enzymatic reaction in amperometric AChE-based biosensors.

The enzyme inhibition mechanism proceeds through the formation of a stable complex of the pesticide with the active site of AChE. Thus, the presence of a pesticide inactivates the enzyme AChE, resulting in a reduction of the amount of thiocholine generated. Therefore, a drop in the intensity of the oxidation current is registered and related to the concentration of the inhibitor (Kukla et al., 1999). In this way, pyrethroid insecticides, including permethrin, have also shown an inhibition effect on AChE activity (Singh and Agarwal, 1987; Rao and Rao, 1995).

In the present work, AChE-based amperometric biosensors were used for the inhibitive determination of permethrin. The enzyme was immobilized by cross-linking on the surface of screen-printed carbon electrodes (SPCEs), with the developed devices (AChE/SPCEs) being the first disposable amperometric sensors used for the sensitive determination of permethrin.

2. Experimental

2.1. Reagents

All solutions were prepared with water purified with a Milli-Q apparatus from Millipore (Bedford, MA, USA).

C10903P14 (carbon ink) from Gwent (Electronic Materials, Torfaen, UK), Electrodag 418 (Ag ink) and Electrodag 6037 SS (Ag/AgCl ink) from Acheson Colloiden (Scheemda, The Netherlands) and 242-SB (dielectric ink) from ESL Europe Agmet Limited (Reading, UK) were used in the fabrication of SPCEs.

All reagents used were of analytical-reagent grade. Electrochemical measurements were carried out using a universal buffer system containing boric acid at 200 mM (Merck, Darmstadt, Germany), citric acid at 50 mM (Panreac, Barcelona, Spain), tri-sodium phosphate 12-hydrate at 100 mM (Merck, Darmstadt, Germany) and KCl at 100 mM (Merck, Darmstadt, Germany).

The pH values of the universal buffer were adjusted with a 1000 mM NaOH (Merck, Darmstadt, Germany) solution.

AChE (E.C.3.1.1.7, 1047 U/mg from electric eel), acetylthiocholine iodide, glutaraldehyde (GA) and bovine serum albumin (BSA) were obtained from Sigma (Steinheim, Germany).

AChE phosphate solutions were prepared by mixing 1 mg of AChE with 1 mL of a 10 mM pH 6 phosphate solution ($NaH_2PO_4 \cdot 2H_2O$, Panreac, Barcelona, Spain).

Permethrin stock solutions were prepared by dissolving appropriate amounts of permethrin (Fluka, Steinheim, Germany) in dimethylformamide (Panreac, Barcelona, Spain).

A commercial sample of lice gel was obtained from OTC Iberica (Barcelona, Spain).

2.2. Apparatus

SPCEs were produced on a DEK 248 printing machine (DEK, Weymouth, UK) using polyester screens with appropriate stencil designs mounted at 45° to the printer stroke.

Amperometric measurements were taken using a PalmSens electrochemical system (PalmSens, The Netherlands).

The pH of the solutions was measured with a Crison Model 2002 (Barcelona, Spain) pH meter.

2.3. Software

Data analysis was processed with a STATGRAPHICS PLUS (Statistical Graphics Corp, 1994–1999) software package for the experimental design process, PROGRESS (Rousseuw, 1989) for the robust regression and DETARCHI (Sarabia and Ortiz, 1994) for the capability of detection.

2.4. SPCE preparation

Home-made SPCEs were used in the determination of permethrin. For the construction of the SPCEs, successive layers of different inks were printed onto a polyester strip substrate following the printing procedure described in previous works (Gonzalo-Ruiz et al., 2007; Domínguez-Renedo and Arcos-Martinez, 2007b).

2.5. AChE immobilization

The biologically sensitive layer of the developed biosensor was formed by cross-linking AChE (0.1% w/v) with BSA (6% w/v) and GA (2.5% w/v) aqueous solution, prepared in 10 mM phosphate buffer pH 6. Firstly, 5 μL of GA, 5 μL of BSA and 10 μL of AChE solutions were mixed. Then, 5 μL of this mixture was dropped on the working electrode surface. Finally, it was left to react 90 min at 4 °C.

2.6. Permethrin amperometric determination procedure

The AChE/SPCEs biosensors were placed in the electrochemical cell containing 5 mL of the universal buffer solution. An adequate potential was applied and, once a steady-state current was set, a defined amount of acetylthiocholine iodide 100 mM stock solution was added to the measuring cell. A large oxidation current was observed due to the addition of acetylthiocholine iodide, and a plateau corresponding to the steady-state response was reached. Then, fixed portions of the permethrin stock solution were added consecutively, reaching a plateau each time. The addition of permethrin solution resulted in a current decrease proportional to the amount of permethrin added.

3. Results and discussion

In order to develop a permethrin sensor, different electrochemical procedures using SPCEs were tested. In a first step, bare electrodes were checked under different experimental conditions, obtaining no analytical signal for permethrin. Different film modified SPCEs were then investigated including mercury (Dominguez-Renedo et al., 2009) and bismuth (Wang et al., 1993) film modifications. These modifications did not lead to analytical results in the determination of the insecticide. Finally, the modification of the SPCE surface with nanoparticles was studied, since silver and gold nanoparticle deposits on SPCEs have demonstrated their utility in the sensitive determination of different analytes (Calvo et al., 2007; Domínguez-Renedo and Arcos-Martinez, 2007a, 2007b). However, no electrochemical response was obtained for permethrin in any case. The development of an AChE/SPCEs biosensor was then proposed.

The AChE/SPCEs biosensor developed produced an amperometric signal which is sensitive to the presence of acetylthiocholine iodide in the electrochemical cell giving a high oxidation current (Fig. 1). After reaching a steady-state current, the addition of permethrin in the electrochemical cell produces an inhibition of the enzyme AChE, which causes a decrease in the acetylthiocholine iodide amperometric signal of the biosensor.

Permethrin inhibition action can be quantitatively evaluated determining the difference between the steady-state current in the absence of permethrin (I_0) and the steady-state current in the presence of permethrin (I). The parameter ΔI ($I_0 - I$) depends on acetylthiocholine iodide concentration, applied potential (E_{ap}) and the pH of the buffer

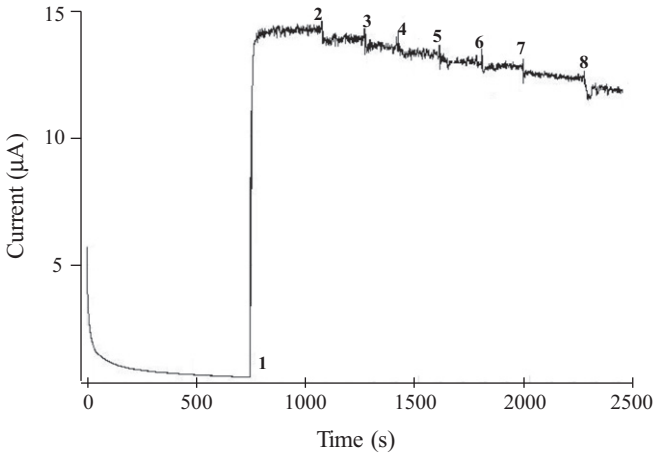

Fig. 1. Amperometric recording obtained at an AChE/SPCE in universal buffer: (1) Addition of 100 μL of a 100 mM acetylthiocholine iodide solution ([acetylthiocholine iodide] = 2 mM), (2–8) additions of 50 μL of a 0.64 mM permethrin solution. E_{ap} = +0.6 V vs. Ag/AgCl SPE, pH = 4.

solution. Therefore, an optimization of these variables was necessary in order to ensure the quality of the results.

Previous experiments showed that the oxidation signal for acetylthiocholine iodide was only observed for a potential of +0.6 V. For this reason this variable was fixed, while the remaining two variables were optimized. In fact, Fig. 2 shows a well defined peak for acetylthiocholine at this potential.

Experimental design has been used as a tool for optimization. In this case, a 2^2 central composite design was applied, with a replication in the central point in order to estimate the residual error. The response to be optimized was ΔI obtained for a sample containing a concentration of permethrin of 0.1 μM. The optimum values obtained in the optimization process were as follows,

[acetylthiocholine iodide] = 2 mM pH = 4.

Under these optimum conditions, the dependence between ΔI and permethrin concentration is linear as shown in Fig. 3.

An important characteristic of any analytical method is, without doubt, its capability of detection. In order to determine this parameter, several calibration curves were carried out in the concentration range from 6.2 to 41 μM for AChE/SPCEs under the optimum working conditions. The existence of anomalous points would lead to incorrect adjustments, altering the method's sensitivity and its capability of detection. In order to avoid this problem least median squares regressions (LMS) were used, which allow the detection of outliers and make it possible to identify a linear range if at least 50% of the data are aligned (Rousseuw,

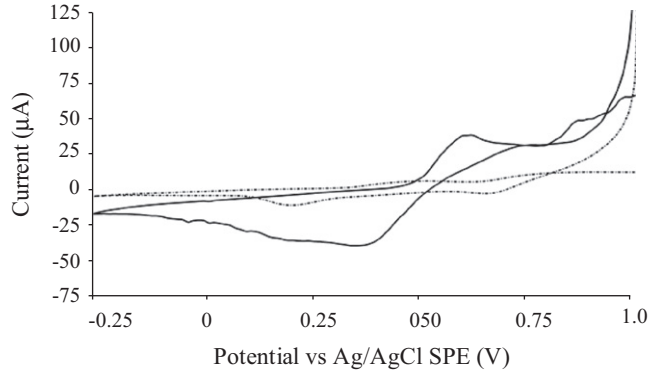

Fig. 2. Cyclic voltammograms obtained in universal buffer pH 4 solution using an AChE/SPCE: (dot line) blank; (solid line) [acetylthiocholine iodide] = 2 mM.

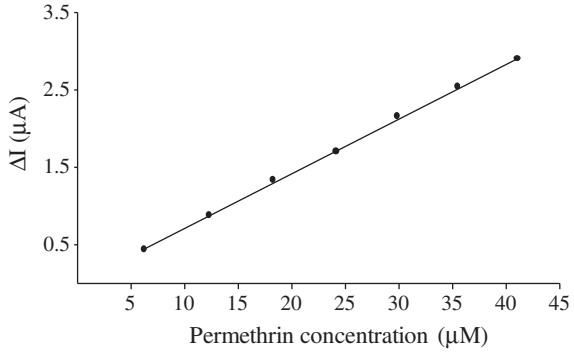

Fig. 3. Relation between ΔI vs. [permethrin]. E_{ap} = +0.6 V vs. Ag/AgCl SPE, pH = 4 and [acetylthiocholine iodide] = 2 mM.

1989). The strategy followed consisted of two steps. In the first, the LMS regression was used to detect anomalous points and, once they were eliminated, a regression based on the ordinary least squares (OLS) criterion was worked out, in order to obtain the optimal precision and accuracy of both the slope and intercept values.

The capability of detection of the developed biosensor was then calculated using the DETARCHI program (Sarabia and Ortiz, 1994). At the chosen probability level of 5% (α = β = 0.05) the capability of detection of the proposed method was (8.1 ± 0.4) μM (n = 3).

3.1. Precision

The precision of the developed AChE/SPCEs was calculated in terms of repeatability and reproducibility. The repeatability of successive amperometric measurements with the same electrode surface was tested. Sets of four successive calibrations for permethrin were carried out yielding a relative standard deviation (RSD) for their slopes of 9.6%. Likewise, the reproducibility of the amperometric signal was checked using the slopes of five regressions carried out with different electrode surfaces. The RSD values obtained were 5.4%. The parameters obtained for the different calibration sets are shown in Table 1. These results suggest that the fabrication procedure of the AChE-based biosensors is reliable, and allows reproducible electroanalytical responses to be obtained with different electrodes constructed in the same manner.

Examination of the repeatability shows that the AChE developed biosensor presents a high stability. Moreover, different studies carried out have shown that this biosensor can be used for the sensitive and quantitative determinations of permethrin during 3 weeks.

Different experiences were carried out in order to improve the selectivity of the developed biosensor. In this way, different mediators were proven with the aim of decreasing the applied potential. Tetrathiofulvalene, ferrycyanide, ferrocenemethanol and tetracyanoquinodimethane resulted unsuitably in permethrin determination, since no response was obtained at the lower potential when they were used.

3.2. Analytical application

In order to check the performance of the developed AChE/SPCEs biosensor in the quantification of permethrin, a lice gel sample containing 1.5% (w/v) of permethrin was analyzed.

The concentration of the sample was calculated by standard addition. With this aim, 100 μL of a diluted lice gel sample (0.02%, w/v) was added to the electrochemical cell. Then, successive additions of 50 μL of 0.64 mM permethrin solution were added and the calibration parameters were calculated. Finally, the permethrin concentration quantified (1.6 ± 0.3) % (w/v) (n = 3; α = 0.05) was in good agreement with the value supplied by the manufacturer from a statistical point of view at α = 0.05 level.

Table 1
Regression parameters obtained in the calibration sets realized for precision determination. Permethrin concentration ranging from 2 μM up to 41 μM.

		Intercept (μA)	Sensitivity × 10^{-3} (μA M^{-1})	S_{yx}	R^2	RSD
Repeatability	1st calibration	−0.004	7.09	0.03	0.999	9.6%
	2nd calibration	0.133	6.51	0.02	0.999	
	3rd calibration	0.038	7.93	0.02	0.999	
	4th calibration	0.127	7.97	0.08	0.994	
Reproducibility	1st calibration	−0.168	7.79	0.07	0.996	5.4%
	2nd calibration	−0.042	8.08	0.05	0.998	
	3rd calibration	0.179	7.67	0.19	0.998	
	4th calibration	−0.105	8.14	0.08	0.993	
	5th calibration	−0.004	7.09	0.03	0.999	

3.3. Recovery

Recovery studies were also carried out in spiked lice gel samples with permethrin. In this way, 0.02%, w/v lice gel solution was prepared by dilution of the commercial sample. Then, a fixed amount of permethrin was added to it giving a final concentration of permethrin of 0.04%, w/v. This last spiked solution was finally analyzed by standard addition.

The result obtained (96 ± 12) % ($n = 3$, $\alpha = 0.05$), shows that no influence of the matrix composition of the lice gel sample is observed.

4. Conclusions

The electrochemical determination of permethrin by conventional electroanalytical methods involving electrodes other than HDME has resulted unviably. However, the use of AChE based inhibitor biosensors using SPCEs enables amperometric determination of permethrin. The inhibition action of this insecticide in AChE activity produces a decrease in the oxidation current of enzymatic product. The measurement of this decrease allows the quantitative analysis of permethrin even in complex samples, such as lice gel.

Moreover, the method developed in this work presents several important advantages, including sensitivity, disposability, ease-of-use and environmentally friendly determination for the analysis of permethrin.

Acknowledgments

Financial support made by Junta de Castilla y León (GR177) and the Spanish Ministry of Science and Innovation (MICINN) (TEC2009-12029 and CENIT-E 2009-INFINITEX) is gratefully acknowledged. M.A. Alonso-Lomillo would like to acknowledge financial support from the MICINN and the European Social Found through a Ramón y Cajal Fellowship.

References

Andreescu S, Barthelmebs L, Marty JL. Immobilization of acetylcholinesterase on screen-printed electrodes: comparative study between three immobilization methods and applications to the detection of organophosphorus insecticides. Anal Chim Acta 2002a;464:171–80.
Andreescu S, Noguer T, Magearu V, Marty JL. Screen-printed electrode based on AChE for the detection of pesticides in presence of organic solvents. Talanta 2002b;57:169–76.
Butte W, Kemper K. A spectrophotometric assay for pyrethroid-cleaving enzymes in human serum. Toxicol Lett 1999;107:49–53.
Calvo MEB, Domínguez-Renedo O, Arcos-Martinez MJ. Determination of lamotrigine by adsorptive stripping voltammetry using silver nanoparticle-modified carbon screen-printed electrodes. Talanta 2007;74:59–64.
Chocholous P, Satinsky D, Sladkovsky R, Pospisilova M, Solich P. Determination of pesticides fenoxycarb and permethrin by sequential injection chromatography using miniaturized monolithic column. Talanta 2008;77:566–70.
Coomber DC, Tucker DJ, Bond AM. Electrochemical oxidation of pyrethroid insecticides at glassy carbon electrodes in acetonitrile. Electroanalysis 1998a;10:163–72.
Coomber DC, Tucker DJ, Bond AM. Electrochemical reduction of the synthetic pyrethroid insecticides tralomethrin and tralocythrin at glassy carbon and mercury electrodes. J Electroanal Chem 1998b;452:5-11.
de Souza Pinheiro A, de Andrade JB. Development, validation and application of a SDME/GC-FID methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water. Talanta 2009;79:1354–9.
Domínguez-Renedo O, Arcos-Martínez MJ. Encyclopedia of sensors. USA: American Scientific Publishers; 2006.
Domínguez-Renedo O, Arcos-Martinez MJ. A novel method for the anodic stripping voltammetry determination of Sb(III) using silver nanoparticle-modified screen-printed electrodes. Electrochem Commun 2007a;9:820–6.
Domínguez-Renedo O, Arcos-Martinez MJ. Anodic stripping voltammetry of antimony using gold nanoparticle-modified carbon screen-printed electrodes. Anal Chim Acta 2007b;589:255–60.
Domínguez-Renedo O, Alonso-Lomillo MA, Arcos-Martinez MJ. Recent developments in the field of screen-printed electrodes and their related applications. Talanta 2007;73:202–19.
Dominguez-Renedo O, Gómez-Gonzalez MJ, Arcos-Martinez MJ. Determination of antimony (III) in real samples by anodic stripping voltammetry using a mercury film screen-printed electrode. Sensors 2009;9:219–31.
Du J, Yan H, She D, Liu B, Yang G. Simultaneous determination of cypermethrin and permethrin in pear juice by ultrasound-assisted dispersive liquid–liquid microextraction combined with gas chromatography. Talanta 2010;82:698–703.
Gonzalo-Ruiz J, Alonso-Lomillo MA, Muñoz FJ. Screen-printed biosensors for glucose determination in grape juice. Biosens Bioelectron 2007;22:1517–21.
Istamboulie G, Sikora T, Jubete E, Ochoteco E, Marty JL, Noguer T. Screen-printed poly(3,4-ethylenedioxythiophene) (PEDOT): a new electrochemical mediator for acetylcholinesterase-based biosensors. Talanta 2010;82:957–61.
Kaushik A, Solanki PR, Ansari AA, Malhotra BD, Ahmad S. Iron oxide–chitosan hybrid nanobiocomposite based nucleic acid sensor for pyrethroid detection. Biochem Eng J 2009;46:132–40.
Kazemipour M, Noroozian E, Tehrani MS, Mahmoudian M. A new second-derivative spectrophotometric method for the determination of permethrin in shampoo. J Pharm Biomed Anal 2002;30:1379–84.
Kukla AL, Kanjuk NI, Starodub NF, Shirshov YM. Multienzyme electrochemical sensor array for determination of heavy metal ions. Sens Actuators B 1999;57:213–8.
Manisankar P, Viswanathan S, Pusphalatha AM, Rani C. Electrochemical studies and square wave stripping voltammetry of five common pesticides on poly 3,4-ethylenedioxythiophene modified wall-jet electrode. Anal Chim Acta 2005;528:157–63.
Manisankar P, Sundari PLA, Sasikumar R, Roy DJ. Voltammetric determination of phenoxybenzyl-type insecticides at chemically modified conducting polymer–carbon nanotubes coated electrodes. Electroanalysis 2008;20:2076–83.
Manisankar P, Sundari PA, Sasikumar R. Square-wave stripping voltammetric determination of some organic pollutants using modified electrodes. Int J Environ Anal Chem 2009;89:245–60.
Marty JL, Mionetto N, Noguer T, Ortega F, Roux C. Enzyme sensors for the detection of pesticides. Biosens Bioelectron 1993;8:273–80.
Mionetto N, Marty JL, Karube I. Acetylcholinesterase in organic-solvents for the detection of pesticides — biosensor application. Biosens Bioelectron 1994;9:463–70.
Oudou HC, Alonso RM, Jimenez RM. Voltammetric study of the synthetic pyrethroid insecticides cypermethrin and deltamethrin and their determination in environmental samples. Electroanalysis 2001;13:72–7.
Ovalle M, Stoytcheva M, Zlatev R, Valdez B. Electrochemical study of rat brain acetylcholinesterase inhibition by chlorofos: kinetic aspects and analytical applications. Electrochim Acta 2009;55:516–20.
Periasamy AP, Umasankar Y, Chen SM. Nanomaterials — acetylcholinesterase enzyme matrices for organophosphorus pesticides electrochemical sensors: a review. Sensors 2009;9:4034–55.
Rao GV, Rao KSJ. Modulation in acetylcholinesterase of rat-brain by pyrethroids in-vivo and an in-vitro kinetic-study. J Neurochem 1995;65:2259–66.
Rousseuw AMLPJ. Robust regression and outlier detection. New York: Wiley; 1989.
Sarabia L, Ortiz MC. DETARCHI — a program for detection limits with specified assurance probabilities and characteristic curves of detection. TrAC-Trends Anal Chem 1994;13:1–6.
Singh DK, Agarwal RA. Effect of the synthetic pyrethroid permethrin on the snail *Lymnaea acuminata*. Sci Total Environ 1987;67:263–7.
Starowicz M, Stypula B, Banas J. Electrochemical synthesis of silver nanoparticles. Electrochem Commun 2006;8:227–30.
Statistical Graphics Corp. Statgraphics Plus for Windows, version 4.0; 1994–1999.
Stoytcheva M, Sharkova V, Panayotova M. Electrochemical approach in studying the inhibition of acetylcholinesterase by arsenate (III): analytical characterisation and application for arsenic determination. Anal Chim Acta 1998;364:195–201.
Thriveni T, Sreedhar NY. Differential pulse adsorptive stripping voltammetric determination of permethrin using hanging mercury drop electrode. Bull Electrochem 2004;20:517–23.

Vazquez RP, Mughari AR, Galera MM. Solid-phase microextraction (SPME) for the determination of pyrethroids in cucumber and watermelon using liquid chromatography combined with post-column photochemically induced fluorimetry derivatization and fluorescence detection. Anal Chim Acta 2008;607:74–82.
Vonderheide AP, Boyd B, Ryberg A, Yilmaz E, Hieber TE, Kauffman PE, et al. Analysis of permethrin isomers in composite diet samples by molecularly imprinted solid-phase extraction and isotope dilution gas chromatography-ion trap mass spectrometry. J Chromatogr A 2009;1216:4633–40.
Wang J, Lu JM, Tian BM, Yarnitzky C. Screen-printed ultramicroelectrode arrays for on-site stripping measurements of trace-metals. J Electroanal Chem 1993;361:77–83.