

Table 1. Characteristics of flow-based biosensing systems for the determination of pesticides.

Biosensor systems based on electrochemical detection (single amperometric detection not included)												
Enzyme	Immobilisation method, support and electrode	Measurement	Pesticides	Analysis time	Working range	LOD	Inhibition time	Enzyme reactivation	RSD	Stability	Real samples	Ref.
AChE V-type from Electric Eel	Covalent binding on activated CPG beads (reactor), tubular H ⁺ -selective membrane electrode	Potentiometry	Diazinon Parathion-ethyl (previously oxidized with bromine)	----	10 ⁻⁵ - 100 μM	0.2 nM 1 nM (IC ₁₀)	30 min	20 μM 2-PAM (20 min) and working buffer (20 min)	----	----	----	36
AChE VI-S-type from Electric Eel	Incorporation in air stable lipid films supported on a methylacrylate polymer, glass electrode	Ion current transients	Carbofuran	----	1 - 100 nM	1 nM	6 min	Substrate injections	----	90% activity after 30 days	Fruits, vegetables and dairy products	58
OPH from recombinant <i>E. coli</i>	Cryoimmobilisation by PVA entrapment in a mini-reactor, glass pH micro-electrode	Potentiometry	Paraoxon	20 min	0.001 - 1 mM	----	Not needed	Not needed	3.5% (n=10, 1 mM)	90% activity after 60 days	----	45
OPH from recombinant <i>E. coli</i>	Cystamine-glutaraldehyde coupling on a thin-film gold electrode / Glutaraldehyde cross-linking on a pH-sensitive Ta ₂ O ₅ /silane-modified EIS	Amperometry (+0.75 V vs. Ag/AgCl) / Potentiometry (constant-capacitance mode, 22 nF)	Paraoxon (amp./pot.) Parathion (amp./pot.) Dichlorvos (pot.) Diazinon (pot.)	< 1 min	1 - 100 μM ---- 2 - 100 μM ----	70 nM / 2 μM ---- 6 μM ---- (s/n = 3)	Not needed	Not needed	1.6% / 3.8% (n= 15, 100 μM paraoxon) 8% (n=15, 100 μM dichlorvos)	100% activity after 30 days (1 or 2 cycles/day)	----	48 49
AChE VI-S-type from Electric Eel	Covalent binding on silica gel, conductivity or pH electrode	Conductimetry / Potentiometry	Carbofuran Carbaryl	37 and 31 min (1 st and 2 nd meas.) / 45 and 35 min (1 st and 2 nd meas.)	0.09 - 36 μM 1.5 - 50 μM	0.09 μM 1.5 μM (IC ₁₀)	5 min / 10 min	----	2.4% / 4.0%	----	Water	59

Biosensor systems based on amperometric detection											
Enzyme	Immobilisation method, support and electrode	Pesticides	Working potential	Working range (WR)	LOD	Inhibition time	Enzyme reactivation	RSD	Stability	Real samples	Ref.
AChE III-type from Electric Eel	Glutaraldehyde/BSA crosslinking onto nylon grids on a GC electrode	Paraoxon Carbaryl	+0.25 V vs. Ag/AgCl	0.5 - 10 μ M 0.5 - 50 μ M	0.1 μ M 0.1 μ M (IC ₅)	----	1.4 mM 2-PAM (4 h) and working buffer (2 h)	3.7% (n= 5, 40 μ M) 4% (n= 5, 8 μ M)	90% activity after 30 days	Lagoon water and kiwis	42
AChE III-type from Electric Eel	Coupling through a cystamine SAM onto a gold-coated nylon mesh attached to a GC electrode	Carbaryl Paraoxon	+0.25 V vs. Ag/AgCl	0.01 - 10 μ M 0.01 - 10 μ M	0.05 μ M 0.05 μ M (IC ₅)	----	1.4 mM 2-PAM (1 h) and working buffer (2 h)	<5% (10 μ M) <5% (10 μ M)	----	----	43
BChE from horse serum	Glutaraldehyde crosslinking on nylon, cellulose nitrate or white tracing paper membranes, covering epoxy carbon-paste electrodes	Diazinon	+0.61 V vs. Ag/AgCl	----	5 nM (in solution) 4 nM (nylon) 1.5 nM (cellulose)	10 min	0.1% TMB-4 (10 min)	----	100% after 10 uses and subsequent regeneration	----	38
AChE from bovine erythrocytes	Glutaraldehyde crosslinking on aminated magnetic particles (magnetic reactor), Pt thick-film electrode	Carbofuran Paraoxon-ethyl Malaoxon Paraoxon-methyl	+0.6 V vs. Ag/AgCl	4.5 - 271 nM 3.8 - 230 nM 3.2 - 191 nM 4.0 - 243 nM	14 nM 12 nM 22 nM 28 nM	10 min	Release of the magnetic particles by switching off the electromagnet	----	----	Drinking and brook water	64
AChE V-S-type from Electric Eel	Immobilisation onto activated nylon membrane covering SP electrodes	Dichlorvos	+0.3 V vs. Ag/AgCl	0.9 - 90 μ M	0.9 μ M	3 min	10 mM substrate or 0.1 mM 2-PAM (3 min)	----	----	----	40
AChE VI-S-type from Electric Eel	Carbodiimide immobilisation onto pretreated RVC or immobilisation by cyanogen bromide activation onto RVC-agarose composite	Paraoxon	+0.25 V vs. Ag/AgCl	5 - 2000 μ M	5 μ M (s/n = 3)	Competitive	----	----	60% activity after 30 days	----	39
AChE III- type from Electric Eel	Carbodiimide immobilisation, with dextran sulfate and lactitol as stabilisers, on CoPC-modified SP electrodes	Dichlorvos Paraoxon	0 V vs. Ag/AgCl	----	6 nM 0.04 nM	20 min	----	11.0% (n= 5) 6.2% (n= 5)	----	River water	65
Wt AChE / E69W <i>Dm</i> AChE mutant	PVA-SbQ entrapment on CoPC-modified SP electrodes	Omethoate	----	0.1 - 10 μ M	2 μ M / 0.1 μ M (IC ₁₀)	15 min	Disposable electrodes	8% (n= 6, 1 μ M with E69W)	----	Water	41
B4-21 / B4-27 / B3 <i>Dm</i> AChE mutants	Co-entrapment during aniline electropolymerisation on sonicated poly(<i>o</i> -PDA)-coated CoPC-modified SP carbon electrodes	Dichlorvos Parathion methyl Azinphos methyl	+0.2 V vs. Ag/AgCl	10 ⁻¹⁷ - 10 ⁻⁸ M 10 ⁻¹⁶ - 10 ⁻⁸ M 10 ⁻¹⁶ - 10 ⁻⁸ M	10 aM 100 aM 100 aM (IC ₂₀)	20 min	----	14% (n= 3, WR) 19% (n= 3, WR) 8% (n= 3, WR)	65% activity after 92 days with stabilisers	----	66
AChE VI-S-type from Electric Eel /	Glutaraldehyde/BSA crosslinking on SP Pt	Carbaryl Heptenophos	+0.35 V vs. pseudoref.	0.005 - 50 μ M 0.004 - 40 μ M	1.0 μ M / 0.48 μ M 2.5 μ M / 0.47 μ M	No pre-incubation	----	4 % 4 %	60-40% activity after	----	67

BChE from horse serum	electrodes		Ag		(IC ₁₀)				150 meas. during 5 days		
AChE VI-S-type from Electric Eel	Adsorption into a nanostructured carbon matrix	Dichlorvos	+0.1 V vs. Ag/AgCl	10 ⁻⁶ - 1 μM	1 pM (IC ₂₀)	10 min	Buffer or 10 mM choline (30 min – 3 h)	----	70% activity after 30 days	----	68
AChE	LbL immobilisation on CNT-modified GC electrodes	Paraoxon	+0.15 V vs. Ag/AgCl	0.001 - 10 nM	0.4 pM (s/n = 3)	6 min	200 μl of 0.1 mM 2-PAM and 10 mM ATCh	< 5.6% (n= 6, WR)	85% activity after 21 days	----	70
AChE VI-S-type	Al ₂ O ₃ sol-gel entrapment on SP electrodes	Dichlorvos	+0.25 V vs. Ag/AgCl	0.1 - 80 μM	10 nM (s/n = 3)	15 min	ATCh substrate	2.9% (n= 6, 1 μM)	93% activity after 25 meas., 90% activity after storage for 5 months	Seawater and river water	71
AChE V-S-type from Electric Eel	PVA-SbQ entrapment on a Pt electrode	Paraoxon	+0.41 V vs. SCE	----	1 nM (IC ₁₀)	----	1 mM 2-PAM (7 min)	----	70% activity after 21 days	----	44
AChE	PVA-SbQ entrapment on a Pt electrode	Paraoxon Carbaryl	+0.41 V vs. Ag/AgCl	10 ⁻¹⁰ - 10 ⁻⁵ M 10 ⁻¹⁰ - 10 ⁻⁵ M	nM (IC ₁₀)	----	0.5 mM 2-PAM (15 min)	----	----	Water	72
AChE V-S-type from Electric Eel	PVA-SbQ entrapment on a Pt wire electrode	Chlorpyrifos Chlorpyrifos-oxon Methyl-chlorpyrifos-oxon	+0.41 V vs. Ag/AgCl	0.1 - 10 μM 0.1 - 10 μM 0.1 - 10 μM	3.14 nM 73 nM 0.88 μM (IC ₁₀)	---- 16 min 8 min	0.4 mM 2-PAM (3 min), partial with buffer when inhibited with MeCPO	---- 6%(n= 3, 1 μM) 40-50% (n= 3, 1μM)	----	----	73
OPH from recombinant <i>E. coli</i>	Covalent immobilisation on activated aminopropyl CPG beads (reactor), carbon paste electrode	Paraoxon Methyl parathion	+0.9 V vs. Ag/AgCl	----	20 nM 20 nM (s/n = 3)	Not needed	Not needed	2% (n= 35, 1 μM) ----	----	Spiked water and simulated well water	46
OPH from recombinant <i>E. coli</i>	Cystamine-glutaraldehyde coupling on a thin-film gold electrode	Paraoxon Methyl parathion	+0.75 V vs. Ag/AgCl	1 - 10 μM 1 - 10 μM	0.1 μM (s/n = 3)	Not needed	Not needed	3.6% (n= 20, 1 μM) ----	100% activity after 4 weeks	----	47
PH from <i>Pseudomonas</i> sp.	Polyethyleneimine-glutaraldehyde coupling on a SP carbon electrode	Parathion	+0.7 (2 s) and +0.85 (1 s) V vs. Ag/AgCl	0.03 - 0.3 μM	0.5 nM	Not needed	Not needed	----	----	Tap water and spiked river water	50