Electrochemical Methods in Pesticides Control

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ABSTRACT

The state of the art of voltammetric and amperometric methods used in the study and determination of pesticides in crops, food, phytopharmaceutical products, and environmental samples is reviewed. The main structural groups of pesticides, i.e., triazines, organophosphates, organochlorides, nitrocompounds, carbamates, thiocarbamates, sulfonylureas, and bipyridinium compounds are considered with some degradation products. The advantages, drawbacks, and trends in the development of voltammetric and amperometric methods for study and determination of pesticides in these samples are discussed.

Key Words: Electrochemical method; Pesticides; Structural groups; Voltammetric and amperometric methods.

1. INTRODUCTION

Agricultural production currently, and increasingly, depends on the use of pesticides. Pesticide is a term used in a broad sense for chemicals, synthetic, or natural, that are used for the control of insects, fungi, bacteria, weeds, nematodes, rodents, and other pests.[1]

These compounds and the products derived from them by degradation or metabolism give rise to residues that may spread through the environment and are particularly frequent contaminants in superficial and groundwaters, in soil and in agricultural and food products.

As many organic compounds used as pesticides contain electroactive groups, voltammetry can be used for their mechanistic and analytical studies.

Electrochemical techniques have been very helpful in the elucidation of processes and mechanisms of oxidation and reduction of pesticides. Moreover, the use of electrochemical data combined with spectroscopic studies could provide important information useful to the understanding of the degradation pathways of pesticides in aqueous solutions and in this way to mimicking the environmental processes.

There is a wide range of studies concerned with analytical methods for monitoring the pesticides in environmental samples. Most applications of chemical analysis to pesticide control involve methods with high sensitivity accompanied by sufficient selectivity, precision, and accuracy. Easy sample pre-treatment and rapid analytical procedures are also desirable. When selecting the method, the cost of the instrumentation and the possibility of performing measurements in the field are also important factors to be considered. Since electrochemical methods satisfy all the above criteria, they were a good choose for the analysis and control of environmental pesticides.

Unfortunately, the determination of pesticides in most samples requires their extraction into organic solvents. The well-known practical difficulties of using organic solvents in electroanalysis to determine scarcely water-soluble compounds can be overcome by working in oil– water emulsions as these are predominantly aqueous.

The principal electrochemical methods are voltammetry, amperometry, potentiometry, and conductimetry. Since electrochemical biosensors for pesticides analysis have been recently reviewed,[2,3] special emphasis will be

given to focus on the developments concerning the voltammetric and amperometric analyses of pesticides.

Classification of pesticides according to structure is given in Table 1. The pesticides considered in this paper are listed in Tables 2 and 3, where the applications are present.

2. ELECTROANALYTICAL METHODS FOR DETERMINATION OF PESTICIDES

In the development of electroanalytical methods for the determination of pesticides, the electrochemical detection performance is strongly influenced by the material of the working electrode. The working electrode is where the reaction of interest occurs. The selection of the working electrode depends primarily on the redox behavior of the target analytes and the background current over the applied potential range.

2.1. Mercury Electrodes

For a long time mercury drop electrodes were the most popular, first in the form of the dropping mercury electrode (DME) and after in the form of static mercury drop electrode (SMDE), and the hanging mercury drop electrode (HMDE).

In the literature, there are several examples (Table 2) of the use of mercury electrodes in the study of the electrochemical behavior of pesticides and in their determination in various matrixes, for example in soil, water, and agricultural products.

Table 1. Structural groups pesticide compounds.

Class	Structural group
I	Organochloride
II	Triazines
III	Nitropesticides
IV	Carbamates and thiocarbamates
V	Organophosphate
VI	Sulphonylureas
VII	Bipyridinium pesticides
VIII	Others

Table 2. Alphabetic list of pesticide compounds reviewed, electrode, technique, electrolyte used in determination and respective potential, detection limit, application, and references relating to their analysis in mercury electrode.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Alachlor	I	SMDE	DPV	Phosphate buffer (pH 7)	21.0	27.0 mg/L	Model samples	[21]
Aldrin	I	DME	DPV	0.1 N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide, and 40% deionized water	21.84[b]	Not reported	Spiked water	[28]
Ametryne	II	DME	DPV	Phosphoric acid 0.1 M (pH 3)	21.0[d]		Industrial waste[c]	[4]
		HMDE	AdSV	Not reported	21.0[b]	0.2 mg/L[d]	River water[d]	[65]
		DME	AdSV	Britton-Robinson buffer (pH 3.5)	21.02[a]	0.179 mg/L	Spiked river water	[71]
Atrazine	II	DME	DPV	Phosphoric acid 0.1 M (pH 3)	20.99[d]		Industrial waste[c]	[4]
		DME	DPV	KCl/HCl buffer (pH 2)	20.93[a]	15 mg/l	Model samples	[67]
		SMDE	AdSV	BR buffer (pH 2.5)	20.83; 20.94[a]	0.96 mg/l	Water samples[d]	[68]
Benfluralin	III	HMDE	AdSV	Britton-Robinson buffer (pH 10.46) with 49% (V/V) methanol	20.58[a]	0.05 mg/mL	Model samples and soil	[69]
Bromofenoxim	III	HMDE	AdSV	Britton-Robinson buffer (pH 7.6)	20.33[a]	0.98 ng/L	Model samples and soil	[69]

Carbaryl	IV	HMDE	AdSV	Determination after	20.65[b]	5 mg/Kg[f]	Soil[d]	[65]
		HMDE[f]	DPV	nitrosation[e] in 0.10 mol/L		0.41 mg/L	Natural water	[36]
		HMDE[f]	DPV	sodium hydroxide product	20.68	0.47 mg/Kg	Soil	[36]
		HMDE[f]	AdSV	1,4-naphthoquinone		0.005 mg/L	Natural water	[36]
		HMDE[f]	AdSV			0.007 mg/Kg	Soil	[36]
CDT	III	DME	DPV	0.05 M Sulfuric acid	0.00[a]	2.6 mg/L	Environmental water	[11]
Chlorothion	III	DME	DPV	Acetate buffer (pH 4)	20.31[b]	1.50 mg/L	Model samples	[70]
Chlorfenvinfos	V	DME	DPV	Universal buffer (pH 4)	20.95[b]	0.36 mg/L	Grains and soil	[17]
Crotoxyphos	V	DME	DPV	Universal buffer (pH 4)	21.12[b]	0.34 mg/L	Grains and soil	[17]
p,p^0-DDT	I	DME	DPV	0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide, and 40% deionized water	20.63[b]	Not reported	Spiked water	[28]
o,p^0-DDT	I	DME	DPV	0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide and 40% deionized water	20.83[b]	Not reported	Spiked water	[28]
Desmetryne	II	SMDE	AdSV	Britton-Robinson buffer (pH 4)	21.08[a]	0.15 mg/L	Water samples[d]	[73]
Dichlorvos	V	DME	DPV	20% Ethanol in a solution of pH 8	21.05[b]	2.6 mg/L	Commercial samples	[16]

(*continued*)

Table 2. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Dicrotophos	V	DME	DPV	Universal buffer (pH 4)	21.05[b]	0.30 mg/L	Commercial samples, grains, and soil	[17]
Dieldrin	I	MME	DPV	0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M BR buffer (pH 6)	20.91[b]	0.11 mg/L	Model samples	[22]
		MME	DPV	Emulsions obtained from 6.0 mL *n*-hexane–ethyl acetate (20 þ 1) effluent fraction. 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 6)	20.98[b]	Not reported	Spiked apples	[24]
		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 6)	20.98[b]	0.14 mg/L	Model samples	[25]
Dieldrin	I	MME	DPV	0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide, and 40% deionized water	21.77[b]	Not reported	Spiked water	[28]

Mixture diedrin-endosulfon (after hydrolysis of endosulfan)		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M BR buffer (pH 12.0)	−0.98; −1.18[b] (respectively)	Not reported	Model samples	[23]
Mixture diedrin-endosulfon-suphate (after hydrolysis of endosulfan-sulfate)		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M BR buffer (pH 13.0)	−0.98[b]	Not reported	Model samples	[23]
Mixture diedrin-*a*-endosulfon (after hydrolysis of endosulfan)		MME	DPV	pH 12 in a HPO_4^{2-}/NaOH buffer	−0.98, −1.18[b] (respectively)	Not reported	Spiked apples	[24]
Dinobutone	III	HMDE	AdSV	Not reported	−0.46[b]	0.6 mg/L[f]	River water[d]	[65]
		DME	DPV	Britton-Robinson buffer (pH 6.1)	−0.24; −0.46[a]	16.5; 20.5 mg/L	Environmental water	[11]
		SMDE	AdSV	Britton-Robinson buffer (pH 6.1)	−0.46[a]	0.614 mg/L	Spiked river water	[71]
Dinoseb	III	HMDE	AdSV	BR (pH 5)	−0.21; −0.36[b]	0.36; 0.11 mg/L	Model samples	[72]
Diquat	VII	SMDE	SWV	Extracted solution neutralized with NaOH (to pH5.6) and 0.003% gelatin	0.56[b]	1 mg/g	Spiked potatoes[d]	[33]
DNOK	III	HMDE	AdSV	Not reported	−0.44[b]	0.1 mg/L[f]	River water[d]	[65]
		DME	DPV	Britton-Robinson buffer (pH 6.1)	−0.3; −0.5V[a]	2.1; 1.5 mg/L	Environmental waste	[11]
		SMDE	AdSV	Britton-Robinson buffer (pH 6.1)	−0.44[a]	0.096 mg/L	Spiked river water	[71]

(*continued*)

Table 2. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Endosulfan-sulfate	I	MME	DPV	0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 6.0)	20.83[b]	0.11 mg/L	Model samples	[22]
Endosulfan-sulfate		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (6.0)	20.90	0.084 mg/L	Model samples	[25]
Endosulfan-sulfate		MME	DPV	Emulsions obtained from 8–18 mL *n*-hexaneacetate (20 þ 1) effluent fraction. 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (6.0)	20.92[b]	Not reported	Spiked apples	[24]
Mixture endosulfon-endosulfon-sulfate (after hydrolysis of endosulfan)		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405 þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (11.0)	21.15; 20.86[b] (respectively)	Not reported	Model samples	[22]

Endrin	I	DME	DPV	0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide and 40% deionized water	21.73[b]	Not reported	Spiked water and commercial samples	[28]
Fluoroglycophen-etyl	III	HMDE	AdSV	Britton-Robinson buffer (pH 11.6) with 20% (V/V) DMF	Not reported	0.55 ng/mL	Model samples and soil	[69]
Glifosate (after nitrosation)	V	DME	DPV	40 mL Eluate solution add 2 mL of sulfuric acid (1 : 1)	20.78[a]	35 mg/L	Natural waters	[20]
Guthion	II	DME	DPV	Britton-Robinson buffer (pH 4.3), in 20% (v/v) MeOH/H_2O medium	20.75[a]	19 mg/L	Model samples	[7]
		SMDE	DPV	Britton-Robinson buffer (pH 5.0–5.5)	Not reported	31 mg/L	Spiked river water; spiked residential well water	[74]
		SMDE	AdSV	Britton-Robinson buffer (pH 5.0–5.5)	Not reported	0.63 mg/L	Spiked river water; spiked residential well water	[74]
		DME	AdSV	Not reported	20.64[f]	0.5 (mg/L)[b]	River water[d]	[65]
		HMDE	AdSV	Not reported	20.71[f]	1.5 (mg/L)[b]	River water[d]	[65]

(*continued*)

Table 2. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
a-	HCH	I	DME	DPV 0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide and 40% deionized water	21.83[b]	Not reported	Spiked water	[28]
b-	HCH	I	DME	DPV 0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide and 40% deionized water	21.90[b]	Not reported	Spiked water	[28]
g-HCH	I	DME	DPV	0.1N Tetrabutylammonium bromide dissolved in a solution which was 40% ethanol, 20% dimethyl formamide and 40% deionized water	21.23[b]	Not reported	Spiked water	[28]

Heptachlor	I	MME	DPV	Emulsions obtained from 20 mL *n*-hexane effluent fraction. 0.2% Triton X-405þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 8)	20.92[b]	Not reported	Spiked apples	[24]
Mixture Heptachlor – endosulfon-sulfate		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 8)	Not reported	Not reported	Model samples	[25]
Mixture Heptachlor – endosulfon-sulfate and dieldrin		MME	DPV	Emulsions obtained from ethyl acetate, 0.2% Triton X-405þ 0.2% hyamine 2389, 0.1M Britton-Robinson buffer (pH 8)	Not reported	Not reported	Spiked apples	[24]
Isomethiozin	II	DME	DPV	Britton-Robinson buffer in 0.1 M $NaClO_4$ at pH 1.9	20.52[b]	0.04 mg/g	Soil	[66]
		HMDE	AdsV	Not reported	20.56[b]	0.9 mg/L[f]	Soil[d]	[65]
Menazon	V	DME	DPV	0.06 M Acetic acid/0.04M sodium acetate	20.84; 21.30[b]	0.15; 0.18 mg/L (respectively)	Model samples	[18]
Hydrolysis products		DME	DPV	Britton-Robinson buffer (pH4.3)	20.44[b]		Model samples	[18]
Metamitron	II	DME	DPV	Britton-Robinson buffer (pH 2)	20.49[b]	0.02 mg/g	Soil	[75]
		HMDE	DPV	AcH/AcNa (pH4.6)	20.70[a]	50 mg/L	Commercial samples	[8]

(*continued*)

Table 2. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
		HMDE	AdSV	AcH/AcNa (pH 4.6)	−0.70[a]	0.5 mg/L	Model samples	[8]
		HMDE	AdSV	Not reported	−0.45[b]	0.4 mg/Kg[f]	Soil	[65]
Methoprotryne	II	HMDE	AdSV	0.1 mol L^{-1} Perchloric acid	−0.87[b]	0.65 mg/L	Spiked irrigation and tap waters	[5]
		HMDE	AdSV	Britton-Robinson (pH 4)	−1.07 [a]	0.07 mg/L	Water samples	[68]
Monocrotophos	V	DME	DPV	20% Ethanol in a solution of pH 2	−1.00[b]	2.2 mg/L	Commercial samples	[16]
Paraquat	VII	SMDE	SWV	Extracted solution neutralized with NaOH (to pH 5.6) and 0.003% gelatin	−0.59[b]	1 mg/g	Spiked potatoes	[33]
		HMDE	AdSV	Not reported	−0.70[b]	1.5 mg/L[f]	Water samples	[65]
Mixture of parathion with PCNB	III	DME	DPV	Britton-Robinson buffer (alkaline solution)	−0.65, −0.52[a] respectively	Not reported	Model samples	[13]
Mixture of parathion with a metabolite (*p*-nitrophenol		DME	DPV	Britton-Robinson buffer (pH 3)	−0.15, −0.24[a] respectively	Not reported	Model samples	[13]

Mixture of parathion with paraoxon (after hydrolyze of paraoxon)		DME	DPV	0.5 M Sodium hydroxide	Not reported	Not reported	Model samples	[13]
Mixture of parathion(I) with paraoxon(II) (after hydrolyze of parathion)		DME	DPV	HAc/Ac with 50% (V/V) of MeOH(pH 8)	−0.74, −0.48[a] respectively	48 mg/L (II) and 23 mg/L (*p*-nitrophenol-hydrolyze product)	Model samples	[14]
Pendimethalin	III	HMDE	AdSV	Britton-Robinson buffer buffer (pH 7.42) with 49% (V/V) methanol	Not reported	0.94 mg/mL	Model samples and soil	[69]
Phenitrothione	III	DME	AdSV	Not reported	−0.32[b]	3 mg/L[f]	River water[d]	[65]
		DME	DPV	0.05 M Sulfuric acid	−0.085; −1.00[a]	5.4 mg/L	Environmental water	[11]
Phosphamidon	V	DME	DPV	20% Ethanol in a solution of pH 4	−1.00[b]	3.8 mg/L	Commercial samples	[16]
Prometryne	II	DME	DPV	KCl/HCl (pH 2)	−0.98[a]	15 mg/L	Model samples	[67]
		HMDE	AdSV	0.1 M $HClO_4$	−0.88[b]	2.17 mg/L	Spiked tap water, well water and soil	[76]
		SMDE	AdSV	Britton-Robinson buffer (pH 4)	−1.02 [a]	0.35 mg/L	Water samples	[68]
		DME	AdSV	Britton-Robinson buffer (pH 3.5)	−1.05[a]	0.951 mg/L	Spiked river water	[71]

(*continued*)

Table 2. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep(V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Simazine	II	DME	DPV	Phosphoric acid 0.1 M (pH 3)	−0.99[a]	Not reported	Industrial waste[c]	[4]
		DME	DPV	2.0 mL Ethyl acetate, 0.1% sodium pentanesulfonate and 0.1 M Britton-Robinson buffer (pH 2.0)	−0.95[a]	44 mg/L	Spiked irrigation	[9]
		DME	DPV	KCl/HCl (PH 2.2)	−0.95[a]	15 mg/L	Model samples	[67]
		HMDE	AdSV	Not reported	−0.75[b]	0.2 mg/L[f]	River water[d]	[65]
Simetryn	II	DME	AdSV	Not reported	−1.0[b]	0.4 mg/L[f]	River water[e]	[65]
		SMDE	DPV	Britton-Robinson buffer (pH 5.0–5.5)	Not reported	21.3 mg/L	Spiked river water; spiked residential well water	[74]

		SMDE	AdSV	Britton-Robinson buffer (pH 5.0–5.5)	Not reported	0.4 mg/L	Spiked river water; spiked residential well water	[74]
Terbutryne	II	HMDE	AdSV	0.1 M Perchloric acid	−0.92[b]	0.58 mg/L	Spiked	[5]
		SMDE	AdSV	Britton-Robinson buffer (pH 4)	−1.06[a]	0.36 mg/L	Water samples	[68]
Terbutylazine	II	SMDE	AdSV	Britton-Robinson buffer (pH 2.5)	−0.87; −0.96[a]	0.12 mg/L	Water samples	[68]
Triflurolin	III	HMDE	AdSV	Britton-Robinson buffer (pH 6.10) 47% (V/V) ethanol	−0.57[a]	0.03 mg/mL	Model samples and soil	[69]

[a]The value of Ep vs. SCE.
[b]The value of Ep vs. Ag/AgCl.
[c]Determination of total *s*-triazines (atrazine, simazine, and ametrine).
[d]The analyte is evaluated after solid phase extraction.
[e]With derivatization.
[f]Only limit of determination is reported.

Table 3. Alphabetic list of pesticide compounds reviewed, electrode, technique, electrolyte used in determination and respective potential, detection limit, application, and references relating to their analysis in solid electrodes.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep (V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Aminocarb	IV	Glassy carbon electrode	DPV	Acetate buffer (pH 6.6)	þ0.74[a]	30 mg/L	Model sample	[38]
Assulam	IV	Glassy carbon electrode	SWV	Britton-Robinson buffer (pH 1.9)	þ0.89[b]	1.63 mg/L	Spiked environmental samples	[77]
		Glassy carbon electrode	Amperometry	Britton-Robinson buffer (pH 1.9)	þ1.2[b]	2.8 mg/L	Spiked environmental samples	[77]
Bendiocarb	IV	Modified carbon paste electrode covered with a enzymatic membrane	Amperometric	Phosphate buffer (pH 7.3)	þ0.4[b]	80 mg/L	Model samples	[56]
Bentazon	VIII	Glassy carbon electrode	SWV	AcH/AcNa (pH 3.4)	þ0.85[b]	2.4 mg/L	Commercial samples	[44]
		Glassy carbon electrode	Amperometry	Acetate bufer (pH 4.5)/NaOH	þ1.10[b]	0.24 mg/L	Estuarine waters	[81]
Bensulfuron-methyl	VI	Glassy carbon electrode	SWV	Britton-Robinson buffer (pH 12.1)	þ1.0[b]	HPLC determination	Commercial samples	[44]
Carbaryl (after hydrolyse)	IV	Glassy carbon electrode	DPV	Solution NaOH/AcH (pH 3.5)	þ0.56[b]	40 mg/L	Commercial samples	[40]
Carbaryl (after hydrolyse)		Glassy carbon electrode	Amperometry	[d]	þ0.75[b]	0.1mg/mL	Vegetables	[42]
Carbaryl		Graphite–CoPC–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.3)	þ0.25[b]	2.2 mg/L	Model samples	[57]

Carbaryl	IV	Glassy carbon electrode covered with a enzymatic grift	Amperometry	(pH 8)	þ0.25[b]	0.20 mg/L	Lagoon water and Kiwi fruits	[78]
		Graphite–epoxy–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.0)	þ0.70[b]	20 mg/L	Model samples	[58]
		Platinum electrode with immobilized cholinesterase	Amperometry	Phosphate buffer (pH 8)	þ0.41[b]	[d]	Freeze-dried water	[79]
Carbaryl (after hydrolyse)		Glassy carbon electrode	Amperometry	Acetate buffer (pH 5)/NaOH	þ0.81[b]	2.0 mg/L	Natural waters	[82]
Carbofuran (after hydrolysis)	IV	Glassy carbon electrode	DPV	Solution NaOH/ AcOH (pH 3.5)	þ0.65[b]	27 mg/L	Commercial samples	[40]
Carbofuran (after hydrolysis)		Glassy carbon electrode	Amperometry	Data not reported	þ1.0[b]	0.1mg/mL	Vegetables	[42]
Carbofuran		Graphite–epoxy–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.0)	þ0.70[b]	2.2 mg/L	Model samples	[58]
Chlorbromuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.29 mg/L	Model samples	[41]
Chlorpropham	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.21 mg/L	Model samples	[41]
Chlortoluron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V/V)	þ1.4[b]	0.21 mg/L	Model samples	[41]
Chloroxuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.29 mg/L	Model samples	[41]
2,4-D	VIII	Monoclonal anti 2,4-D antibody immobilized on the gold electrode	Amperometry	Phosphate buffer (pH 7.3)	20.3[b]	0.1 mg/L	Model samples	[80]

(*continued*)

Table 3. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep (V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
Dichlorvos	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.40[b]	HPLC determination	Model samples	[56]
		Graphite–CoPC–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.3)	þ0.25[b]	0.26 mg/L	Model samples	[57]
Dichlorvos	V	Graphite– epoxy– AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.0)	þ0.70[b]	22 mg/L	Model samples	[58]
Dinoseb	III	Mercury film on a glassy carbon electrode	AdSV	AcOH/AcONa (pH 5.0)	20.22[b]	0.026 mg/L	Spiked apple juice	[53]
Disulfiram	IV	Graphite–poly(tetrafluoroethylene) electrode	LSV	Phosphate buffer (pH 7.4)	þ0.70[a]	5.9 mg/L	Model samples	[50]
		Graphite–poly(tetrafluoroethylene) electrode	Amperometry	Phosphate buffer (pH 7.4)	þ1.0[b]	5.9 mg/L	Spiked tap waters and well waters	[51]
Diuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.23 mg/L	Model samples	[41]
Fenamiphos	V	Platinum electrode with immobilized cholinesterase	Amperometry	Phosphate buffer (pH 8)	þ0.41[b]	HPLC determination	Freeze-dried waters	[79]
Fenitrothion	V	Platinum electrode with immobilized cholinesterase	Amperometry	Phosphate buffer (pH 8)	þ0.41[b]	HPLC determination	Freeze-dried waters	[79]
Fenuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.16 mg/L	Model samples	[41]

Fluormeturon	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.23 mg/L	Model samples	[41]
Heptenophos	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	0.3 mg/L	Model samples	[56]
Linuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.24 mg/L	Model samples	[41]
Metabromuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.27 mg/L	Model samples	[41]
Methidation	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Methiocarb	IV	Glassy carbon electrode	Amperometry	Data not reported	þ1.0[b]	0.1 mg/mL	Vegetables	[42]
Methyl-Parathion	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Molinuron	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.22 mg/L	Model samples	[41]
Molinate	IV	Glassy carbon electrode	SWV	BR (pH 1.9)	þ1.5[b]		Commercial samples	[44]
Oxadiazon (after hydrolyse)	VIII	Glassy carbon electrode	SWV	30% ethanol in KCl//NaOH solution (pH 12.8)	20.1 [b]		34.5 mg/L Commercial samples	[45]
Paraoxon	III	Graphite–CoPC–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.3)	þ0.25	0.82 ng/L	Model samples	[57]
		Glassy carbon electrode covered with a enzymatic grift	Amperometry	Phosphate buffer (pH 8)	þ0.25	0.28 mg/L	Lagoon water and kiwi fruits	[78]

(*continued*)

Table 3. Continued.

Pesticide	Class	Electrode	Technique	Electrolyte	Ep (V) vs. SCE[a] or Ag/AgCl[b]	Detection limit	Application	References
		Graphite–epoxy–AchE biocomposite electrode	Amperometry	Phosphate buffer (pH 7.0)	þ0.70	27 mg/L	Model samples	[58]
Paraquat	VII	Carbon paste electrode chemically modified with Amberlite XAD-2	CSV (cathodic stripping voltammetry)	Ammonium acetate buffer (pH 6)	20.70[b]	0.10 mg/L	River water	[52]
Parathion-ethyl	V	Platinum electrode with immobilized cholinesterase	Amperometry	Phosphate buffer (pH 8)	þ0.41[b]	HPLC determination	Freeze-dried waters	[79]
Phosphamidon	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Phosalone	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Phosmet	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Pirimiphos-methyl	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Promecarb	IV	Glassy carbon electrode	Amperometry	Data not reported	þ1.0[b]	0.1 mg/mL	Vegetables	[42]
Propham	IV	Glassy carbon electrode	Amperometry	Acetate buffer with 50% ethanol (V/V)	þ1.4[b]	0.18 mg/L	Model samples	[41]
Propoxur	IV	Glassy carbon electrode	Amperometry	Data not reported	þ1.0[b]	0.1 mg/mL	Vegetables	[42]

Quinalphos	V	Modified carbon paste electrode covered with a enzymatic membrane	Amperometry	Phosphate buffer (pH 7.3)	þ0.4[b]	HPLC determination	Model samples	[56]
Sulfometuron-methyl (via its N-chloroderivative)	VIII	Platinum electrode	DPV	Eluant acidified to (pH 1.3)	þ0.44[b]	HPLC determination	Model samples	[37]
Thiram	IV	Graphite poly(tetrafluoroethylene) electrode	LSV	Phosphate buffer (7.4) (pH 7.4)	þ0.7[a]	12.9 mg/L	Spiked strawberries	[50]
		Graphite poly(tetrafluoroethylene) electrode	Amperometry	Phosphate buffer (7.4) (pH 7.4)	þ1.0[b]	10.3 mg/L	Spiked tap waters and well waters	[51]
Zectram	IV	Glassy carbon electrode	DPV	Acetate buffer (pH 6.6)	þ0.65	30 mg/L	Model samples	[38]
Sodium diethyldithio-carbamate	IV	Tyrosinase-based thick-film electrodes	Amperometry	No supporting electrolyte	20.2	[b] Untreated river water	10^{-6} M	[59]
Chlorpyrifos-oxon (metabolite of chlorpyrifos)	V	Platinum wire coated with a mixture of cholinesterase enzyme and photocrosslinkable PVA- SbQ	Amperometry	Phosphate buffer (pH 8.0)	þ0.41[b]	10^{-6} M	Model samples	[60]
Chlorpyrifos-oxon (metabolite of chlorpyrifos)	V	Disposable cholinestrase biosensor based on screen-printed electrodes	Amperometry	Phosphate buffer (pH 7) with 5 –10% organic solvent	þ0.10[b]	1 ppb	Model samples	[61]
Maneb	IV	Aldehyde dehydrogenase entrapped in PVA-SBQ	Amperometry	Phosphate buffer (pH 7.5)	þ0.25[b]	1.5 ppb	Model samples	[62]

[a]The value of EP vs. SCE.

[b]The value of EP vs. Ag/AgCl.

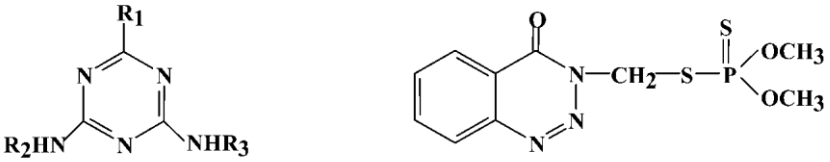
2.1.1. Triazine Pesticides

Triazines and their derivatives have been used as herbicides in agriculture. Basically two groups are distinguished, *s*-triazine and asymmetrical triazine (Fig. 1).

s-Triazines are aromatic heterocyclic compounds whose generic structural formula is shown in Fig. 1(a). Their properties are defined, basically, by the chemical group represented as R_1.[4,5] Results obtained by polarography demonstrated that *s*-triazine reduction occurs in the – C55N– bond of the heterocyclic ring.[4,6] For atrazine, simazine, and ametryne, the mechanism of electrochemical reduction begins with *s*-triazine molecule protonation, most probably on nitrogen in the ortho position with respect to carbon, binding a chloro, or methylthio group. Protonation enables reduction of one double bond in the ring, including participation of one additional proton.[4]

The mechanism of reduction of asymmetrical triazines depends on the structure of the molecule. Thus guthion has been shown by several methods to be reduced at the – N55N – bond of the heterocyclic ring[7] although, the reduction of the metamitron involve the functions –C55N– and $N-NH_2$ that are present in the molecule.[8]

Estimation of triazines or other pesticides usually requires pre-treatment of the sample involving extraction with organic solvents. The well-known difficulties associated with organic solvents in electroanalysis and the low solubility of pesticides in water led to the search for alternative conditions. One of these was the polarographic study of simazine in water– oil solutions and in micellar solutions.[9]



a) b)

R_1 = Cl; OCH_3; SCH_3

R_2 e **R_3** = Alkyl Groups (1 to 4 carbon atoms)

Figure 1. Structure of triazine: (a) *s*-triazine; and (b) example of asymmetrical triazine (guthion).

It should be noted that in the quantitative determination of this group of pesticides the techniques of differential impulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) are the most used (Table 2).

2.1.2. Nitropesticides

Pesticides with nitro-containing structural groups are most efficient, but have very toxic properties and it is, therefore, extremely important to have accurate and reliable methods for determination of these products in environmental samples.

The reduction mechanism of aromatic compounds containing the nitro group with consequent formation of hydroxylamines or the corresponding amines is currently a well-defined process.[10,11] Within this group of pesticides, there are essentially four groups nitrorganophosphates, nitrophenol derivatives, dinitroaniline derivatives, and nitrorgano-chlorides.

Parathion, a pesticide belonging to the nitrorganophosphate group, was determinate in the presence of two of its metabolites, paraoxon and *p*-nitrophenol.[12] Parathion and *p*-nitrophenol show different reduction potentials, respectively 20.39 and 20.68 V relative to SCE, and therefore do not interfere. With respect to parathion and paraoxon, the simultaneous determination is possible due the process of adsorption of the parathion.

In another work, a similar simultaneous determination of parathion and its main metabolites[13] showed that parathion and *p*-nitrophenol do not interfere with each other. The determination together of parathion and paraoxon was made possible due to the selectivity of the alkaline hydrolysis of the two compounds in the experimental conditions that were used.

In a later study, the estimation of parathion and paraoxon mixtures was based on the fact that palladium(II) only catalyses the hydrolysis of parathion.[14]

As with the triazines, some of these pesticides contain nitro groups that can be adsorbed onto the surface of mercury electrodes, and therefore a large number of studies report the use of AdSV for the quantification of this group of pesticides in samples containing very small amounts of these contaminants.

2.1.3. Organophosphate Pesticides

The pesticides belonging to this family maybe divided into six groups schematically represented in Fig. 2.

It is known that the electrochemical activity of a compound is intimately related to its chemical structure. The oscillopolarographic behavior of a group of organophosphoric esters reinforces this fact.[15] Thus the compounds

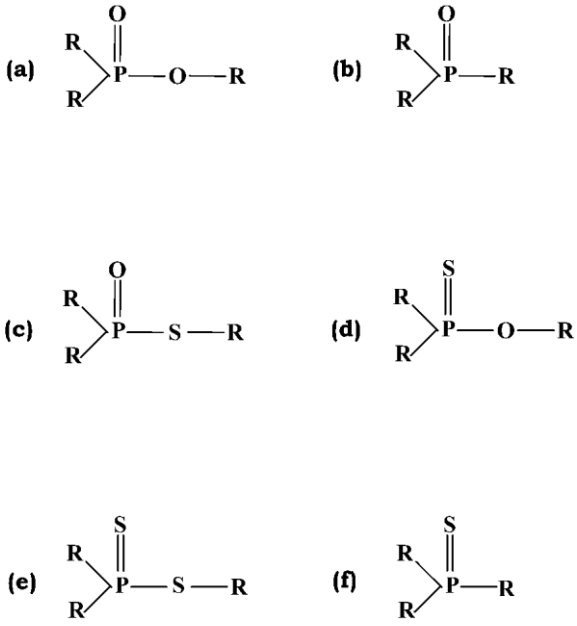


Figure 2. Structures of the six organophosphate pesticide groups.

belonging to this group and which possess bonds of the type –P55S– and –S–P55 [groups (c), (d), (e), and (f)], show intense adsorption peaks, which allow the estimation of concentrations lower than 1 mM.

Another work confirmed that pesticides belonging to group (a) with C55C bonds in the chemical group represented as R, Fig. 3, of which some examples are dichlorvos, dicrotophos, chlorfenvinphos, crotoxyphos, are electroactive at mercury electrodes.[16,17] The electrochemical behavior of these compounds was examined over the pH range 2.0 – 12.0 and for each of them was found a single well-defined wavepeak. This peak was attributed to reduction of the carbon– carbon double bound in a two-electron process.[16]

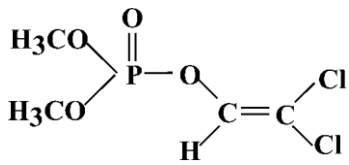


Figure 3. Structure of a group (a) pesticide (dichlorvos) containing a C55C bond.

Methods for the determination of pesticides and/or their degradation products are of considerable interest. In the case of menazon an electronalytical study of the pesticide and its hydrolysis products,[18] showed that at high pH the compound is rapidly hydrolyzed, producing 4,6-diamino-1,3,5-triazin-2-methyl-mercaptan and the corresponding thiosphosphate. The responses of different species are studied for analytical utility and reaction mechanisms are proposed.

Studies of malathion and glyphosate are two examples of indirect determination, applicable when the pesticide is unstable or the compound is inactive at a mercury electrode.[19,20] For malathion, the polarographic method developed is based upon the determination of the stable breakdown product of hydrolyze, i.e., fumaric acid. For glyphosate, the polarographically active derivative of glyphosate is obtained by nitrosation.

2.1.4. Organochlorides pesticides

Pesticide members of this group are notorious for their toxicity due to the capacity for bioaccumulation.

Several electrochemical studies were consistent in their conclusion of a reaction mechanism involving the removal of one atom of chlorine.[21,22]

The electrochemical behavior of some of the cycloalkene-containing compounds of this group (dieldrin, heptachlor, endosulfan, and endosulfan-sulfate), whose structure is shown schematically in Fig. 4, has been widely reported.[22 – 26] For reasons already mentioned, these studies were all performed in micellar solutions. The effect of the addition of several surfactants on the electrochemical behavior of solutions of these pesticides was studied in order to obtain a better signal to noise ratio. The chosen mixture was Hyamine (cationic surfactant) and Triton X-405 (neutral surfactant).

It was possible to assay simultaneously the pesticides heptachlor and endosulfan-sulfate, because the potential difference observed was about 0.18 V vs. Ag/AgCl. For the other pesticides, by controlling the rate of hydrolysis, determination of the following mixtures was possible: endosulfan/dieldrin, endosulfan-sulfate/dieldrin, and endosulfan/endosulfan-sulfate.

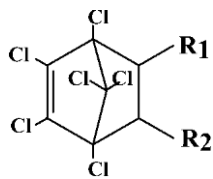


Figure 4. Structure common to dieldrin, heptachlor, and endosulfan.

In another work, the adsorption behavior of alachlor and its electrochemical reaction products in the presence of different surfactants were studied in order to improve the signal/noise ratio.[21] It was proven that these compounds are adsorbed in the surface of the mercury electrode to the detriment of the pesticides and/or their reaction products. Because in this group of pesticides, the reduction reaction gives rise to a negatively charged species, the adsorption of a cationic detergent on the surface of the electrode will produce an attractive electrostatic effect and thereby favor the reduction of alachlor. Similarly, the adsorption of a neutral detergent will prevent adsorption of either pesticides or their reaction products causing an inhibitory effect. In the case of anionic surfactants, they will be almost completely desorbed from the surface of the electrode at the negative applied potential at which the reduction of the pesticide takes place and consequently, will have no effect on the process.

The pesticides *p*,*p*^{0}-DDT and dieldrin have similar electrochemical behavior. Thus Fe(II) was added to solutions of these two compounds, because the dieldrin forms a metallic complex with it, which is electroactive at the mercury electrode and has a different potential compared with *p*,*p*^{0}-DDT. The reaction of the metallic ion with dieldrin maybe explained by the fact that it contains an epoxy group and a C5C bond, absent in *p*,*p*^{0}-DDT.[27]

In the literature, the techniques more used for the determination of these group of pesticides were DPV and AdSV.

Using differential pulse voltammetry eight compounds of the three classes of organochlorine pesticides were determined in water.[28] These were: *a*-HCH, *b*-HCH, *g*-HCH, *o*,*p*-DDT, *p*,*p*-DDT, aldrin, dieldrin, and endrin. Correlating the chemical structures of these pesticides with their limits of detection, it was noted that the detection limit obtained was lowest for compounds containing aromatic rings (*o*,*p*-DDT; *p*,*p*-DDT). For non-aromatic compounds, the detection limit was lower for compounds that contain no double bonds such as hexachlorocyclohexanes (a-HCH; b-HCH, g-HCH) than it was for double bond-containing compounds (aldrin; dieldrin, and endrin).

2.1.5. Sulphonylureas

The sulfonylureas constitute a less dangerous group of pesticides as they have low toxicity in mammals, they are selective for specific pests and in their usual applications they only require low dosages to be effective.[29]

The general structure of sulfonylureas consists of three distinct parts: an aryl group, the sulphonylurea bridge, and a nitrogen-containing heterocycle. As an example of the family of herbicidal sulfonylureas, the structural formula of chlorsulfuron is presented as Fig. 5.

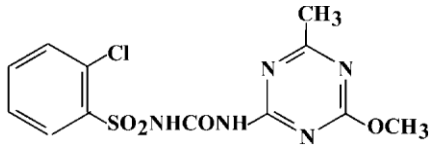


Figure 5. Structure of chlorsulfuron.

In the literature, there are few works that are based on electrochemical methods for the determination of the sulfonylureas. Of these, the most important is the determination of chlorsulfuron, metsulfuron-methyl, DPX-M6316, and chlorimuron-ethyl using the technique of DPV.[29] The electroanalytical behavior of these sulfonylureas is strongly dependent on the pH of the solution. The best signals were obtained at pH 2.5. Mechanistic studies of the electrode reaction were not pursued.

2.1.6. Bipyridinium Pesticides

The bipyridium pesticides are known as "viologens," V_L. The general structural formula is shown in Fig. 6.

Voltammetric studies suggested the mechanism of reduction at the mercury electrode given in Eq. (1).[30–33]

$$V_L^{2+} \overset{+e}{\rightleftharpoons} V_L^{+} \overset{+e}{\rightleftharpoons} V_L \qquad (1)$$

These studies showed not only the two peaks corresponding to the two-electron transfer steps but also two peaks corresponding to the reduction of the cations, V_L^{2+} and V_L^{+}, adsorbed on the surface of the electrode.

Not all the pesticides in this family are electroactive. The necessary but not sufficient condition for electroactivity in these compounds at mercury electrodes is the coplanarity of the two heterocyclic nuclei. The coplanarity enables the reversible formation of a free-radical cation after the uptake of a single electron. Understanding that the biological activity of these substances is mediated by the degree of formation of this cation, it appears probable that the electrochemical reduction of these herbicides at mercury

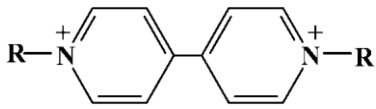


Figure 6. Structure of a viologen.

electrodes maybe used as a model for the monitoring of processes that occur in plants.[32]

Paraquat and diquat are the selective contact herbicides most frequently used of this family. The two compounds are usually called "methylviologen" because, on reduction, they give rise to stable, blue or violet radicals.

2.1.7. Carbamate and Thiocarbamate Pesticides

Metallic complexes of dithiocarbamates are much used as pesticides. By means of polarographic studies, it has been possible to determine, for some of these compounds, the stoichiometric ratio of the metal– dithiocarbamate complex and to study, kinetically, their decomposition in acid solution.[34]

As has been noted and justified previously, the electrochemical methodologies developed for the determination of some pesticides required as a first step a pre-treatment either by hydrolysis or derivatization. Another example of this is nitrosation followed by carbaryl hydrolysis; in this article; other techniques such as nuclear magnetic ressonance (NMR) and thin layer chromatography (TLC) were used to characterize the products of reaction.[35]

Because carbaryl is not electroactive at a mercury electrode another method was developed, based on indirect determination using a colorimetric oxidation reaction.[36]

2.2. Solid Electrodes

The materials most frequently used for the construction of solid electrodes are carbon, platinum, gold, and silver. Few studies have used solid electrodes to investigate the electrochemical behavior of pesticides directly on the surface of the electrodes.

Sulfometuron-methyl has been quantitated using platinum electrodes in a reduction reaction after derivatization.[37]

The great majority of published works have used glassy carbon electrodes (Table 3). To exemplify this, one study used glassy carbon electrodes to study the oxidation of 13 carbamates. Of these only four, pirimicarb, methiocarb, aminocarb, and zetran, were shown to be electrochemically active. In this work, the variation of peak potential with the pH of the solution and analysis of the voltammograms are consistant with a mechanism that involve the formation of a cationic radical. Consideration of the oxidation potentials suggested an analytical method for the determination of aminocarb and zetran, using DPV, which would achieve a detection limit for either compound of 30 mg L^{-1}.[38]

In later work, also using DPV, the mechanism of electrochemical oxidation of four other pesticides in the carbamate family, fenuron, diuron, clorotoluron and fluometuron, was studied. The authors reached a similar conclusion; that oxidation of these compounds involved the formation of a radical and that this then dimerized.[39]

A more recent work, also using DPV, quantitatively analyzed carbaryl and carbofuron in phytopharmaceutical preparations after alkaline hydrolysis and the formation of phenolic derivatives.[40]

The oxidation of two carbamates, profam and chlorprofam, and nine ureas, molinuron, linuron, clorobromuron, metabromuron, fenuron, diuron, clorotoluron and cloroxuron were studied with glassy carbon electrodes. Determination of these herbicides was performed in a continuous flow system with an amperometric "wall-jet" detector both with and without high-performance liquid chromatographic (HPLC) separation.[41]

In another work, a HPLC determination of residues of some carbamate insecticides with electrochemical detection after degradation of molecules as phenols are developed.[42]

Using a glassy carbon electrode, several methods were developed for the estimation, in phytopharmaceutical preparations, of a group of five herbicides used in rice culture (bentazone, molinate, bensulfuron-metyl, oxadiazon and propanyl).[43 – 46]

Electrochemical oxidation of propanil in deuterated solutions was studied by using a glassy carbon microelectrode. The results are supported by electrochemical and spectroscopic studies of acetanilide in deuterated solutions.[47] The association of electrochemical and NMR data made the elucidation of the mechanism of oxidation possible and soon will lead to a better understanding of the (bio)degradation processes of anilide pesticides in the environment.

In recent times, electrochemists have become interested in the purposeful modification of electrodes by adsorbing, coating, or otherwise attaching specific molecules to the surface. This deliberate and controlled modification of the electrode surface will produce electrodes with new and interesting properties that may form the basis of new applications in electrochemistry and will allow the development of novel devices.[48]

To study the electrochemical behavior of herbicides and growth regulators belonging to the family of quaternary ammonium compounds, a special electrode was constructed in which an ion-exchange polymer was intercalated between the carbon surface and a dialysis membrane.[49]

The oxidative voltammetric behavior of the herbicides thiram and disulfiram at graphite–poly(tetrafluoroethylene) (PTFE) composite electrodes has been studied. As an application, the determination of thiram in spiked strawberries was carried out with good results.[50] With the same electrodes,

it was possible to develop a continuous flow analysis system employing an amperometric detection technique.[51]

To quantitate paraquat in riverine waters, the electrode used was a carbon paste electrode chemically modified with Amberlite XAD-2 resin, the limit of detection attained was 0.10 mg mL^{21}.[52]

Despite the advantages and characteristics of the glassy carbon electrode with a mercury film (MFE) being well known for the determination of metals, the number of works describing the estimation of organic compounds is small. Two applications using this type of electrode are the determination of triazines in environmental samples using HPLC with an electrochemical detector[5] and the measurement of dinoseb in contaminated apple juice using AdSV.[53]

There are also many reports of the use of biosensors in which the surface of the electrode is chemically modified and then a biological material is immobilized on to it for the detection of a specific pesticide.

Electrochemical biosensors maybe conveniently divided into three groups: immunosensors, whole cell and organite-base sensors, and enzyme sensors.

Immunosensors are based on the antibody–antigen reaction (Ab–Ag) and are constructed by immobilizing either the antibody or the hapten of the antigen on the surface of the electrode. There are few reports of the development of immunosensors for the estimation of pesticides, usually, the antigen/hapten-antibody interaction cannot be converted directly into an analytically quantitatable signal, especially for small molecules (:S1000 Da); therefore, labeled molecules are needed for indirect determination of the analyte-antibody reaction. Unlike enzymes, antibodies show no catalytic activity, and the analyte-antibody reaction is troublesome to regenerate, especially with high-affinity antibodies, making many measurements difficult and often involving multistep procedures.[54]

In the whole cell or organites sensors, the cells or organites were immobilized by different techniques such as entrapment in alginete or agar gels and immobilization by cellulose acetate or cellulose nitrate membranes to the surface of a conventional oxygen (clark) electrode.[54,55] The measurement is based on biochemical oxygen demand (BOD) or the quantification of photosynthesis.

It was, therefore, the development of techniques for the immobilization of enzymes and thereby the construction of enzyme sensors that made a substantial contribution to the growth of biosensors in the determination of trace amounts of pesticides in various types of sample. Biosensors based on immobilized selected enzyme such as cholinesterases, tyrosinase, alkaline and acid phosphatase, ascorbate oxidase, acetolactate synthase, and aldehyde dehydrogenase[54 – 62] have been widely used for the quantification of pesticides. In the field of environmental monitoring, the principal objective of

this type of biosensor is be used in situ. Because analytical matrixes are much more complex and include hundreds of analytes, such as agrochemicals and other environmental contaminants, market needs are harder to predict.

3. PRESENT AND FUTURE TRENDS IN THE ANALYSIS OF PESTICIDES RESIDUES

The majority of the studies found in the literature have as their objective the quantitative measurement of pesticides in a wide variety of sample types and in this area, it has already been shown that voltammetric methods are very useful due to their selectivity.

Besides the sensors commonly used in voltammetry (Hg, Pt, Au, glassy carbon and carbon paste electrodes, various types of modified electrodes), ultramicroelectrodes with dimensions smaller than 10 mm are promising. At these tiny electrodes, voltammetric waves are obtained, rather than conventional peaks even at high voltage scan rates. Because of the low current, the voltage drop in solution is negligible and the supporting electrolyte is not essential in the solution. Thus even organic solvents can be employed without the necessity of using a potentiostat. The use of microelectrodes clearly opens the way for studies in numerous systems of environmental concern.[63]

During the last decade, the study of the degradation mechanisms of pesticides and pesticide-induced oxidative stress as a possible mechanism of toxicity has been a focus of chemistry research. In this study, the association of electrochemical and spectroscopic methods made the elucidation of the mechanism of oxidation possible and soon will lead to a better understanding of the (bio)degradation processes of pesticides in the environment.

Biosensors will undoubtedly play an important role in future for analysis of pesticides residues, some critical parameters such stability, accuracy, and reliability are being improved due to a rapid progress in development of biosensor in recent decade.[2]

The electrochemical DNA-biosensor has been used recently to investigate the interactions between DNA and some pesticides. This study is very important because the use of this biosensor revealed the occurrence of a time-dependent interaction of all the herbicides with DNA.[64]

4. CONCLUDING REMARKS

Examples have been presented here of the application of voltammetry and amperometry in the analysis of pesticides for environmental control. In the

past, the technical complexity of these techniques has overshadowed their power and thus inhibited their use. Now, the improvements in electronics and computers make voltammetric and amperometric techniques available to the user in a practical way. New chemical or biological recognition processes and advances in modified solid electrodes and microelectrodes should lead to many applications for electroanalysis including the analysis of pesticides.

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