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Voltammetric Analysis of Pesticides

Ignas Tonle K.^{1,2} and Emmanuel Ngameni¹

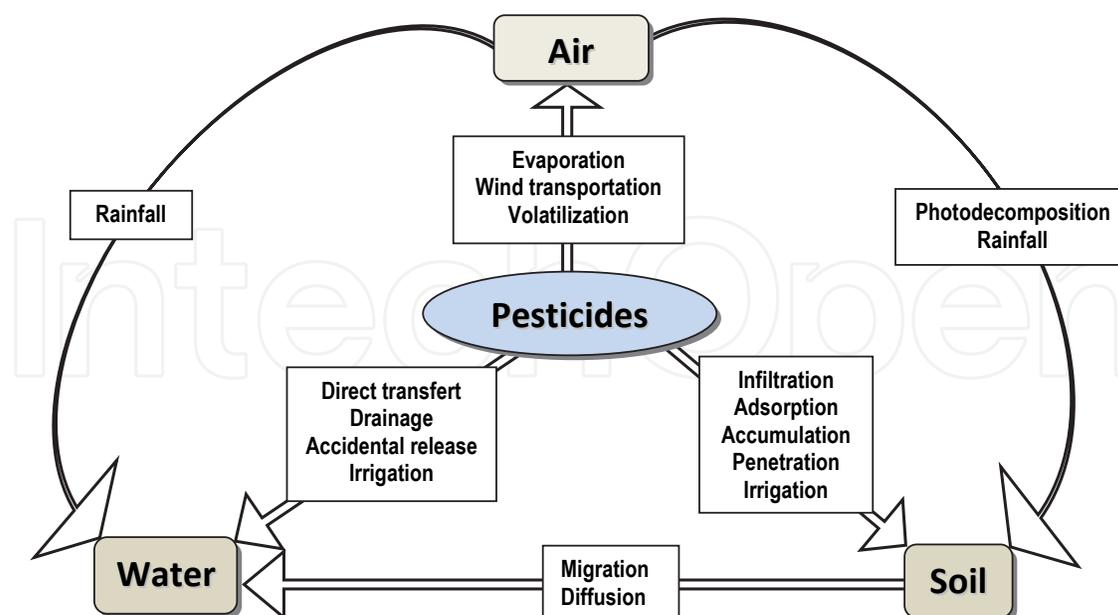
¹Laboratory of Analytical Chemistry, University of Yaounde

²Department of Chemistry, University of Dschang
Cameroon

1. Introduction

Pollution due to pesticides is a daily and growing problem, closely related to the intensification of agricultural activities devoted to the satisfaction of human needs in terms of food. In fact, throughout the world, pesticides are intensively used as defoliants or against weed and pests in a large variety of crops (Castanho et al., 2003; De Souza & Machado, 2005a). Also known as persistent organic pollutants due to their low solubility and degradation in the environment, pesticides are thus inherently toxic since their accumulation in living organisms can induce serious diseases.

Several analytical techniques have been used for the analysis of pesticides, which include fluorimetry (Anson & Wade, 1976; Eremin et al., 1996; Coly & Aaron, 1998a,b), capillary electrophoresis (Tomita et al., 1992; Pico et al., 2003), spectrophotometry (Shivhare & Gupta, 1991; Jain et al., 1993), mass spectroscopy (Moyano & Galceran, 1996; Leandro et al., 2006) and mainly gas or liquid chromatography (McGarvey, 1993; Castro et al., 2000; Fillion et al., 2000; Corasaniti & Nistico, 1993). These techniques operate quite well but they present a certain number of disadvantages: they are limited to laboratories, time consuming, expensive, and have to be performed by highly trained technicians (Mulchandani, 2001). During the past decade, scientific works devoted to the implementation of electrochemical devices suitable for the sensing of pesticides have gained growing interest. The main proposal of these studies is the development of convenient, sensitive, selective and low cost tools that could be exploited for a rapid monitoring of pesticides (Tapsoba et al. 2009; Tcheumi et al., 2010). In fact, when pesticides are applied, only a small fraction actually reaches target organisms formed by crop pests and vectors of diseases. Consequently, traces amounts of these chemicals can be detected in surrounding and ground water, in the soil and in the air. Scheme 1 summarizes the most common pathways involved in the dissemination of pesticides in the environment. In another hand, the determination of pesticides and their residues or metabolites in either water or soil solutions is a critical problem for several reasons: (i) the number of chemicals involved is too large, (ii) each of these chemicals displays a specificity in term of reactivity, and (iii) several active ingredients of pesticides are often present in the same matrix. Therefore, the need to design convenient tools for the electroanalysis of pesticides in environmental matrices and in food remains a permanent and challenging question. Following these lines, there is an interest to properly adapt electrochemical methods to build sensors, due to some of their advantageous characteristics such as simple operations, short analysis times, accuracy and high sensitivity (Parham & Rahbar, 2010; Tcheumi et al., 2010).



Scheme 1. Common pathways for the dissemination of pesticides in the three parts of the environment.

In this chapter, the potential contribution of electrochemical methods to the monitoring of pesticides will be exposed. Since chemically modified electrodes have gained great interest for pesticides analysis, a focus will be given to the description of new sensors fabricated in recent years. The future trends in the design of new electrode configurations likely to modernize the electroanalysis of pesticides will be also discussed.

2. Overview of voltammetric methods for the determination of pesticides

2.1 Fundamental concept of voltammetric methods

Voltammetric techniques are undoubtedly the most useful tools in analytical sciences, especially for studies in aqueous media or at solid state of electroactive species. As most chemical and biochemical compounds are either reducible or oxydable, modern research laboratories are usually equipped with electrochemical techniques. Yet, these methods can be used to study the kinetics and thermodynamics of electron and ion transfer processes (Bagotsky, 2005), to investigate adsorption phenomena likely to occur at the electrode surface and to study the reaction mechanisms in organic chemistry or in biochemistry (Bard & Faulkner, 2001). In most voltammetric methods, an electrochemical cell is required which consists of three electrodes: (i) the indicator (or working) electrode at which the electrochemical reaction involving electron transfer takes place, (ii) the reference electrode characterized by a constant potential over time and (iii) the auxiliary electrode at which a counter reaction to that at the working electrode takes place to balance the total charge in the whole system (Gulaboski & Pereira, 2008). From a practical point of view, when a potential E is applied to the working electrode in contact with an electroactive probe, this probe is either oxidized or reduced. Consequently, a change in its concentration occurs at the electrode surface, causing mass transfer towards the electrode. A current then flows through the electrode. By sweeping the potential with time and recording the current (i), a

curve called voltammogram is obtained which is obviously equivalent to record the current as a function of applied potential. The application of voltammetric methods for analytical purposes is due to the fact that the current recorded at the indicator electrode is directly proportional to the analyte concentration (Wang, 2006). There are many voltammetric techniques each characterized by the nature of the potential applied to derive the electron transfer reaction and by the shape of the i versus E curve, that is of the voltammogram whose physical parameters are easy to exploit for quantitative analysis.

Concerning the electroanalysis of pesticides most of which are organic compounds bearing electroactive functional groups, cyclic voltammetry and pulse voltammetric techniques (namely differential pulse voltammetry, square wave voltammetry and differential pulse polarography) are frequently used. A brief description of each of these techniques in conjunction with some typical applications will be provided in the forthcoming section.

2.2 Cyclic voltammetry (CV)

Amongst voltammetric methods, CV is quite popular and is generally used to first investigate the electrochemical behaviour of new redox systems (Gulaboski & Pereira, 2008). It offers a rapid location of redox potentials of these systems and a convenient evaluation of the effect of media on the redox process involved (Wang, 2006). CV consists of first applying a linear sweep potential to the working electrode from an initial potential (E_i) to a final one (E_f). After reaching E_f , the sweep is reversed and the potential returns to E_i . During this experiment, a current resulting from the potential applied at a precise scan rate is recorded. The recorded cyclic voltammogram is characterized by five main features: the cathodic and anodic peak potentials (denoted E_c and E_a respectively) to which correspond the cathodic and anodic peak currents (i_c and i_a), and the half-peak potential ($E_{1/2}$). The values of these parameters and the relationship between them provide the basis for classifying cyclic voltammograms as reversible, irreversible or quasi-reversible systems. For adsorption processes and coupled chemical reactions, quantitative data on the kinetics of electron transfer reaction and on the thermodynamics of the redox reaction can be derived, mainly when multiple cycles are subsequently recorded between E_i and E_f . For pesticides analysis, the shape of cyclic voltammograms can provide informations about the type of working electrode reaction, the number of electrons involved in the electrochemical reaction and about additional process that can eventually occur such as adsorption or coupled chemical reactions (Zoski, 2007). A typical example illustrating the usefulness of cyclic voltammetry in pesticides analysis is presented in Figure 1 where the interfacial behavior of methylparathion was investigated using repetitive cyclic voltammetry in 0.1 M acetate buffer (pH 5), on a glassy carbon electrode covered with a thin film of a gemini surfactant intercalated montmorillonite (Tcheumi et al., 2010). As shown, the electrode response is made of two redox systems: (i) the first one (characterized by $E_{a1} = 0.03$ V and $E_{c1} = 0.00$ V) is reversible while the second one formed by one reduction peak ($E_{c2} = -0.60$ V) is irreversible. One can notice that a global increase of the reversible system's peaks is observed upon continuous cycling, indicating a progressive adsorptive accumulation of methylparathion by the organoclay on the glassy carbon electrode. During the first cyclic scan performed from +0.03 V, the peak of the reversible system did not appear but arises only when the second cathodic peak was formed. This observation showed that the reversible system thus resulted from a species generated by the irreversible system.

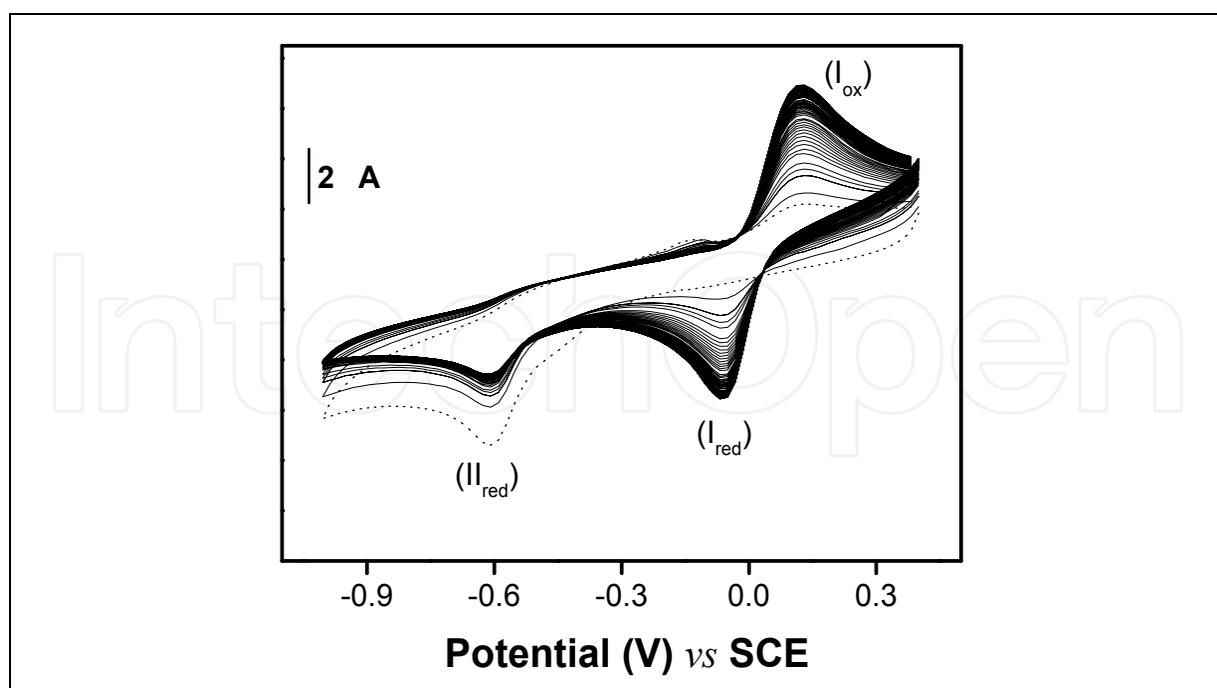
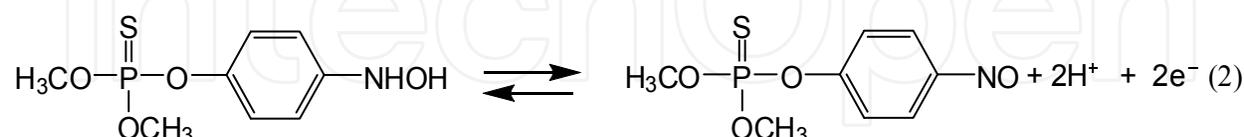
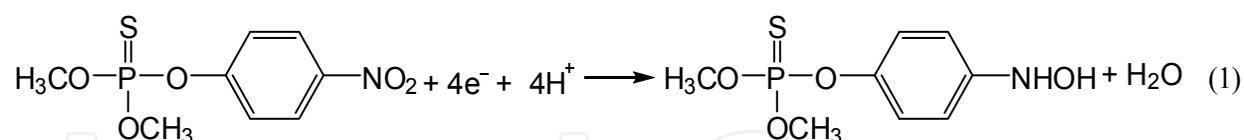


Fig. 1. Multisweep cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} for $41.5 \mu\text{M}$ methylparathion in 0.1 M acetate buffer (pH 5) on a glassy carbon covered with a gemini surfactant intercalated montmorillonite (From Tcheumi et al, 2010).

Such a behavior was reported for the same pesticide on a nafion coated GCE (Zen et al., 1999), and the irreversible peak was attributed to the reduction of the nitro group of methylparathion to hydroxylamine group (Equation (1)), whereas the reversible system correspond to an electron transfer process indicated in Equation (2) (Zen et al., 1999, Sbai et al., 2007).



2.3 Pulse voltammetric techniques

Pulse voltammetric techniques were introduced in electrochemistry by Barker and Jenkin (1952) to resolve a crucial problem, the lowering of the detection limits of voltammetric measurements which is achieved upon substantially increase the ratio of faradaic to capacitive current (Wang, 2006). In such techniques, the basic principle is the same: a sequence of pulsed potentials is applied to the working electrode, after the potential is stepped, the quite undesirable capacitive current decays exponentially with time to

a negligible value while the faradaic current decays more slowly for the same reaction. This leads to a negligible capacitive current and concomitantly to a significant faradaic current which is related to the electrochemical reaction of interest (Wang, 2006; Gulaboski et al., 2008). There are various pulse voltammetric techniques in modern electrochemistry, classified according to the pulse-wave form and the current sampling mode. The most important instrumental parameters of these techniques are the pulse amplitude (height of the potential pulse), the pulse width (duration of the potential pulse) and the sampling period. The electrode response consists of current peaks the height of which is directly proportional to the concentration of the analyte. Thanks to their great performance, pulse techniques can be exploited via anodic, cathodic or adsorptive stripping modes. Square wave voltammetry, differential pulse voltammetry and differential pulse polarography are the most used pulse techniques for the electroanalysis of pesticides molecules.

2.3.1 Square wave voltammetry (SWV)

SWV is the most advanced and efficient of pulse voltammetric techniques (Osteryoung & O'Dea, 1986; Stojek, 2001). A potential, consisting of symmetrical square-wave pulses superimposed on a staircase-wave form is applied to the working electrode. During each square-wave cycle, the current is sampled twice: once at the end of the forward pulse that gives rise to the oxidative current component, and once at the end of the backward pulse that gives rise to the reduction current component. The difference between the two measurements is plotted versus the base staircase potential and the resulting peak-shaped voltammogram is proportional to the analyte concentration (Kounaves, 1997; Wang, 2006; Gulaboski & Pereira, 2008). Many excellent works dealing with the detection of low amounts of pesticides in food and environmental samples have been published. Figure 2 displays typical square-wave voltammograms obtained on a glassy carbon electrode covered by drop-coating of an organophilic modified clay film. The modified electrode was used to analyze diluted solutions of methylparathion, with concentrations ranging from 4.0×10^{-7} to 8.5×10^{-6} M (Tcheumi et al., 2010). For this particular case, the electrochemical procedure used for the electroanalysis stripping SWV involved two successive steps: an open-circuit accumulation of the pesticide followed by a voltammetric detection in a separate medium. Preconcentration was achieved by dipping the working electrode in a stirred solution of methylparathion at a given concentration, this operation is performed to facilitate the transport followed by the accumulation of the pesticide on the organoclay material. As shown by the inset in Fig. 2, peak currents increase with methylparathion concentration, displaying a linear relationship behavior which was exploited to attain a detection limit of 7×10^{-8} M. SWV has also been shown to be an important technique for the detection of paraquat, a toxic herbicide used to control herbal growth in terrestrial and aquatic environment (El Mhammedi et al., 2007). The working electrode consisted of a carbon paste electrode chemically modified by a synthesized Ca-hydroxyapatite. Many other unique applications of square wave voltammetry include the use of non-modified (Liu & Lin, 2005) and modified (Parham & Rahbar, 2010) carbon paste electrodes for the sensing of organophosphate pesticides, the quantification of pesticides in real water samples using ionomer clay-modified electrode (Zen et al., 1996) and even on non modified electrodes (Garrido et al., 1999, 2001).

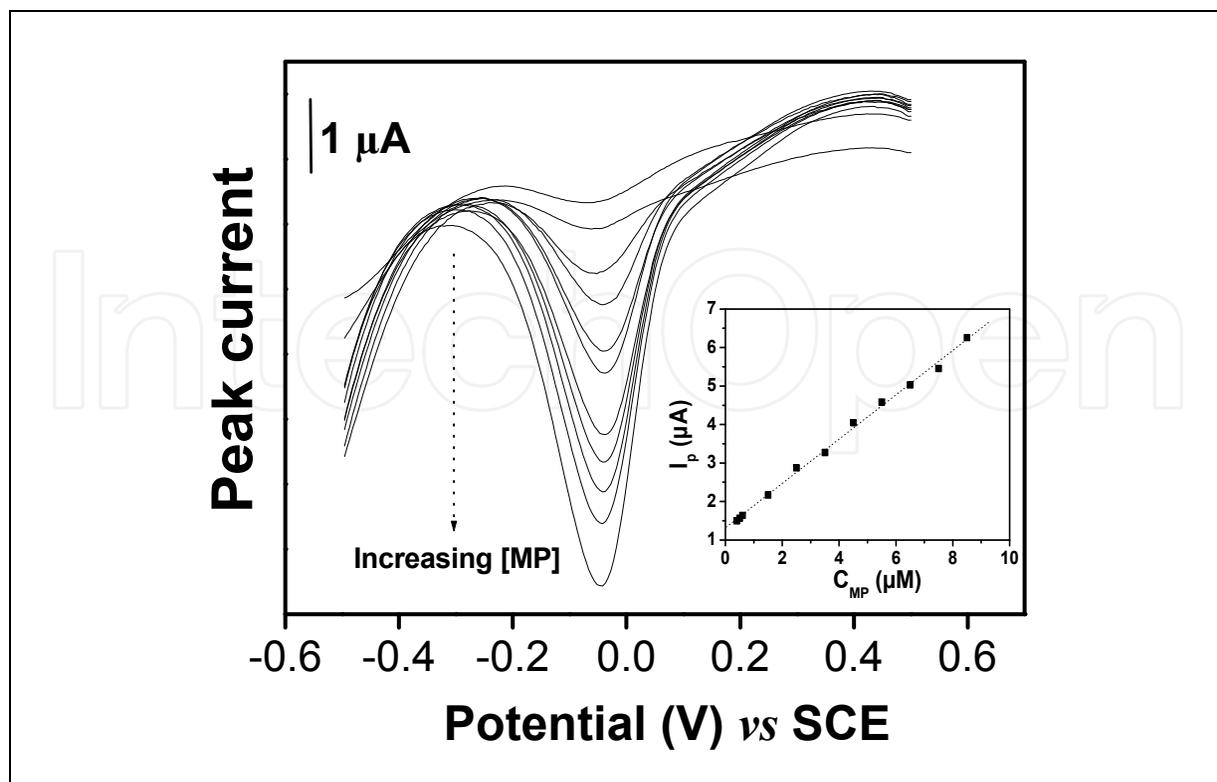


Fig. 2. Square wave voltammograms obtained at a glassy carbon electrode modified by a positively charged gemini surfactant intercalated montmorillonite. The curves were recorded using the “preconcentration at open-circuit/detection sequence”. The inset shows a linear relationship between the electrode response and the pesticide concentration ranging from 4×10^{-7} to 8.5×10^{-6} M (From Tcheumi et al., 2010).

Some recent advances and applications of SWV were described, for which the stripping voltammetry was combined with solid-phase extraction often used in separation science (Gong et al., 2009, 2010). Such a combination was shown to be suitable for decentralized point-of-care or field determination of pesticides in the environment with portable instruments, providing a fast, simple and sensitive electrochemical method for the detection of organophosphate pesticides.

2.3.2 Differential pulse stripping voltammetry (DPV)

Amongst voltammetric methods, DPV is of extreme usefulness as the technique is particularly designed for measuring trace levels of organic and inorganic species (Bagotsky, 2005; Wang, 2006). It consists of small pulses of constant magnitude, superimposed like in SWV on a staircase-waveform. Once more, the current is sampled twice, just before the pulse application and then in the pulse life when the capacitive current has decayed (Skoog et al., 1997; Wang, 2006). The electrode signal, actually the difference between the currents measured for each single pulse consists of peaks the height of which is directly proportional to the concentration of the corresponding analyte. The widespread application of DPV is also due the peak-shaped of voltammograms which results in improved resolution between two species with similar redox potentials as peaks separated by 50 mV may be measured (Wang, 2006). Some recent applications of the technique for the fabrication of sensors include the use of carbon paste electrodes for the detection of either dinitrophenolic

herbicides (Sreedhar et al., 2003) or neonicotinoid insecticides (Papp et al., 2010). Differential pulse voltammetric determination of herbicides at a clay-modified electrode has been also reported by Manisankar et al. (2004a,b; 2005a).

2.3.3 Differential pulse polarography (DPP)

DPP is a subclass of voltammetry in which the operational principles of DPV are applied using either a dropping mercury electrode or a static mercury drop electrode as indicator electrode. Although mercury is highly toxic and thus less present in electrochemistry laboratories, DPP remains nowadays a useful analytical technique for pesticides analysis, for two main reasons: (i) various functional groups (i.e. carbonyl, nitro, disulfide, azo, quinone) present in pesticide molecules are reducible at mercury electrodes which display wide cathodic ranges (surtension), (ii) many organic and inorganic compounds tend to be adsorbed at mercury electrode; this fact can be favourably exploited for their accumulation prior to their detection. Thus, Sreedhar et al. (1997) reported the utilization of DPP for voltammetric sensing of three fungicides; namely folpet, phosmet and dialifos that contain carbonyl group. In this study, both standard addition and calibration methods were used to determine folpet and phosmet at nanomolar level. Castanho et al. (2003) developed a differential pulse polarographic method to detect methylparathion in water and soil suspensions. Their method allowed the recording of the sorption isotherms of the pesticides on three Brazilian soils. Another recent relevant work was reported by Balaji et al. (2010a) who described a method to study the voltammetric behaviour of fluazinam, a dinitropesticide. This method was successfully employed for the detection of the pesticide in various environmental matrices. These authors also developed a differential pulse polarographic method to determine fluochloralin in formulations, grains, soils and spiked water samples (Balaji et al., 2010b).

These studies reveal that pulse voltammetric techniques are particularly designed for measuring very low levels of pesticides in the environment, mainly when they are used in connection with modified electrodes as we will also discuss in this chapter. Taken together, SW and DP voltammetries are commonly exploited via adsorptive stripping mode where traces of pollutants are accumulated by adsorption. This approach offers improvement in selectivity and sensitivity. For this to be achieved, the active surface of solid electrode substrate (glassy carbon, platinum, SnO₂ for example) is modified by a compound or a material exhibiting some chemical affinity towards the target analyte (Walcarius et al., 2003; Tonle et al., 2005). These modified electrodes, engineered to respond selectively and sensitively to pesticides are focussed on electrochemical sensors and biosensors.

3. Electrochemical sensors based on chemically modified electrodes

During the past years, analytical systems based on modified electrodes have been developed, aiming at providing researchers with efficient amperometric sensors of diverse nature. These electrodes which combine the individual and specific properties of each of their components can be classified on the basis of their physical and chemical configurations. Hereafter will be described the major chemically modified electrodes used for the detection of pesticides. The most described chemically modified electrodes in the field of pesticide control include carbon nanotubes modified electrodes, carbon paste electrodes, clay film-modified electrodes and immobilized enzyme electrodes.

3.1 Carbon nanotubes modified electrodes

During the last years, several research teams have exploited either single-wall carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) to build amperometric sensors by means of modified electrodes. Yet, CNTs are of special interest due to their inherent electronic, metallic and structural properties (Ajayan, 1999), and can be directly used as electrode modifier, or in combination with another component dotted with attractive properties. MWCNTs served as excellent electrode material on a chitosan matrix for the sensitive detection of triazophos pesticide (Du et al., 2007). Some other works have been reported in which MWCNTs were combined with conductive polymers to form composite structures which then associated the properties of both components: the well-known electrocatalytic and adsorption characteristics of MWCNTs, and the bound active surface functionalities of conductive polymers. Following the same line, an efficient sensor was obtained by covering a MWCNT modified glassy carbon electrode with polypyrrole and polyaniline, and used to electrochemically reduce isoproturon, voltage and difocol (Manisankar et al., 2008). More recently, a viable nanocomposite platform formed by a basal plane pyrolytic carbon electrode nanostructured with Ni(II)-phtalocyanine and MWCNTs has been shown to exhibit sensitive electrocatalytic properties towards the detection of asulam pesticide (Siswana et al., 2010). Two years before, these authors described the electrocatalytic detection of amitrole on MWCNTs using the basal plane pyrolytic graphite electrode modified by a Fe(II) tetra-aminophthalocyanine (Siswana et al., 2008). The results show that CNTs can lead to a widespread range of electrochemical sensors for the detection of pesticide contaminates.

3.2 Carbon paste electrodes (CPEs)

CPEs, invented by Adams (1958) are formed by a mixture of carbon (graphite) powder, a pasting liquid (binder) and usually a third component (in solid state) whose behaviour is to be studied or which displays favourable interactions towards a target analyte. Recently, a well documented review was published on the electrochemistry and electroanalytical applications of CPEs, on the occasion of the half-of-century anniversary of their discovery (Svancara *et al.*, 2009). Undoubtedly, CPE remains a powerful and useful tool with a wide diversity of applications, especially for the building of low-cost and sensitive sensors for the detection of extremely low concentration of electroactive species (the lowest limits of detection achieved at CPEs lie between 10^{-11} and 10^{-16} M, as summarized in the review by Svancara *et al.* (2009)). These applications are closely related to some of their typical properties such as low background currents, long-time stability, high polarization limits (both in anodic and cathodic directions), easy fabrication and comfortable renewal of the paste (Svegl & Ogorevc, 2000; Svancara *et al.*, 2009).

During the past decade, CPEs have been shown as attractive tools for the detection of pesticides. A mixed-ion fluorohectorite heterostructure incorporated in a CPE was used as an electrochemical sensor for the detection of the herbicide 2,4-dichlorophenoxyacetic acid, reaching concentrations up to 20 μ M (Ozkan *et al.*, 2002). A highly sensitive amperometric method based on a ferophtalocyanine chemically modified CPE coupled with enzymes co-immobilized onto the surface of a dialysis membrane was developed for the detection of organophosphorous pesticides (Anton *et al.*, 2003). This work opened the way to the construction of an amperometric biosensor for paraoxon and carbofuran pesticides detected at concentrations up to 10^{-10} M. Using a bare CPE and a sepiolite (clay material) modified CPE, Sreedhar *et al.* (2003) described a sensitive adsorptive stripping voltammetric method

for the determination of dinoseb and dinoterb herbicides. More recently, Papp et al. (2010) performed the voltammetric investigation of thiamethoxam (a neonicotinoid insecticide) using a tricresylphosphate-based CPE. The so-developed method allowed a direct determination of the insecticide in a river water samples. One could also cite a relevant work by Parham & Rahbar (2010) who quantitatively detected methylparathion in water samples by the means of a ZrO_2 -nanoparticles modified CPE.

As demonstrated by these examples, CPE remain actually a very useful tool for the electroanalytical detection of pesticides. Thus, new electrochemical sensors could be favourably tailored for a specific analytical task, depending on the nature and the chemical reactivity towards the pesticide, of the compound added to the matrix formed by carbon particles and the binder.

3.3 Clay film-modified electrodes (CFMEs)

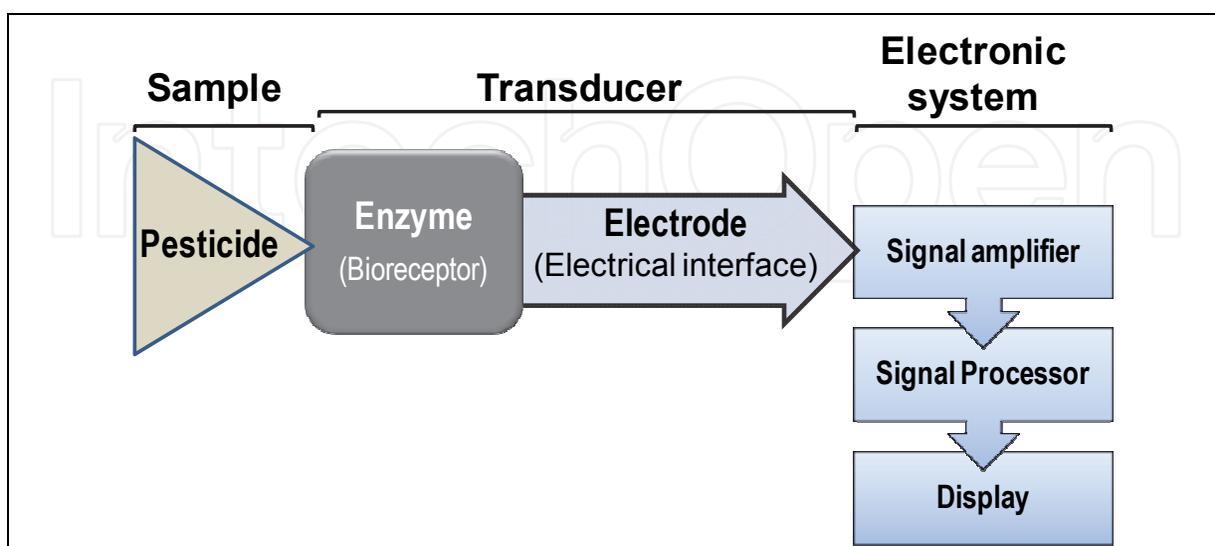
CFMEs are obtained by covering the surface of conductive solid substrates (glassy carbon, Au, Pt, SnO_2 or pyrolytic graphite) by a thin membrane of clay. They were first introduced by Ghosh and Bard (1983) to elucidate charge phenomena in the film, and the effect of the film structure on the mobility of the electrochemical probe to the electrode surface (Naegeli et al., 1986; Subramanian & Fitch, 1992; Fitch et al., 1996). This particular type of electrodes has been actively investigated for its potential applications in electrocatalysis (Premkumar & Ramaraj, 1997; Moronta, 2004; Paramasivam & Anandhan, 2005), in the electroanalysis of organic and inorganic compounds (Ballarin et al, 2000; Jieumboue et al., 2009, Tonle et al., 2009) and in biochemical analysis (Coche-Guerente et al. 1998; Mbouguen et al. 2007). It has been shown that the diffusion of an electroactive species within the film at a CFME depends on several factors such as the pore structure of the film, the size of the probe, its concentration, the ionic strength and the composition of the supporting electrolyte (Naegeli et al., 1986; Fitch et al. 1996). Two main approaches are usually used to build CFMEs: (i) the spin-coating of a colloidal suspension enriched with clay particles, (ii) the drop-coating on the active surface of the electrode of the clay suspension, both followed by drying either in air or in an oven at a given temperature. As stated by Navratilova & Kula (2003), the way of drying, the type of clay and the size of clay particles are crucial factors for obtaining a film with required stability, uniformity and thickness.

The high adsorption power of clays and clay minerals, combined with their particular colloidal properties allowed their exploitation as suitable modifiers for the elaboration of clay film-modified electrodes used to analyze pesticides. In such electrodes, pesticide molecules containing functional polar groups are directly bound to negatively charged smectite-type clay particles either by electrostatic interactions or by an ion exchange process. Yet, smectites are characterized by internal surfaces accessible by polar organic molecules and by flexible adsorptive properties (Villemure & Bard, 1990). As smectites can act as carrier of organic contaminants, sensitive voltammetric methods were developed by several authors. Manisankar et al. (2004b) studied the redox behaviour of endosulfan and orthochlorophenol using a sodium montmorillonite clay-modified glassy carbon electrode (GCE), and demonstrated the suitability of the modified electrode for the determination of these pesticides by means of differential pulse stripping voltammetry. The same research team reported the development of an electrochemical trace determination method for isoproturon and carbendazim in soil and water spiked samples, using once more a sodium montmorillonite clay-modified GCE, in the presence and in the absence of cetyltrimethylammonium bromide (CTAB) surfactant (Manisankar et al., 2005b). Following

these lines, they showed that the presence of CTAB at a heteropolyacid montmorillonite clay-modified GCE enhanced the electrode response and hence the stripping voltammetric determination of isoproturon (ISO), carbendazim (CAR) and methylparathion (MP), leading to low limits of detection (1, 10 and 20 ng mL⁻¹ for ISO, CAR and MP respectively; Manisankar et al., 2006). Significant advances have also been noticed in the field of CFMEs via the use as electrode modifiers of organoclays issued from the intercalation of cationic surfactants in the interlayer space of montmorillonite. In fact, the presence of surfactant within the clay gallery changes the inherent properties of the latter from hydrophilic to organophilic, leading thereby to a hybrid material useful for the uptake of organic pollutants. Thus, Tcheumi et al. (2010) exploited a gemini surfactant intercalated montmorillonite complex to efficiently accumulate methylparathion pesticide. By increasing the concentration of the dimeric surfactant in the clay, they observed the enhancement of the electrode response due to the hydrophobic character of the organoclay and to favourable hydrophobic-type interactions towards MP. This modified electrode allowed the stripping determination of methylparathion with a detection limit of 7×10^{-8} M.

3.4 Immobilized enzyme electrodes

Electrochemical biosensors have attracted much attention over the last two decades for environmental chemistry. A biosensor can be defined as an analytical device which tightly converts a biological response to a quantifiable and processable signal (Grieshaber et al., 2008). The basic principles and architectures of electrochemical biosensors have been reviewed by several authors (Pohanka et al., 2001; Mulchandani et al., 2001; Mostafa, 2010). A typical biosensor for pesticides detection is formed by three main components: the bioreceptor (enzyme) coupled to an electrochemical interface (electrode), and an electronic system designed to convert the biological response from the electrode into a quantifiable and processable signal (Scheme 2). The steps involved in the analysis process, described in detail by Davis et al. (2007) are summarized as follows: once the electrode is exposed to a pesticide solution, an interaction occurs between the pesticide and the enzyme, diminishing or destroying completely its activity.



Scheme 2. Major components of a typical biosensor for pesticide detection

This inhibition can then be easily quantified by further exposure to the initial substrate concentration and comparison with the response prior to pesticide exposure. Numerous works have been undertaken during the last couple of decades on the exploitation of electrochemical biosensors for pesticides monitoring, and some of the best limits of detection (LOD) achieved are summarized in Table 1.

Pesticide	*Biorecept or	Technique	Limit of detection	Reference
Parathion	PH	Amperometry	1 ng L ⁻¹	Sacks et al., 2000
Parathion Paroxon	PH	Amperometry	15 nM 20 nM	Chough et al., 2002
Parathion Carbaryl	AChE	Cyclic voltammetry	**9.0- 0.3 µg L ⁻¹	Pedrosa et al., 2008
Carbaryl	AChE	Amperometry	5 x 10 ⁻⁵ M	Josiane & Sergio, 2008
Paraoxon Parathion	OPH	Potentiometry	2 x 10 ⁻⁶ M	Schöning et al., 2003
Paraoxon Methylparathion	OPH	Amperometry	9 x 10 ⁻⁸ M 7 x 10 ⁻⁸ M	Mulchandani et al., 2001
Carbofuran Paraoxon	AChE BuChE	Amperometry	0.2 nM 0.6 nM	Albareda et al., 2001
Carbofuran Dichlorvos	ChO ChE	Amperometry	0.01 ppb 1.3 x 10 ⁻³ ppb	Snejdarkova et al., 2003
Carbofuran	AChE	Amperometry	1 nM	Olga & Jon, 2007
Carbaryl Carbofuran	AChE ChO	Amperometry	2 µg mL ⁻¹	Palchetti et al., 1997
Methylparathion Diazinon Carbofuran Carboy	Tyr	Amperometry	6 ppb 19 ppb 5 ppb 10 ppb	Yaico et al., 2007
Diazinon Dichlorvos	Tyr	Amperometry	5 µM 75 µM	Everett & Reichnitz, 1998
Ziram Diram	Tyr	Amperometry	0.074 µM 1.3 µM	Perez-Pita et al., 1997
Ethylparaoxon	AsO	Amperometry	1 ppm	Rekha et al., 2000

*See section 6 for abbreviations - **The detection range is for both pesticides

Table 1. Description of some enzymatic biosensors used for direct detection of pesticides

The detection of pesticides at low levels can't easily be achieved by direct detection of the pesticide itself, but rather by the detection of its inhibitory effects on enzyme reaction (Davis et al., 2007). However, Schöning et al. (2003) realized a miniaturized enzyme biosensor for the direct determination of organophosphorus pesticides using an organophosphorus hydrolase modified semiconductor. This sensor showed certain selectivity and stability as it allowed the discrimination between organophosphorus and other pesticides, requiring a single-step and showing a long period of stability. A wide range of immobilization techniques were investigated on mutant acetylcholinesterase enzymes, giving rise to

sensitive and selective sensors which were used to measure concentrations of several enzymes down to levels hitherto undetectable (Davis et al., 2007).

One could also mention a quite simple method proposed by Pedrosa et al. (2008) for the detection of parathion and carbaryl in natural waters and in food samples using a self-assembled monolayer (SAM) acetylcholinesterase electrochemical biosensor. From this investigation, the usefulness of the SAM for the fabrication of the biosensor was demonstrated as its deposition on the gold electrode used as electrical interface did not inhibit the electron transfer process between this gold electrode and the electrolyte. Despite these relevant works, the lack of selectivity in most cases is to be mentioned. In fact, immobilized enzymes are often inhibited by many chemicals such as heavy metals and other electroactive species likely to coexist in the matrix to be analysed. Additionally, multi-step protocols are required for analysis with inhibition based sensors, limiting thereby their application for on-site monitoring (Schöning et al., 2003). At present, there are several types of electrochemical biosensors exploited for the recognition followed by the quantification of pesticides. The works exposed in this section have shown that the construction of new and efficient biosensors could be expected by different immobilization strategies taking into consideration the nature of the transducer material, the long-term stability and the selectivity of the final device.

4. Practical considerations and validation of voltammetric methods

The first thing to be considered for an electrochemical experiment is the availability of equipments. The required basic instruments includes an electrochemical cell (in a three electrode configuration in most cases), the voltamperometric analyser formed by a potentiostat (main component) coupled to a computer in modern tools. Some other specific components such as a faradaic cage or a deoxygenating gas tube could be added when required, depending on the exigencies of the experiment.

Nowadays, a large number of voltammetric analysers are commercially supplied at relatively modest prices, so that from 5000 € (in 2011) one can intend to perform experiments on a voltammetric system interfaced to a computer. For more information on modern and miniaturised instrumentation, one can consult the current suppliers websites presented in Table 2.

After the instrumentation, some practical criteria to be taken into consideration for a voltammetric method designed for environmental monitoring are closely related to selectivity, sensitivity and accuracy. For sensors, the stability, the reproducibility and the cost of the global sensing procedure are some key parameters to be properly evaluated.

Table 3 summarizes some low detection limits achieved at carbon paste and film electrodes chemically modified within the past two decades. For practical guidance, the electrode configuration and the nature of the supporting electrolyte are provided.

The characteristics of sensors are hereafter summarized according to definitions formulated by the Analytical Chemistry Division of the International Union of Pure and Applied Chemistry (Kutner et al., 1998).

Concerning the selectivity and sensitivity, the modifier agent for biosensors and modified electrodes should be conveniently chosen on the basis of selective and favourable interactions towards the analyte, improving thereby the device selectivity. Moreover, the detection limit should be sufficiently low for the purpose envisaged.

Supplier name	Website
Radiometer analytical (France)	www.radiometer-analytical.com
BASi (USA)	www.BASInc.com
EG&G PAR (USA)	www.egg.inc.com/par
BioLogic (USA)	www.bio-logic.us
Eco Chemie (The Netherlands)	www.brinkmann.com
Solartron (USA)	www.solartron.com
Palm Instruments (The Netherlands)	www.Palmsens.com
CH-Instruments (USA)	www.chinstruments.com
Dropsens (Spain)	www.dropsens.com

Table 2. Some common electrochemical instrumentation suppliers

*Electrode configuration	*Supporting electrolyte	Analyte	LOD	Reference
CPEs modified with a ferophthalocyanine and immobilized enzyme	50 mM PB (pH 7.5)	Paraoxon Carbofuran	10 ⁻¹⁰ M	Anton et al., 2003
CPE modified with tricresylphosphate	BRB (pH 7.0)	Thiamethoxam	7.29 µg mL ⁻¹	Papp et al., 2010
CPE modified with sepiolite (clay)	BRB (pH 4.0)	Dinoseb Dinoterb	10 ⁻¹⁰ M 5.4 x 10 ⁻¹⁰ M	Sreedhar et al., 2003
Blank CPE	0.2 M AB (pH 5.2)	Methylparathion	0.05 µM L ⁻¹	Liu & Lin, 2005
CPE modified with ZrO ₂ nanoparticles	AB (pH 5.25)	Methylparathion	2 ng mL ⁻¹	Parham & Rahbar, 2010
CPE modified by amberlite XAD-2 resin	0.1 M AB (pH 6)	Paraquat	0.1 mg L ⁻¹	Alvarez et al., 1992
CPE covered by a enzymatic membrane	PB (pH 7.3)	Heptenophos	0.3 mg L ⁻¹	Skladal, 1992
GCE modified by PEDOT*	C ₂ H ₅ OH/H ₂ O (50%, v/v) of 0.1 M H ₂ SO ₄ /0.1 M KOH or BRB	Dicofol Cypermethrin Monocrotophos Chlorpyrifos Phosalone	11.20 mg L ⁻¹ 2.50 µg L ⁻¹ 2.23 µg L ⁻¹ 305 µg L ⁻¹ 1.80 µg L ⁻¹	Manisankar et al., 2005a
GCE covered by a thin film of sodium MMT	0.1 M H ₂ SO ₄ in C ₂ H ₅ OH/H ₂ O (50%, v/v) /0.1 M KOH / 0.1 M KCl or BRB	Carbendazim Isoproturon	5 ng mL ⁻¹ 1 ng mL ⁻¹	Manisankar et al., 2005b
GCE covered by a film of heteropolyacid MMT	0.1 M H ₂ SO ₄ in C ₂ H ₅ OH/H ₂ O (50%, v/v)	Isoproturon Carbendazim Methylparathion	1 ng mL ⁻¹ 10 ng mL ⁻¹ 20 ng mL ⁻¹	Manisankar et al., 2006
MWCNT-GCE PAN-MWCNT-GCE PPY-MWCNT-GCE	C ₂ H ₅ OH/H ₂ O (50%, v/v) of 0.1 M H ₂ SO ₄ /0.1 M NaOH or BRB	Isoproturon Voltage (RS) Dicofol	0.1 µg L ⁻¹ 0.01 µg L ⁻¹ 0.05 µg L ⁻¹	Manisankar et al., 2008
GCE modified by a dimeric surfactant intercalated MMT	0.1 M AB (pH 5)	Methylparathion	7 x 10 ⁻⁸ M	Tcheumi et al., 2010
Fe-TAP-MWCNTP-PGE	0.1 M PB (pH 12) + 0.05 M Na ₂ SO ₄	Amitrole	0.5 nM	Siswana et al., 2008
Graphite covered by PTFE	PB (pH 7.4)	Thiram	12.9 µg L ⁻¹	Fernandez et al., 1995
pNITSPc/Nafion-CFME	0.2 M AB (pH 5.2)	Methylparathion	0.1 mg mL ⁻¹	Sbai et al., 2007
pNITSPc/p-PPD-CFME	0.2 M AB (pH 5.2)	Methylparathion	40 µg L ⁻¹	Tapsoba et al., 2009

*See section 6 for abbreviations.

Table 3. Some best detection limits achieved within the two past decades on carbon paste and film coated electrodes for pesticide analysis.

The linear concentration range should be as large as possible, and the calibration highly reproducible. The modification procedure leading to the chemically modified electrode or to the biosensor should be easy to perform; for biosensor especially, the immobilization of the bioreagent should be permanent whilst the enzyme activity is kept free from deterioration and devaluation. The measurements should be sufficiently reliable and repeatable.

5. Future trends in pesticides control by voltammetric methods

In this chapter, the role voltammetric methods play for the monitoring of pesticides both in environment and food has been examined. This was done by reviewing momentary various methods and their possible combinations leading to efficient tools for the electroanalysis of pesticide molecules. Key learnings on the electrochemical sensors were discussed, and the summarizing of the recent advances demonstrates that the sensors up-to-date described offer high sensitivity and fast analysis, and can be used under field conditions. As proven by the number of applications reviewed, it appears that voltammetric methods are extensively applied for the detection of pesticides in various matrices. Moreover, voltammetry constitutes an alternative to chromatographic and spectroscopic methods usually used for the determination of pesticides.

Concerning the monitoring of pesticides, future trends will be the development of innovative technology for miniaturised and disposable tools combining the following features: stability, high selectivity, highest accuracy and low detection limits. These tools may also meet the requirements for on field detection and real-time analysis by non specialised operators. Thus, some key areas offering great promise in the elaboration of new electroanalytical strategies may be properly developed, which include new electrode configurations, miniaturized devices and the preparation of new nanocomposite materials.

5.1 New electrode configurations

In order to improve the sensing ability of voltammetric techniques, significant efforts are being made nowadays. The miniaturization of working electrodes has led to the emergence of microelectrodes that are electrodes with at least one dimension not greater than 25 μm (Wang, 2006). In comparison with conventional working electrodes, such electrodes present several advantages: their small size allows their use in the study of reactions and electrodic processes in lower conductivity solvents and in the absence of the supporting electrolyte, thereby minimizing the cost of sample manipulations. Moreover, microelectrodes can be used to explore microscopic domains, to measure local concentration profiles (in vivo analysis) whilst offering lowered limits of detection in microflow systems.

A wide operability of microelectrodes was demonstrated by de Souza et al. who reported the use of gold microelectrode and square wave voltammetry for the analytical determination of low concentration of dichlorvos pesticide in pure and natural water samples (2005a) in one hand, and trace amounts of paraquat in lemon and orange juice samples (2005b), in natural water, food and beverages (2006) in the other hand. Experiments were performed without any pre-purification or preparation step of the samples.

Sbai et al. (2007) reported for the first time the use of a carbon fiber microelectrode modified with combinations of nickel(II) tetrasulfonated phthalocyanine and nafion films for a rapid detection of methylparathion pesticide. The advantage of nickel complexes-based associated to nafion coating as new electrode material was thus demonstrated. That work was further extended by Tapsoba et al. (2009) who exploited the same nickel(II) complex but now

electroformed, in combination with a para-phenylenediamine electropolymerized coating to detect methylparathion for concentrations up to 40 $\mu\text{g/L}$. Taking in to advantage the practical applicability of wall-jet electrode in stripping analysis, that is maintaining under well-developed convection-diffusion conditions the flux of electroactive analyte to the working electrode; Manisankar et al. (2005a) studied the electrochemical behaviour of some pesticides on a poly 3,4-ethylenedioxythiophene modified wall-jet electrode. These few examples reveal the possibility to exploit unmodified or chemically modified microelectrodes for the construction of sensitive devices for pesticide monitoring.

5.2 Miniaturized devices

The development of miniaturized and disposable voltammetric sensors is undoubtedly a challenge for coming research work devoted to environmental and food control. Although the size of a sensor is not so important for environmental monitoring, the growing tendency towards miniaturization is observed nowadays for several reasons: (i) research laboratories need to reduce the amount of used chemicals which have an impact not only on the environment (secondary pollution) but also on the economy (Suzuki, 2000; Rodriguez-Mozaz et al., 2004); (ii) inexpensive, easy-to-handle and small size sensors are suitable for on-field screening applications; (iii) the need to minimize sample pre-treatment in order to reduce analysis time and allow probing of natural speciation (Brett, 2001).

Biosensing is extremely important for pesticides control; fortunately, electrochemical biosensors do not require heavy and sophisticated equipment for the signal processing (Pijanowska & Torbicz, 2005). In addition, biosensors are easy to calibrate. Hence, miniaturized biosensors able to provide results in real time are regarded as cost-effective and portable analytical tools. In this sense, disposable carbon paste electrodes with embedded enzyme, screen-printed electrodes covered by a pesticide recognition compound are also potential options for the elaboration of sensitive working electrodes. Screen-printed electrodes based on thick-film hybrid technology offer a number of advantages: they are convenient for works on microvolumes and for decentralized assays. The feasibility of this particular aspect has been proven by Suprun et al. (2005) who reported on the use of a screen-printed carbon electrode for the detection of aldicarb, paraoxon and methylparathion

5.3 New electrode materials for biosensors

The preparation of nanomaterials-modified electrochemical transducers could be extended, based for example on the conjugation of adsorptive carbon nanotubes and electroactive polymers on which enzymes as organophosphatase should be immobilized for the detection of organophosphorus pesticides. Such a combination may improve the electrochemical properties of transducers: fast electron transfer or high signal to noise ratio along with sensitivity and selectivity. Some key reviews on the nanotechnology immobilization of enzymes for the elaboration of biosensors have been published (Merkoci & Alegret, 2005; Davis et al., 2007; Kumar, 2007; Merkoci, 2009; Stoytcheva et al., 2011) that demonstrate the interest of several nanomaterial-enzyme configurations.

6. List of abbreviations

AB: Acetate buffer

AChE: Acetylcholine esterase

ADH: Aldehyde deshydrogenase

AsO: Ascorbate oxydase
BRB: Britton Robinson buffer
BuChE: butyrylthiocholine esterase
CFME: Carbon fiber microelectrode
ChE: Choline esterase
ChO: Choline oxydase
CPE: Carbon paste electrode
Fe-TAP-MWCNT-PGE: Iron(II) tetra-aminophthalocyanine electropolymerized onto a MWCNT-modified basal plane pyrolytic graphite electrode
GCE: Glassy carbon electrode
MMT: Montmorillonite
MWCNT: Multiwalled carbon nanotubes
MWCNT-GCE: MWCNT film coated GCE
OPH: Organophosphorus hydrolase
PAN: Polyaniline
PAN-MWCNT-GCE: PAN electrodeposited on MWCNT-GCE
PB: Phosphate buffer
PEDOT: Poly 3,4-ethylenedioxythiophene
PH: Parathion hydrolase
pNITSPc/Nafion-CFME: Polytetrasulfonated phthalocyanine/nafion film coated on a CFME
pNITSPc/p-PPD-CFME: Polytetrasulfonated phthalocyanine/*para*-phenylenediamine film coated on a CFME
PPY: Polypyrrole
PPY-MWCNT-GCE: PPY electrodeposited on MWCNT-GCE
PTFE: Polytetrafluoroethylene
Tyr: Tyrosinase

7. Conclusion

A description of the state of art and a global overview of voltammetric methods currently developed and applied for the determination of pesticides residues in real environmental matrices and food were provided. By a comparative approach, the usefulness of voltammetry and its advantages towards classical methods of pesticides analysis were also demonstrated. A focus has been given to practical considerations, as pesticides form a wide range of compounds, the electrochemical behavior of each of them being strongly related to its physicochemical properties. The constitution, the preparation methods and the specific features of chemically modified electrodes that have found numerous important applications for the detection of pesticides during the past two decades were also presented, and a brief discussion on future trends in the electroanalysis of pesticides using non conventional electrodes discussed.

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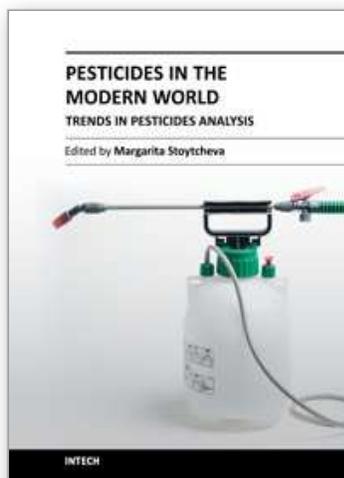
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The book offers a professional look on the recent achievements and emerging trends in pesticides analysis, including pesticides identification and characterization. The 20 chapters are organized in three sections. The first book section addresses issues associated with pesticides classification, pesticides properties and environmental risks, and pesticides safe management, and provides a general overview on the advanced chromatographic and sensors- and biosensors-based methods for pesticides determination. The second book section is specially devoted to the chromatographic pesticides quantification, including sample preparation. The basic principles of the modern extraction techniques, such as: accelerated solvent extraction, supercritical fluid extraction, microwave assisted extraction, solid phase extraction, solid phase microextraction, matrix solid phase dispersion extraction, cloud point extraction, and QuEChERS are comprehensively described and critically evaluated. The third book section describes some alternative analytical approaches to the conventional methods of pesticides determination. These include voltammetric techniques making use of electrochemical sensors and biosensors, and solid-phase spectrometry combined with flow-injection analysis applying flow-based optosensors.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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