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# Organophosphorus Pesticides Analysis

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## 1. Introduction

The organophosphorus (OP) pesticides are synthetic esters, amides, or thiol derivatives of the phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids (Corbett et al., 1984; Eto, 1974; Gupta, 2006; Hassall, 1982; Quin, 2000). The structural diversity of this family of compounds is reflected in their physicochemical and biological properties: vapour pressure, solubility in water, chemical stability and toxicity (Corbett et al., 1984; Hassall, 1982; WHO, 1986), which determine their specific application (Hassall, 1982). Compared to the mostly banned in U.S. and Europe organochlorine pesticides, the OP ones are less persistent in the environment, are not subject of bioaccumulation and biomagnification, and do not release toxic break down products (Krieger, 2001). These features justify their application in the agricultural and veterinary practices of the modern world. In 1999 the OP insecticides represented  $\approx 37\%$  of the pesticides in use at a global scale (Table 1) and 72% of the insecticides used in U.S. (Kiely et al., 2004). The top ten OP insecticides active ingredients include malathion, chlorpyrifos, terbufos, diazinon, methyl-parathion, phorate, acephate, phosmet, azinphos-methyl, and dimethoate (Kiely et al., 2004).

Consumption, tons	Year								
	1990	1991	1992	1993	1994	1995	1996	1997	1998
OP insecticides	49446	48919	52472	53961	50321	63998	66620	71338	65578
Pesticides total	318528	311415	304063	276699	307901	327488	320934	324942	193491
% OP	15.52	15.70	17.25	19.50	16.34	19.54	20.76	21.95	33.89

Consumption, tons	Year								
	1999	2000	2001	2002	2003	2004	2005	2006	2007
OP insecticides	62653	48685	32507	13829	15495	20944	26724	18629	12377
Pesticides total	167912	252176	245064	179724	180897	202817	232515	234688	105940
% OP	37.31	19.31	13.26	7.69	8.56	10.33	11.49	7.94	11.68

Table 1. Summary of the annual OP insecticides consumption (metric tons of active ingredients) and of the annual total pesticides consumption (metric tons of active ingredients), according to the Statistics Division of the Food and Agriculture Organization of the United Nations (FAOSTAT, 1990-2007).

Nevertheless, because of the high acute toxicity of the OP pesticides (Eddleston et al., 2008; Gupta, 2006; Roberts & Aaron, 2007), as well as because of the registered chronic effects (Gupta, 2006), the OP pesticides residues limits in food, drinking water and environmental

samples are subject of regulation and control. The European Council Directive 98/83/EC on the quality of water intended for human consumption (Council Directive 98/83/EC, 1998) sets the limit value of the individual pesticides in drinking water at  $0.1 \mu\text{g L}^{-1}$  and that of the total pesticides at  $0.5 \mu\text{g L}^{-1}$ . According to the U.S. Environmental Protection Agency Office of Ground Water and Drinking Water (OGWDW), the health advisory levels for some OP pesticides in drinking water are: diazinon  $3 \mu\text{g L}^{-1}$ , parathion-methyl  $2 \mu\text{g L}^{-1}$ , disulfoton  $1 \mu\text{g L}^{-1}$ , fenamiphos  $2 \mu\text{g L}^{-1}$ , etc., the following 22 OP pesticides being on the U. S. National Pesticide Survey List: diazinon, dichlorfos, dicrotophos, dimethoate, diphenamiphos, sulfone, disulfoton, disulfoton sulfone, disulfoton sulfoxide, fenamiphos sulfone, fenamiphos sulfoxide, fenitrothion, methyl paraoxon, mevinphos, monocrotophos, omethoate, parathion ethyl, phosphamidon, stirophos, terbufos, tetrachlorvinphos, and merphos. At this time, four European Council Directives (Council Directive 76/895/EEC, 1976; Council Directive 86/362/EEC, 1986; Council Directive 86/363/EEC, 1986; Council Directive 90/642/EEC, 1990) set the maximum residue limits (MRLs) for pesticides in food commodities. Other organisations involved in establishing the pesticide residues levels are the World Health Organization (WHO), the Food and Agricultural Organization of the United Nations (FAO), the Codex Alimentarius Commission, and the U.S. Environmental Protection Agency (EPA). Currently, EPA is reassessing pesticide residue limits in food to ensure that they met the safety standard established by the Food Quality Protection Act of 1996 (FQPA, 1996). Some relevant data on MRLs are presented in Table 2.

Pesticide	MRLs (varie according to the product, $\text{mg kg}^{-1}$ )		Pesticide	MRLs (varie according to the product, $\text{mg kg}^{-1}$ )	
	EC	Codex		EC	Codex
acephate	0.05-0.2	0.01-50	malathion	0.02-8	0.01-20
azinphos-methy	0.01-0.5	0.05-10	Parathion-methyl	0.02-5	0.05-1
chlorpyrifos	0.05-5	0.01-5	phorate	0.02-1	0.05-0.1
diazinon	0.01-5	0.01-5	phosmet	0.05-10	0.05-0.2
dimethoate	0.02-2	0.05-5	terbufos	0.01	0.05-0.3

Table 2. Maximum residue limits (MRLs) of pesticides in or on food and feed of plant and animal origin, set by the European Council (EC) regulation No 396/2005 (Reg. EC No 396/2005), and MRLs in food set by the Codex Alimentarius Commission (Codex pesticides residues in food online database, 1996)

The MRL of a number of OP pesticides is set up at or about the limit of their determination by the currently available analytical methods. Thus, in this work are reviewed the developed during the last years (2005-2011) procedures for OP pesticides analysis, including sample pretreatment and determination in the context of the implementation of modern reliable, high sensitive, selective, rapid, cost-effective and environmental friendly analytical techniques for OP pesticides residues quantification. This overview comments on their advantages and limitations.

## 2. Organophosphorus pesticides analysis

The revision of 115 original publications covering the period 2005-2011 and of 40 reviews demonstrated that the techniques applied for OP pesticides analyses are mostly

chromatographic (gas chromatography and liquid chromatography), electrochemical, immunochemical, and biosensors based ones (Fig. 1).

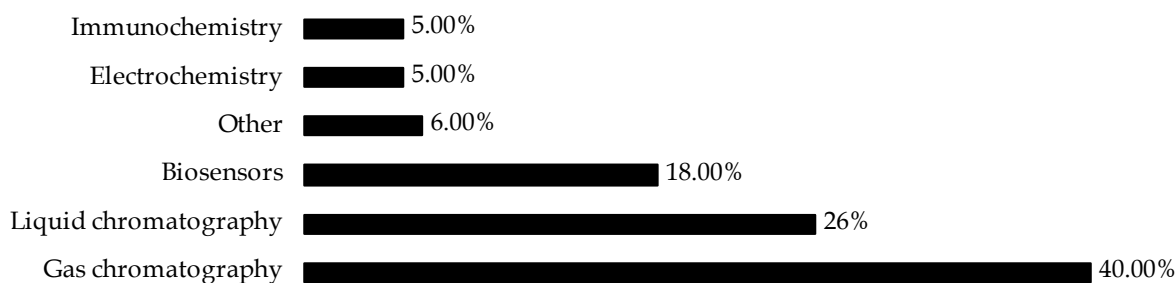


Fig. 1. Techniques applied for OP pesticides analysis (2005-2011)

### 2.1 Chromatographic methods for OP pesticides analysis

Chromatography is considered as a powerful analytical technique regarding the analysis of complex matrices. However, the method requires sample pretreatment, which reaches 60% of the total analysis time. Hence, the development of time-saving, jointly with effective and economic procedures is of crucial importance. Some recent publications provide an overview of the promising techniques: solid-phase extraction, solid-phase microextraction, stir-bar sorptive extraction, matrix solid-phase dispersion, solvent extraction, liquid-phase microextraction, super critical fluid extraction, ultrasonication extraction, microwave-accelerated extraction, and membrane-assisted methods, applied to various matrices (Beyer & Biziuk, 2008; Gilbert-López et al., 2009; Hyötyläinen & Riekkola, 2008; Picó et al., 2007; Pinto et al., 2010; Rial-Otero et al., 2007).

The tendencies in the application of gas chromatography and liquid chromatography to pesticides residues determination in environmental samples and food, together with sample preparation procedures are revised by several authors (Le Doux, 2011; Pareja et al., 2010; Sharma et al., 2010; Yusà et al., 2009). The trends in liquid chromatography-mass spectrometry and liquid chromatography-tandem mass spectrometry development are highlighted in the published in 2007, 2009, and 2010 reviews (Kuster et al., 2009; Malik et al., 2010; Petrovic et al., 2010; Soler & Picó, 2007).

The original research works devoted to OP pesticides analysis applying various chromatographic techniques: gas chromatography-mass spectrometry (Baugros et al., 2008; Chen & Huang, 2006; Cortés-Aguado et al., 2008; Cunha et al., 2009; Filho et al., 2010a, 2010b; Hassan et al., 2010; Kolberg et al., 2011; Lavagnini et al., 2011; Lesueur et al., 2008a, 2008b; Li et al., 2011b; Libin et al., 2006; López-Feria et al., 2009; Nguyen et al., 2008; Nguyen et al., 2010; Pang et al., 2006; Rodrigues et al., 2010; Silva et al., 2008; Sinha et al., 2006; Toledano et al., 2010; Wang et al., 2007; Wang et al., 2011; Wu et al., 2011; Yang et al., 2011), gas chromatography-tandem mass spectrometry (Barco-Bonilla et al., 2010; Camino-Sánchez et al., 2008; Frenich et al., 2006; Fuentes et al., 2008, 2009; García-Rodríguez et al., 2010; Lee et al., 2008; Qu et al., 2010; Walorczyk, 2008; Walorczyk & Gnusowski, 2009), gas chromatography-ion trap mass spectrometry (González-Rodríguez et al., 2008; Przybylski & Hommet, 2008), gas chromatography time-of-flight mass spectrometry (Hernández et al., 2010; Portolés et al., 2011), high performance liquid chromatography (Akkad et al., 2010; Al-Degs et al., 2009; He et al., 2009; Pérez-Ruiz et al., 2005; Wu et al., 2010; Zhu et al., 2007), high performance liquid chromatography-electrospray ionization-mass spectrometry (Sinha et al., 2010), liquid

chromatography-ion trap-triple stage mass spectrometry (Blasco et al., 2005; Lesueur et al., 2008b), liquid chromatography-mass spectrometry (Inoue et al., 2007; Liu et al., 2005, 2006), liquid chromatography tandem mass spectrometry (Baugros et al., 2008, 2009; Chung & Chan, 2010; Dagnac et al., 2009; Díaz et al., 2008; Dujaković et al., 2010; García-Valcárcel & Tadeo, 2009; Hernández et al., 2006; Kujawski & Namieśnik, 2010; Pang et al., 2006; Pinxteren et al., 2009; Radišić et al., 2009; Salma et al., 2009), and nano-liquid chromatography (Buonasera et al., 2009) comment on the sample preparation procedure, the detection system, and the analytical performances of the method with emphasis on its optimization.

Sample preparation procedures include a large variety of techniques: solid-phase extraction (Al-Degs et al., 2009; Dujaković et al., 2010; Portolés et al., 2011; Wang et al., 2010; Yang et al., 2011; Zhu et al., 2007), solid-phase extraction using carbon nanotubes (López-Feria et al., 2009; Wang et al., 2007), solid-phase microextraction (Chai et al., 2009; Cortés-Aguado et al., 2008; Filho et al., 2010a, 2010b; Tsoutsis et al., 2006), solid-phase microextraction using a new sol-gel hybrid coating (Ibrahim et al., 2010), solid-phase dispersion (Libin et al., 2006; Radišić et al., 2009; Ramos et al., 2009; Silva et al., 2008), headspace-solid-phase microextraction (Rodrigues et al., 2010), microwave-assisted extraction coupled to solid-phase extraction or different clean-up methods (Fuentes et al., 2008, 2009), single-drop microextraction (Ahmadi et al., 2006; Xiao et al., 2006; Pinheiro et al., 2009), cloud point extraction coupled with ultrasonic-assisted back-extraction (Zhao et al., 2011), solvent extraction (Dugo et al., 2005; Fenoll et al., 2007; Georgakopoulos et al., 2009; González-Rodríguez et al., 2008; He et al., 2009; Hernández et al., 2006; Liu et al., 2005; Pang et al., 2006; Sinha et al., 2006, 2010; Walorczyk & Gnusowski, 2009), accelerated solvent extraction and gel permeation clean-up (Wu et al., 2011), membrane-assisted solvent extraction (Pinxteren et al., 2009), ultrasonic solvents extraction (García-Valcárcel et al., 2009; Lesueur et al., 2008b; Wu et al., 2010), liquid-liquid extraction (Kujawski & Namieśnik, 2010; Nguyen et al., 2010), low density miniaturized homogeneous liquid-liquid extraction (Hassan et al., 2010), liquid-liquid extraction and low temperature purification (Pinho et al., 2010), liquid extraction and programmed temperature vaporization (García-Rodríguez et al., 2010), dispersive liquid-liquid microextraction (Cunha et al., 2009), pressurized liquid extraction (Barco-Bonilla et al., 2010; Baugros et al., 2009; Blasco et al., 2005), hollow fiber sorptive extraction (Li et al., 2011b), hollow fiber-protected liquid-phase microextraction (Chen & Huang, 2006), stir-bar sorptive extraction-thermal desorption (Lavagnini et al., 2011), as well as the developed in 2003 (Anastassiades et al., 2003) quick, easy, cheap, effective, rugged and safe (QuEChERS) method (González-Curbelo et al., 2011; Kolberg et al., 2011; Lee et al., 2008; Lesueur et al., 2008a; Nguyen et al., 2008; Walorczyk, 2008). Some of these techniques like solid phase extraction and solid-phase microextraction in particular are commonly accepted. Advantage of the solid phase microextraction is the possibility of automation. Liquid-phase microextraction, as a relatively new procedure, does not find a large application at this time. The developed approaches are intended to reduce the sample preparation time, the solvent consumption and the amount of the sample, and to achieve high selectivity, applying simple, rapid, effective, and inexpensive methods, compatible with modern analytical techniques.

Other methods aimed to ensure a high sensitivity of the determination, in concert with the reliable sample preparation technique, apart of the mentioned above, are: gas chromatography with nitrogen-phosphorus detection (Fenoll et al., 2007; Georgakopoulos et al., 2009; Pagliuca et al., 2005; Ravelo-Pérez et al., 2008), gas chromatography with flame thermionic detection (Tsoutsis et al., 2006), gas chromatography with electron capture detection (Chai & Tan, 2009; Guardia-Rubio et al., 2007; Ibrahim et al., 2010; Pinho et al.,



2010; Ramos et al., 2009), gas chromatography with flame photometric detection (Ahmadi et al., 2006; Wang & Du, 2010; Xiao et al., 2006; Zhao et al., 2011), gas chromatography with flame ionization detection (Pinheiro, & Andrade, 2009), liquid chromatography with electrochemical flow detection (Trojanowicz, 2010), liquid chromatography with UV detection (Buonasera et al., 2009), high performance liquid chromatography with UV detection (Zhu et al., 2007), high performance liquid chromatography with fluorimetric detection (Pérez-Ruiz et al., 2005), and high performance liquid chromatography with diode array detection (Wu et al., 2010).

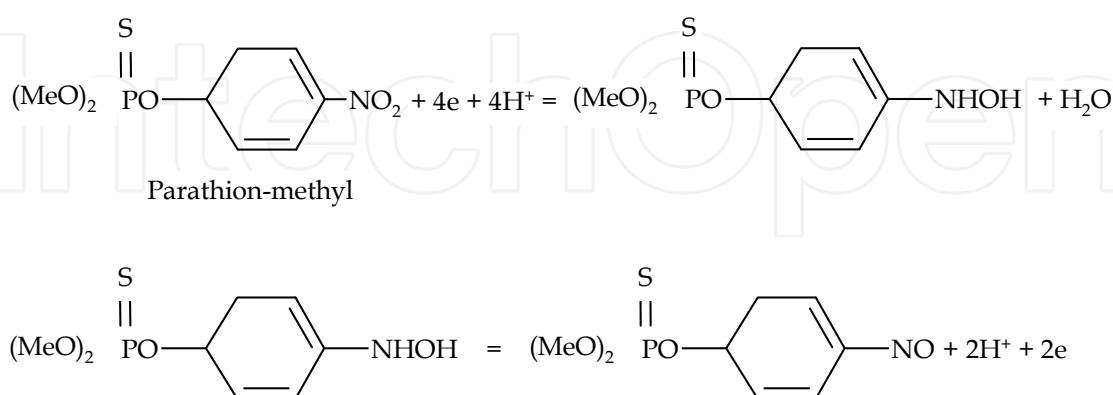
Relevant data collected for the period 2010-2011, revealing the analytical performances of some selected chromatographic methods are summarized in Table 3.

Pesticide	Detection Method	Sample preparation	LOD	References
Atrazine	LC-MS/MS	SE	0.06 $\mu\text{g L}^{-1}$	Sinha et al., 2010
	GS-MS	TOTAD	0.05 $\mu\text{g L}^{-1}$	Toledano et al., 2010
Chlorpyrifos	GC-MS	LLSE	0.13 $\mu\text{g kg}^{-1}$	Hassan et al., 2010
	GC-ECD	LLE	14.0 $\mu\text{g kg}^{-1}$	Pinho et al., 2010
Diazinon	GC-QqQ MS/MS	DSPE	0.37 $\mu\text{g kg}^{-1}$	Qu et al., 2010
Dichlorvos	GC-MS	ASE	6.00 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	GC-MS	HS-SPME	3.80 $\mu\text{g L}^{-1}$	Rodrigues et al., 2010
	GC-QqQ MS/MS	DSPE	1.50 $\mu\text{g kg}^{-1}$	Qu et al., 2010
Paraoxon	GC-MS	ASE	1.10 $\mu\text{g kg}^{-1}$	Wu et al., 2011
Malathion	GC-MS	ASE	0.20 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	GC-MS	SPME	0.03 $\mu\text{g L}^{-1}$	Filho et al., 2010b
	GS-MS	TOTAD	0.07 $\mu\text{g L}^{-1}$	Toledano et al., 2010
	GC/PFPD	SPE	0.03 $\mu\text{g L}^{-1}$	Wang et al., 2010
	GC-MS	SPME	2.00 $\mu\text{g kg}^{-1}$	Filho et al., 2010a
	GC-QqQ MS/MS	DSPE	0.22 $\mu\text{g kg}^{-1}$	Qu et al., 2010
Parathion	GC-MS	ASE	0.20 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	GC-MS	HS-SPME	4.70 $\mu\text{g L}^{-1}$	Rodrigues et al., 2010
	HPLC-DAD	UASEME	0.10 $\mu\text{g L}^{-1}$	Wu et al., 2010
	GS-MS	TOTAD	0.12 $\mu\text{g L}^{-1}$	Toledano et al., 2010
	GC/PFPD	SPE	0.02 $\mu\text{g L}^{-1}$	Wang et al., 2010
	GC-QqQ MS/MS	DSPE	1.50 $\mu\text{g kg}^{-1}$	Qu et al., 2010
Parathion-methyl	GC-MS	ASE	0.80 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	GC-MS	HS-SPME	10.9 $\mu\text{g L}^{-1}$	Rodrigues et al., 2010
	HPLC-DAD	UASEME	0.10 $\mu\text{g L}^{-1}$	Wu et al., 2010
	GC-MS	SPME	0.02 $\mu\text{g L}^{-1}$	Filho et al., 2010b
	GC/PFPD	SPE	0.03 $\mu\text{g L}^{-1}$	Wang et al., 2010
	GC-MS	SPME	5.00 $\mu\text{g kg}^{-1}$	Filho et al., 2010a
Phosmet	GC-MS	ASE	0.50 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	HPLC-DAD	UASEME	0.10 $\mu\text{g L}^{-1}$	Wu et al., 2010
Phorate	GC-MS	ASE	0.70 $\mu\text{g kg}^{-1}$	Wu et al., 2011
	GC-QqQ MS/MS	DSPE	0.62 $\mu\text{g kg}^{-1}$	Qu et al., 2010
Trichlorfon	GC-MS	SPME	0.07 $\mu\text{g L}^{-1}$	Filho et al., 2010b
	GC-MS	ASE	5.1 $\mu\text{g kg}^{-1}$	Wu et al., 2011

Table 3. Analytical performances of some chromatographic methods applied to OP pesticides analysis, namely LOD.

## 2.2 Electrochemical methods for OP pesticides analysis

The electrochemical activity of the OP pesticides containing nitro-phenyl groups: parathion-methyl, parathion, paraoxon, fenitrothion, etc. makes possible their direct electrochemical determination. The mechanism of the redox process, selecting parathion-methyl as a model, is the following:



The electrochemical method of choice applied to OP pesticides analysis, considering the period 2005-2011, is square-wave voltammetry (Li and al., 2011; Parham and Rahbar, 2010; Sbaï et al., 2007; Tan et al., 2010; Wang and Li, 2008). It is recognized as a high sensitive regarding the detection of organic molecules. Current efforts are directed toward sensitivity and selectivity improvement by chemical modification of the electrode surface. The reported techniques include: nano-ZrO<sub>2</sub> modification of a carbon paste electrode (Parham and Rahbar, 2010), fabrication of ZrO<sub>2</sub>/Au nano-composite films on alumina substrates (Wang and Li, 2008), electrodeposition of molecularly imprinted porous silicate (Tan et al., 2010) or of gold-sodium dodecylbenzene sulfonate nanoparticles onto a glassy carbon electrode (Li and al., 2011a), tetrasulfonated phthalocyanine electrodeposition combined with Nafion coating of carbon fibres (Sbaï et al., 2007), etc. ZrO<sub>2</sub> nanoparticles in particular, used as a selective sorbents for solid-phase extraction, demonstrate excellent performance in OP pesticides detection, because of their affinity toward the phosphate group on OP pesticide molecule (Parham and Rahbar, 2010; Wang and Li, 2008).

The developed electrochemical methods are applied for OP pesticides determination in pears (Li and al., 2011; Tan et al., 2010), and in water samples (Parham and Rahbar, 2010). Some relevant data revealing the sensitivity of the determinations are presented in Table 4.

Pesticide	Electrode	Electrode modification	LOD	References
Parathion-methyl	CFME	poly-NiTSPc/Nafion	0.1 mg L <sup>-1</sup>	Sbaï et al., 2007
Parathion-methyl	GC	imprinted silicate	2.5 µg L <sup>-1</sup>	Tan et al., 2010
Parathion-methyl	GC	nano-ZrO <sub>2</sub>	2.0 µg L <sup>-1</sup>	Parham and Rahbar, 2010
Parathion-methyl	GC	nano-Au/SDBS	25 µg L <sup>-1</sup>	Li and al., 2011
Parathion	GC	ZrO <sub>2</sub> /Au	3.0 µg L <sup>-1</sup>	Wang and Li, 2008

Table 4. Analytical performances of square wave voltammetry, applied to OP pesticides analysis, namely LOD.

The analysis of the reported studies confirms that the electrochemical methods have the advantage to be rapid, sensitive, selective, and accurate. In addition, they use affordable, portable, and miniaturized instrumentation. These characteristics make them appropriate for the “*in field*” determination of the low persistent in the environment OP pesticides.

### 2.3 Immunochemical methods for OP pesticides analysis

Only few immunochemical methods for OP pesticides analysis were reported during the surveyed period 2005-2011. Gui and al. (2006) synthesize two haptens of the OP insecticide triazophos and develop an enzyme-linked immunosorbent assay based on monoclonal antibody, demonstrating high affinity and specificity to triazophos. Guo and al. (2009) investigate two formats of gold-labeled antibody lateral-flow strips for the simultaneous detection of triazophos and of the carbamate pesticide carbofuran. The application of the immunogold labeling technique in immunoassays is reviewed by Lai et al. (2010). Garcés-García and al. (2006) point out the development of plate immunoassays for routine determination of residues: diazinon, fenthion, malathion, and chlorpyrifos in extra virgin olive oil. The achieved by the mentioned methods LOD is shown in Table 5.

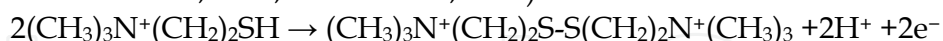
Pesticide	Method	LOD	References
Diazinon	ELISA	46 $\mu\text{g L}^{-1}$	García and al., 2006
Fenthion	ELISA	10 $\mu\text{g L}^{-1}$	García and al., 2006
Malathion	ELISA	16 $\mu\text{g L}^{-1}$	García and al., 2006
Chlorpyrifos	ELISA	17 $\mu\text{g L}^{-1}$	García and al., 2006
triazophos	ELISA	0.1 $\mu\text{g L}^{-1}$	Gui and al., 2006

Table 5. Analytical performances of some immunochemical methods, applied to OP pesticides analysis, namely LOD.

### 2.4 Biosensors based methods for OP pesticides analysis

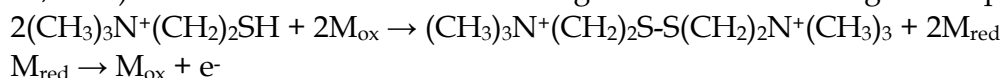
The overview of the publications covering the period 2005-2011 shows that almost all of the described biosensors for OP pesticides analysis are electrochemical ones. The OP pesticides determination is based on the quantification of the acetylcholinesterase inhibition, they provoke. The enzyme activity is determined by electrochemically monitoring the thiocholine formed upon enzymatic hydrolysis of acetylthiocholine. Three alternative routes are explored as response-generating electrochemical reactions:

- i. Direct electrochemical oxidation of thiocholine at 0.80 V/Ag, AgCl (Ivanov et al., 2010; Marinov et al., 2010; Ovalle et al., 2009):



It is important to note that potential lowering and hence interferences elimination could be achieved by using nanostructured materials for electrode modification. Nanoparticles reduce the working potential by catalysing the electrochemical thiocholine oxidation (Du, 2007).

- ii. Mediated thiocholine oxidation at lower electrode potential (0.1÷0.45 V/Ag, AgCl), using cobalt phtalocyanine (Alonso et al., 2010; Law & Higson, 2005), tetracyanoquinodimetane (Hildebrandt et al., 2008) or hexacyanoferrate (III) (Ovalle et al., 2009) as electron mediators in a heterogeneous or in a homogeneous phase:



- iii. Chemisorption of thiocholine at -0.7 V/Ag, AgCl and electrochemical desorption in KOH, giving a measurable reductive peak current (Du et al., 2008).

The majority of the publications report the application of screen-printed electrodes (Alonso et al., 2010; Dondo et al., 2006; Hildebrandt et al., 2008, Law & Higson, 2005) as transducers. Recent developments in the field of screen-printed electrodes and their related applications



are comprehensively reviewed by Renedo et al. (2007). Disposable screen-printed electrodes are considered as an alternative to the traditional electrodes for “*in situ*” analysis.

As immobilization matrices in electrochemical acetylcholinesterase-based sensors for OP pesticides determination were preferentially used various nanomaterials: nanostructured polymer membranes with integrated multiwall carbon nanotubes (Ivanov et al., 2010) or gold nanoparticles (Marinov et al., 2010), multiwall carbon nanotubes-chitosan composite (Du et al., 2007), etc., to achieve sensitivity increase and sensor stability improvement. Recent trends and challenges in developing nanomaterials-based biosensors for OP pesticides detection are discussed by a number of authors (Balasubramanian & Burghard, 2006; Eftekhari, 2008; Gorton, 2005; Guo & Wang, 2007; Kerman et al., 2008; Kumar, 2007; Liu et al., 2008, Luo et al., 2006; Merkoçi & Alegret, 2005; Merkoçi, 2009; Pumera et al., 2007, Wang & Lin 2009).

The alternative route leading to biosensors sensitivity, selectivity and stability increase involves the incorporation in the biosensing platform of biorecognition elements with tailor designed properties. Genetically modified enzymes are extensively used in inhibition based biosensors for OP pesticides determination (Bucur et al., 2005; Marques et al., 2005; Valdés-Ramírez et al., 2008), allowing attaining LOD as low as  $10^{-17}$  M (Sotiropoulou et al., 2005). Current research efforts are reviewed by Campás et al. (2009).

Another important issue associated with electrochemical biosensors development is that concerning chemometrics. It was demonstrated that artificial neural networks implementation could resolve mixtures of pesticides (Alonso et al., 2010).

Exhaustive reviews on enzyme inhibition-based biosensors, including inhibition determination in organic phase are provided by Amine et al. (2006) and López et al. (2006). The application of various enzymes: acetylcholinesterase, acid phosphatase, alkaline phosphatase, organophosphorus hydrolase, and tyrosinase for the quantification of OP pesticides in the environment is extensively revised by Van Dyk et al. (2011).

Another group of electrochemical biosensors for OP pesticides analysis is that of the microbial sensors. Such sensors, based on Clark dissolved oxygen electrode modified with recombinant p-nitrophenol degrading/oxidizing bacteria endowed with OPH activity were reported by Lei et al. (2005, 2006). The surface-displayed OPH catalyzes the hydrolysis of OP pesticides with nitrophenyl substituent to release products, metabolized by the bacteria while consuming oxygen. The oxygen consumption is measured and correlated to the OP concentration.

A microbial biosensor for direct determination of nitrophenyl-substituted organophosphate nerve agents using genetically engineered *Moraxella* sp. has been proposed by Mulchandani et al. (2006). However, the reached LOD is over the OP concentration in environmental samples and higher than that for acetylcholinesterases inhibition-based sensors, immunoassays, and gas, liquid and thin layer chromatography (Mulchandani et al., 2006).

Recently, an electrochemical hybrid biosensor for OP pesticides trace level concentrations determination was developed and characterized (Stoytcheva et al., 2009). It integrates a hybrid biorecognition element consisting of immobilized *Arthrobacter globiformis* and free acetylcholinesterase (ACh) with a Clark type oxygen probe transducer. The bacteria convert the ACh-generated choline to betaine with oxygen consumption measured as a Clark probe current change. This change, representing the sensor response, correlates to the concentration of the OP pesticides inhibiting the ACh catalyzed acetylcholine hydrolysis to choline. Current progress in microbial electrochemical and optical biosensors are reported by Su and al. (2011).

Finally, the few works commenting on optic- and immuno- biosensors development and application to OP pesticides analysis have to be pointed out, too (Llorent-Martínez et al., 2011; Mauriz et al., 2006a, 2006b; Suri et al., 2009). Special attention should be paid to the overview of Jiang and al. (2008), presenting the various transduction systems used in immunosensors: electrochemical, optical, piezoelectric, and nanomechanic, and the immobilization protocols.

Some relevant data are presented in Table 6.

Pesticide	Electrochemical biosensor	LOD	References
Azinphos	Ach/polyaniline carbon/cobalt phtalocyanine	$10^{-10}$ $\mu\text{M}$	Law et al., 2005
Dichlorvos	Ach/polyaniline carbon/cobalt phtalocyanine	$10^{-11}$ $\mu\text{M}$	Law et al., 2005
Chlorpyrifos-oxon	Ach/polyvinyl alcohol/TCNQ/C	$2 \mu\text{g L}^{-1}$	Hildebrandt et al., 2008
Malathion	Ach/AuNPs/chitosan/Au	$0.03 \mu\text{g L}^{-1}$	Du et al., 2008
Paraoxon	Ach/MWCN/poly-(acrylonitrile-methyl-methacrylate-sodium vinylsulfonate)/Pt	$1.39 \times 10^{-6} \mu\text{g L}^{-1}$	Ivanov et al., 2010
Paraoxon	Ach/AuNPs poly-(acrylonitrile-methyl-methacrylate-sodium vinylsulfonate)/Pt	$7.39 \times 10^{-5} \mu\text{g L}^{-1}$	Marinov et al., 2010
Parathion	Ach/polyaniline carbon/cobalt phtalocyanine	$10^{-10}$ $\mu\text{M}$	Law et al., 2005
Triazophos	Ach/MWCNT-chitosan/GCE	$10^{-2}$ $\mu\text{M}$	Du et al., 2007

Table 6. Analytical performances of some biosensors-based methods, applied to OP pesticides analysis, namely LOD.

## 2.5 Chemometrics applied to OP pesticides analysis

Current progress on the application of chemometrics to evaluate the occurrence of organic pollutants, including OP pesticides in the environment are reviewed by Mas et al. (2010). The interpretation of the results of the analytical determination of these substances, applying chemometric approaches is among the addressed issues.

On the improvement of the electroanalytical techniques in particular with the aid of chemometrics (partial least squares, artificial neural networks, and multiple curve resolution methods) comment Ni and Kokot (2008). Some of the suggested methods are successfully applied to OP pesticides analysis.

The strategies for the enhancement of the spectroscopic photochemistry by chemometrics are discussed in the overview presented by Liu et al. (2009). The chemometric methods revealed their efficacy for the simultaneous and selective enzymatic spectrophotometric determination of carbamate (carbofuran, carbaryl) and OP pesticides (chlorpyrifos, dichlorvos, phoxim) (Ni and al., 2007; Rhouati and al., 2010), and for the simultaneous determination of OP pesticides residues: dipterex, dichlorvos and omethoate in vegeable samples by continuous-flow chemiluminescence without any previous separation (Li et al., 2007).

## 3. Conclusion

The continuous lowering of the maximum residue limits of the OP pesticides in food and in the environment calls for the development of sensitive methods for their determination. Such high effective techniques, well suited for testing complex matrices, are the chromatographic ones. Nevertheless, the review of the advances in OP pesticides analysis

during the period 2005-2011 demonstrated that despite of the efforts to reduce solvent consumption and to simplify sample pretreatment, the chromatographic determinations remain expensive and time consuming. In addition, they require experienced personnel and sophisticated laboratory equipment, inappropriate for “*in field*” application. Therefore, a number of alternative electrochemical and biosensors-based techniques were suggested. Because of the inexpensive instrumentation, the simple operation procedure without or with a minimum sample pretreatment, and the high sensitivity, they gain more and more importance in OP pesticides analyses, as an excellent complement to the classical analytical techniques, for “*in situ*” and “*on line*” determinations.

#### 4. List of abbreviations

Ach: acetylcholinesterase; ASE: accelerated solvent extraction; AuNPs: gold nanoparticles; CFME: carbon fibre microelectrode; DSPE: dispersive solid phase extraction; ELISA: enzyme-linked immunosorbent assay; EPA: U.S. Environmental Protection Agency; FAO: Food and Agricultural Organization of the United Nations; FQPA: Food Quality Protection Act; GC: glassy carbon; GCE: glassy carbon electrode; GC-ECD: gas chromatography using electron-capture-detector; GC-QqQ-MS/MS: chromatography-triple quadrupole mass spectrometry; GC/PFPD: gas chromatography/pulsed flame photometric detector; HPLC-DAD: highperformance liquid chromatography with diode array detection; HS-SPME: solid-phase microextraction in mode headspace; LLE: liquid-liquid extraction; LLSE: liquid-liquid solvent extraction; LOD: limit of detection; M: mediator; MRLs: maximum residue limits; MWCN: multiwall carbon nanoparticles; MWCNT: multiwall carbon nanotubes; NiTSPc: nickel(II) tetrasulfonated phtalocyanine; OGWDW: U.S. Environmental Protection Agency Office of Ground Water and Drinking Water; OP: organophosphorus; OPH: organophosphoro hydrolase; QuEChERS method: quick, easy, cheap, effective, rugged and safe method; SDBS: sodium dodecylbenzene sulfonate; SE: solvent extraction; SPE: solid phase extraction; SPME: solid-phase microextraction; TCNQ: tetracyanoquinodimetane; TOTAD: through oven transfer adsorption desorption; UASEME: ultrasound-assisted surfactant-enhanced emulsification microextraction; WHO: World Health Organization.

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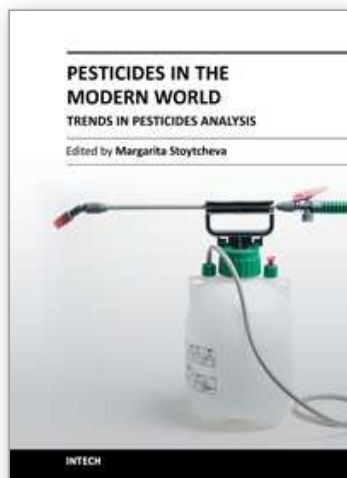
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## **Pesticides in the Modern World - Trends in Pesticides Analysis**

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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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