

New Methods for Electrochemical Determination of Pesticides (A Review)

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Abstract: The review briefly summarizes the present situation in the field of electroanalytical determination of various types of pesticides. It is focused on papers published in years 2010 – 2012 with special emphasis on methods developed in UNESCO Laboratory of environmental electrochemistry in Prague in the framework of the Czech – American S&T Cooperation in association with the laboratory of Joseph Wang, Department of Nanoengineering, University of California, San Diego, based on project NEMVAD (New electrode materials for voltammetric and amperometric detection) supported by AMVIS (American Science Information Center) in Prague and by Ministry of Education, Youth and Sports of the Czech Republic.

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Introduction

Agriculture is one of the important areas for maintaining the development of our civilization. Due to the increase of agricultural production, it is necessary to use plant growth stimulators and effective pesticides. Therefore, large amounts of biologically active substances are intentionally introduced into our environment.

The concentrations of these (sometimes toxic, ecotoxic or even genotoxic) substances must be effectively monitored and many new analytical techniques for the determination of pesticides are thus developed every year. Most of them are based on various separation techniques. Separation methods are generally very sensitive and selective but they are quite expensive and do not allow field applications.

Electrochemical methods, however, can serve as an inexpensive alternative to separation methods for screening purpose or for field applications to check whether the concentration of a given pesticide does not reach maximal allowable concentration. The features of electrochemical monitoring systems make them particularly attractive for controlling actual environmental problems and to answer challenges of green chemistry [3]. From Fig. 1 it is obvious that attention to the electrochemical behavior of pesticides is constantly increasing. Development of modern electrochemical techniques also requires the development of advanced electrochemical materials suitable for specific applications [2].

The application of modern electrochemical methods for pesticides determination was treated in extensive previous review [1]. This review, however, involved only contributions until 2009. Therefore, in the presented review we pay attention to new electroanalytical methods for electrochemical determination of pesticides developed in years 2010 – 2012 (see Table 1). Special attention is paid to methods developed in our UNESCO Laboratory of environmental electrochemistry at Charles University in Prague which are mostly based on non-traditional electrode materials and arrangements. Hence, different electrode materials and their applications for electroanalytical determination of various pesticides are briefly outlined in following paragraphs the main classification being based on working electrode material.

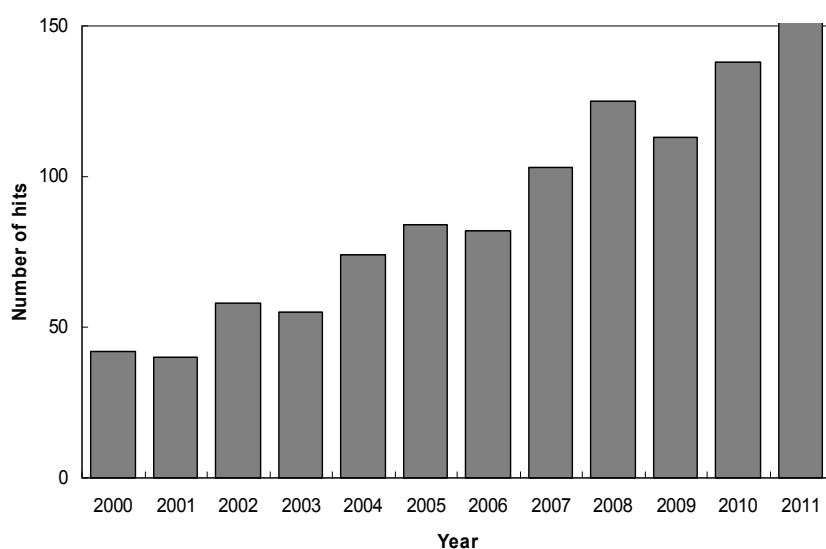


Fig. 1:
The number of publications related to “electrochemistry of pesticides” in the database SciFinder of Chemical Abstracts Service (CAS).

Table I: *Recent electrochemical studies of pesticides*

Pesticide name [CAS#]	Technique / Electrode (concentration range, $\mu\text{mol.L}^{-1}$) \ \ remark ^a \ [ref.]
2,4-DB [94-82-6]	CV, A/CoP-PtE (200 – 2000) \R\ [4]
Aclonifen [74070-46-5]	DPV/m-AgSAE (0,0002 – 0,1) \R\ [5]; TP/DME (3 – 100) \R\ [6]; DPP/DME (0,2 – 100) \R\ [6]; DCV/HMDE (0,01 – 10) \R\ [7]; SV/HMDE (0,001 – 0,1) \R\; DPV/HMDE (0,06 – 10) \R\ [7]
Alachlor [15972-60-8]	AdSV/HMDE (0,007 – 0,1) \R\ [8]
Ametryn [834-12-8]	A/CPE (0,01 – 10) \O\ [9]; PA/AuPLE (0,001 – 1000) \R\ [10]
Amitrole [61-82-5]	A/CPE (0,01 – 10) \O\ [9]
Anilazine [101-05-3]	DPV/m-AgSAE (0,2 – 100) \R\ [11]
Atraton [1610-17-9]	A/CPE (0,01 – 10) \O\ [9]
Atrazine [1912-24-9]	A/CPE (0,01 – 10) \O\ [9]; PA/AuPLE (0,001 – 1000) \R\ [10]
Carbaryl [63-25-2]	A/PtE (1 – 100) \O\ [12]; SWV/BDDE (3 – 50) \O\ [13]
Carbendazim [10605-21-7]	AdSV/TCP-CPE (0,3 – 10) \O\ [14]
Carbofuran [1563-66-2]	A/PtE (1 – 100) \O\ [12]
Clothianidin [210880-92-5]	DPV/TCP-CPE (10 – 200) \R\ [15]
Crotamiton [483-63-6]	DPP/DME (10 – 1000) \R\ [16]
Flumetralin [62924-70-3]	DPP/DME (0,02 – 10) \R\ [17]
Fomesafen [72178-02-0]	DPP/DME (1 – 100) \R\ [18]; DPV/m-AgSAE (1 – 100) \R\ [18]; DPV/HMDE (2 – 100) \R\ [18]
Halosulfuron methyl [100784-20-1]	SV/GCE (9 – 100) \O\ [19]
Chlormethoxyfen [32861-85-1]	DPP/DME (0,002 – 10) \R\ [20]
Chlorfenvinphos [470-90-6]	SV/HMDE (0,003 – 0,01) \R\ [8]
Chlortoluron [15545-48-9]	DPV/CPE (0,08 – 100) \O\ [21]; A/CPE (0,03 – 100) \O\ [21]
Imazamethabenz acid [89318-81-0]	DPP/DME (200) \R\ [22]; CV/GCE (200) \R\ [22]
Imazamethabenz methyl [81405-85-8]	DPP/DME (100) \R\ [23]; CV/HMDE (100) \R\ [23]; CV/GCE (200) \R\ [23]
Imidacloprid [138261-41-3]	DCP/DME (100 – 500) \R\ [24]; DPV/CuC-CCE (0,3 – 100) \R\ [25]; DPV/TCP-CPE (7 – 100) \R\ [15]
Ioxynil [1689-83-4]	TP/DME (1500) \R\ [26]; CV/HMDE (1500) \R\ [26]
Isoprocarb [2631-40-5]	A/PtE (1 – 100) \O\ [12]
Linuron [330-55-2]	SV/CPE (0,09 – 40) \O\ [27]
Methidathion [950-37-8]	SV/HMDE (0,7 – 3) \R\ [28]
Methomyl [16752-77-5]	A/PtE (10 – 300) \O\ [12]
Methyl parathion [298-00-0]	CV/GCE (1) \O\ [29]; SWV/ ZnO ₂ NP-CPE (0,02 – 1) \R\ [30]; CV, SWV/ZnO ₂ -CPE (0,01 – 10) \R\ [31]; SWV/BaDO ₄ -CE (0,4 – 9) \R\ [32]; SV/PtNP-GCE (0,02 – 4) \O\ [33]
Monalide [7287-36-7]	DPP/DME (0,001 – 10) \R\ [34]
Nabam [142-59-6]	A/CuFE (0,2 – 10) \R\ [35]
Nitenpyram [150824-47-8]	DPV/TCP-CPE (9 – 100) \R\ [15]
Nitroxoline [4008-48-4]	SV/HMDE (0,0009 – 1) \R\ [36]

Table I (continued)

<i>Pesticide name [CAS#]</i>	<i>Technique / Electrode (concentration range, $\mu\text{mol.L}^{-1}$) \</i> <i>\ remark ^a \ [ref.]</i>
Oxabetrinil [74782-23-3]	SV/HMDE (0,1 – 10) \R\ [37]
Parathion [56-38-2]	SV/ECPs (0,001 – 100) \R\ [38]
Pendimethalin [40487-42-1]	SWV/HMDE (0,7 – 9) \R\ [39]
Promecarb [2631-37-0]	A/PtE (1 – 100) \O\ [12]
Propoxur [114-26-1]	A/PtE (1 – 100) \O\ [12]
Simazine [122-34-9]	PA/AuPLE (0,001 – 1000) \R\ [10]
Triazophos [24017-47-8]	CV/AuNT-GCE (0,2 – 10) \O\ [40]
Triclosan [3380-34-5]	DPV/CPE (0,4 – 100) \O\ [41]
Valone [83-28-3]	DPP/DME (10 – 1000) \R\ [42]

Legend: ^a O = oxidation; R = reduction.

Mercury and Mercury Based Electrodes

Mercury electrode is one of the most reproducible of all working electrodes. Classical dropping mercury electrode (DME) is today only rarely used for determination of pesticides by DC polarography (DCP) [24] or TAST polarography (TP) [6,26]. More common is the use of DME in combination with differential pulse polarography (DPP), which provides higher sensitivity and eliminates many problems with electrode passivation due to periodical renewal of its surface [6,16-18,20,22,23,34,42].

Hanging mercury drop electrode (HMDE) gives generally more sensitive results than DME. HMDE is often used for the study of reduction mechanisms by cyclic voltammetry (CV) [23,26], for voltammetric determination with the differential pulse (DPV [7,18]) or square wave (SWV [39]) potential ramp or also enables adsorptive accumulation of the substance to be determined, which results in further increase of the sensitivity when using the stripping voltammetric (SV) mode [7,8,28,36,37,39].

Because of fears from toxicity of mercury, there is the increasing pressure to substitute mercury by new more environmentally friendly materials. A very promising alternative seems to be electrodes based on amalgam. These electrodes minimize work with liquid mercury, and keep very similar properties. Very useful in this context are electrodes based on mercury meniscus modified silver solid amalgam (m-AgSAE) [5,11,18]. The example of voltammetric determination of Fomesafen shows that the sensitivity of determination using amalgam and mercury electrodes is fully comparable [18]. When the determination is combined with appropriate preconcentration methods, extremely low subnanomolar concentrations can be determined as was shown on example of aclonifen [5].

Carbon Based Electrodes

Carbon as the electrode material is used in a number of structural forms. Among the most advanced carbon materials for working electrodes is boron-doped diamond (BDDE) [43]. Its extremely wide potential window allows to determine otherwise hardly oxidizable pesticides [13]. Electrodes based on carbon paste (CPE) are most commonly used [44]. These electrodes allow very easy surface renewal and therefore are suitable for the determination of pesticides in complicated matrices [9,21,27,41]. Glassy carbon electrode (GCE) is another successfully used sensor. For the determination of pesticides it has been used in both reducing and oxidizing areas, as well as to study the mechanisms of electrochemical transformations and sensitive stripping analysis [19,22,23].

Metal based and modified electrodes

In pesticide analysis, bare metal electrodes are not too frequently used. They are most often used as a part of miniaturized sensors, like using platinum wire electrode [12] or photolithographic gold electrodes on a glass substrate [10]. Complex of copper and pesticide nabam allows to construct selective sensor based on copper film electrode [35]. Nanoparticles of platinum [33] and gold [40] immobilized on electrode surface lead to increase of their sensitivity. Molecular imprinting technique and electropolymerization method was used for preparing of polyquercetin-polyresorcinol-gold nanoparticles modified capacitive sensor sensitive to organophosphate pesticides [29]. The electrochemical synthesis of a metal complex-based molecularly imprinted polymer of Cu(II)-phthalocyanine on Pt- [4] or carbon ceramic electrode [25] has been applied to develop a selective electrochemical sensor for different pesticides. Carbon pastes based on tricresyl phosphate [14,15], zirconia [31] and Zr^{IV}-nanoparticles [30] were used to increase of sensitivity of this popular electrode.

Determination in flowing systems

Combination of selective electrochemical detection and flow system brings many benefits. Flow system can decrease the time of analysis or to divide the complex sample into individual analytes. Larger group of carbamate insecticides was determined using capillary zone electrophoresis (CZE) [12] and lab on chip with integrated amperometric detector was used for separation and determination of several amitrol and triazine herbicides [9].

In our laboratory the combination of chromatographic separation and electrochemical detection, was used to increase both the selectivity and the sensitive compared to direct voltammetric determination [21].

Conclusions

It can be seen from the above mentioned results and findings that modern electroanalytical methods may even today play a very useful role in the field of monitoring of various types of pesticides in different matrices (such as environmental samples, food and rinks, aquatic samples etc.). Especially new electrode materials and arrangements can greatly stimulate further development in this field. Modern types of solid amalgam electrodes can be particularly useful for on site monitoring of electrochemically reducible pesticides both in bath and flow arrangements.

The most promising electrode materials for electrochemically oxidizable pesticides seem to be various forms of carbon pastes. Probably the most promising material applicable for both anodic oxidations and cathodic reductions is a boron doped diamond film with extremely low noise and charging current, broad potential window and high resistance to passivation. Further development in above outlined field will undoubtedly open new possibilities for electroanalytical determination of trace amounts of pesticides in a broad spectrum of different matrices.

Abbreviations Used

A	=	Amperometry
AuNT- GCE	=	Gold nanoparticle-carbon nanotube modified GCE
AuPLE	=	Gold photolithographic electrodes
BaDO4-CE	=	Surfactant intercalated clay composite electrode
BDDE	=	Boron doped diamond electrode
CoP-PtE	=	Co-porphyrin modified PtE
CPE	=	Carbon paste electrode
CuFE	=	Copper film electrode
CuP-CCE	=	Copper(II) phthalocyanine modified carbon ceramic electrode
CV	=	Cyclic voltammetry
DCP	=	Direct current polarography
DME	=	Dropping mercury electrode
DPP	=	Differential pulse polarography

DPV	=	Differential pulse voltammetry
GCE	=	Glassy carbon electrode
HMDE	=	Hanging mercury drop electrode
IS	=	Impedance spectroscopy
m-AgSAE	=	Meniscus modified silver solid amalgam electrode
PA	=	Pulse amperometry
PtE	=	Platinum electrode
PtNP-GCE	=	Platinum nanoparticle in Ni/Al layered double hydroxides modified GCE
QRAuNP-GCE	=	Polyquercetin-polyresorcinol-gold nanoparticles modified GCE
SV	=	Stripping voltammetry
SWV	=	Square wave voltammetry
TCP-CPE	=	Carbon paste electrode containing tricresyl phosphate
TP	=	Tast polarography
ZnO ₂ -CPE	=	Zirconia modified carbon paste electrode
ZnO ₂ .n-CPE	=	Zirconia nanoparticles modified CPE

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