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Electroanalysis of Insecticides at Carbon Paste Electrodes with Particular Emphasis on Selected Neonicotinoid Derivatives

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1. Introduction

1.1 Recent trends in the use of insecticides

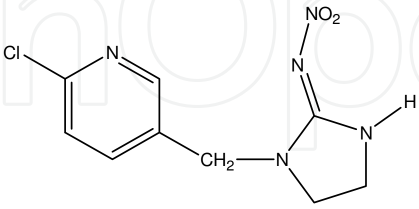
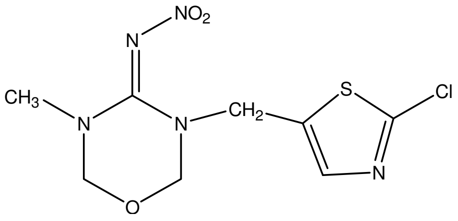
Insecticides are substances from the group of pesticides intended for preventing, destroying, repelling or mitigating insects (Pesticide, 2011). Although there are benefits to the use of insecticides, there are also drawbacks, such as potential toxicity to humans and other animals. Residues in fruit and vegetables, cereals, processed baby food and foodstuffs of animal origin are controlled through a system of statutory maximum residue limits (MRLs) (Tuzimski, 2011).

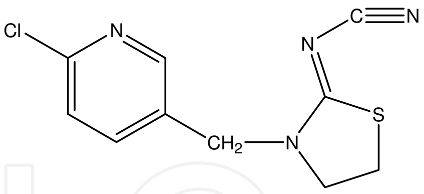
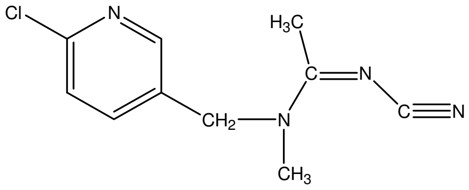
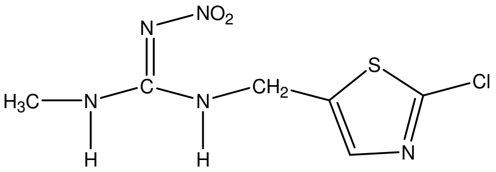
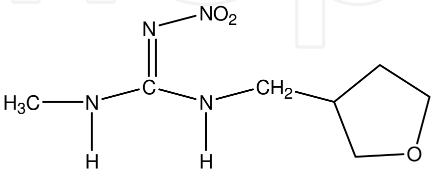
The increasing use of pesticides, especially herbicides and insecticides, in agriculture, forestry, and domestic activities for controlling pests causes pollution of the water resources, environment, as well as of many food stuff. The leaching run-off from agricultural and forest lands; deposition from aerial applications and residua from the industrial wastewater treatment are mainly responsible for the water contamination (Gupta, 2004). The pesticides form a strong class of water and environment pollutants, as they are sometimes non biodegradable. The toxicity of pesticides and their degradation products make these chemical substances potentially hazardous contaminants of the environment (Schultz et al., 2003). According to the Stockholm Convention on Persistent Organic Pollutants, nine of the dozen of the most harmful and persistent organic chemicals are pesticides (Ridding the World of POPs: A guide to the Stockholm Convention on Persistent Organic Pollutants, 2005; Pesticide, 2011).

The insecticides can be grouped by means of sorting into chemical families. Major insecticide families include organochlorines, organophosphates, carbamates, and neonicotinoids. Organochlorine hydrocarbons (e.g. DDT) could be separated into dichlorodiphenylethanes, cyclodiene compounds, and other related compounds. They operate by disrupting the sodium/potassium balance of the nerve fiber, forcing the nerve to transmit continuously. Their toxicities vary greatly, but they have been phased out because of their persistence and potential to bioaccumulate (Kamrin, 1997). For instance, due to extreme stability of highly toxic organochlorines, these formerly popular products (like the above-mentioned DDT) have largely been replaced by organophoshates and carbamates. Nevertheless, they are toxic as well, operating through inhibition of the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis. Moreover, organophosphates are quite toxic to vertebrates, and have to be, in some cases, been replaced by less toxic carbamates (Kamrin, 1997), or by thiocarbamates and dithiocarbamates as the subclasses of carbamates.

Thus, there was a demand for less harmful compounds, which would become the case of **neonicotinoid insecticides** whose successful story had started in 1991 with the launching of a forerunner, *Imidacloprid*, by Bayer Crop Science, being the world's largest selling insecticide for many years (Nauen et al., 2008). Today, neonicotinoids (see **Table 1**), acting on the level of nicotinic acetylcholine receptor (nAChR) of insects, are one of the most important categories of insecticides introduced to the global market since the synthetic pyrethroids (Jeschke & Nauen, 2008; Jeschke et al., 2011). Up until now, neonicotinoids are the most important class of insecticides introduced to the global market since the synthetic pyrethroids, when the former are registered globally in more than 120 countries, regarded as the most effective insecticides to control sucking insect pests such as aphids, whiteflies, leaf and planthoppers, thrips, some micro-Lepidoptera, and a number of coleopteran pests (Jeschke & Nauen, 2008).

The outstanding development of neonicotinoid insecticides for modern crop protection, consumer / professional products, and animal health markets in the last two decades reflects the enormous importance of this chemical class. In 1990, before the launch of the first neonicotinoid insecticide, imidacloprid, the agrochemical market (total volume of ca. eight billion EUR was dominated by organophosphates (OPs) (43%), pyrethroids (18%), and carbamates (16%). In 2008, the neonicotinoids had gained a 24% share of a slightly decreased total market of €6.330 billion, mainly at the expense of OPs (13.6%) and carbamates (10.8%) (see internal data from *Bayer Crop Science* in Jeschke et al., 2011). As a logical step, massive and still expanding application of neonicotinoids requires also new analytical measurements that can be operated in very diverse samples, including recently demonstrated monitoring of photodegradation process(es).

Trivial name	**IUPAC name**	**Structural formula**	**Typical use**
Imidacloprid	(*E*)-1-(6-chloro-3-pyridylmethyl)- -*N*-nitroimidazolidin- -2-ylideneamin		Applied by soil or tree injection, or in granular form. Effective to protect maize, sunflower
Thiamethoxam	3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4- -ylidene(nitro)amine		Effective against aphids, thrips, beetles, centipedes, millipedes, sawflies, leaf miners, stem borers and termites

Trivial name	IUPAC name	Structural formula	Typical use
Thiacloprid	(*Z*)-3-(6-chloro-3-pyridylmethyl)-1,3-thiazolidin-2-ylidenecyanamide		Applied by soil or tree injection, or in granular form. Effective against sucking and chewing insects, primarily aphids and whiteflies
Acetamiprid	(*E*)-*N*^{1}-[(6-chloro-3-pyridyl)methyl]-*N*^{2}-cyano-*N*^{1}-methylacetamidine		Effective to control sucking insects on crops such as leafy vegetables, citrus fruits, pome fruits, grapes, cotton, cole crops, and ornamental plants. It is also a key pesticide in commercial cherry farming due to its effectiveness against the larvae of the cherry fruit fly.
Clothianidin	(*E*)-1-(2-chloro-1,3-tiazol-5-ylmethyl)-3-methyl-2-nitroguanidine		Effective to seed treatment for corn and canola
Dinotefuran	(*RS*)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl)guanidine		Effective for the control of insect pests such as aphids, whiteflies, thrips, leafhoppers, leafminers, sawflies, mole cricket, white grubs, lacebugs, billbugs, beetles, mealybugs, and cockroaches on leafy vegetables, in residential and commercial buildings, and for professional turf management

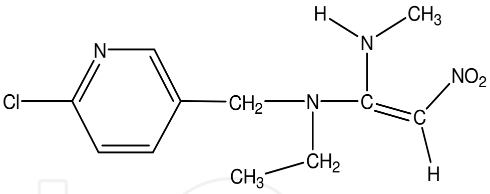
Trivial name	IUPAC name	Structural formula	Typical use
Nitenpyram	(*E*)-*N*-(6-chloro-3-pyridylmethyl)--*N*-ethyl-*N*′-methyl-2-nitrovinylidenediamine		Used in agriculture and veterinary medicine to kill insect external parasites of livestock and pets

Table 1. The commercial neonicotinoid insecticides (assembled according to Jeschke et al., 2011).

Besides a great number of benefits that these insecticides have, it is important to note that there is a hypothesis that neonicotinoid insecticides used for seed coating of agricultural crops – mainly corn, sunflower and seed rape – are related to the extensive death of honey bees. The death of honey bees, *Apis mellifera L.*, and the consequent colony collapse disorder causes major losses in agriculture and plant pollination worldwide. The phenomenon showed increasing rates in the period of 2008-2010, although its causes are still awaiting a clear answer. Many hypotheses, such as infections of parasitic mites (Cox-Foster et al. 2007), viruses (Anderson and Gibbs, 1988), chronic exposure to sub-lethal doses of insecticides (Desneux et al., 2007; Yang et al., 2008; Johnson et al., 2009; Alaux et al., 2010) or acute effects of neonicotinoid insecticides (Suchail et al., 2000) were formulated to account for bee decline. Although neonicotinoid systemic insecticides used for seed coating of agricultural crops were suspected as possible reason, studies so far have not shown the existence of unquestionable sources capable of delivering directly intoxicating doses in the fields. Guttation is a natural plant phenomenon causing the excretion of xylem fluid at leaf margins. Recently was found that leaf guttation drops of all the corn plants germinated from neonicotinoid-coated seeds contained amounts of insecticide constantly higher than 10 mg L^{-1}, with maxima up to 100 mg L^{-1} for thiamethoxam and clothianidin, and up to 200 mg L^{-1} for imidacloprid. The concentration of neonicotinoids in guttation drops can be near those of active ingredients commonly applied in field sprays for pest control, or even higher. When bees consume guttation drops, collected from plants grown from neonicotinoid-coated seeds, they encounter death within few minutes (Girolami et al., 2009; Tapparo et al., 2011).

1.2 Instrumental analysis of insecticides. A survey of contemporary trends

Due to the growing use of insecticides, their accumulation in the environment and foodstuff is evident. For these reasons, it has been necessary to develop sensitive analytical methods for monitoring the low levels of insecticide residues in soil, water, and agricultural products. The leading analytical techniques in the monitoring of insecticides in different complex matrices seem to be the techniques that combine separation and determination steps which allowed multiresidue, multiclass, and trace level analysis. Chromatographic techniques like gas chromatography (GC) and high performance liquid chromatography (HPLC) combined with different types of detectors, mainly mass spectrometric detector (MS) or tandem MS detector are on the leader position (Rocío et al., 2011; Feo et al., 2011). The choise of the chromatographic technique depends on the nature of investigated compound(s), first of all their polarity and basic-acid properties (Lambropoulou and Albanis, 2007), and the type of the sample matrix. In the case of GC in combination with MS, there is a database for the identification of the insecticides from the samples. For the GC analysis advantage have the volatile compounds, but after their appropriate derivatisation in more volatile compound the low volatile or thermolabile compounds can be analysed, also. On the other hand, HPLC is recommended for the analysis of low volatile compounds and for compounds that are unstable when heated. Capillary electrophoresis (CE) and capillary electrochromatography (CEC) are convenient also for the determination of different target insecticides from different complex matrices (Cooper et al., 2000; Picó et al., 2003; Hernández-Borges et al., 2004; Lin et al., 2009). However, the chromatographic techniques are the most powerful tools for examining the contents of a very different insecticides in complex samples, these instruments are related primarily to laboratories, the samples (either liquid or solid samples) very often undergoes preliminary extractions before the chromatographic measurements, when their purchase- and operational costs are always considerably high.

Furthermore, there is a wide spectrum of alternative, mostly portable, non-chromatographic analytical equipments, first of all portable sensors, which are often used for the first screening of target analyte(s). Different techniques from molecular spectrometry (UV/Vis spectrophotometry, fluorimetry, colorimetry, infrared spectrometry), surface plasmone resonance sensors or immunochemical recognitions are used as screening techniques for the obtaining information about pesticide content in very different samples. The biorecognition elements can stay as independent techniques (e.g. Van Dyk and Pletschke, 2011 and the references herein), but they are often combined with other techniques, allowing higher specificity for identification and determination of the target analytes (Shankaran et al., 2007).

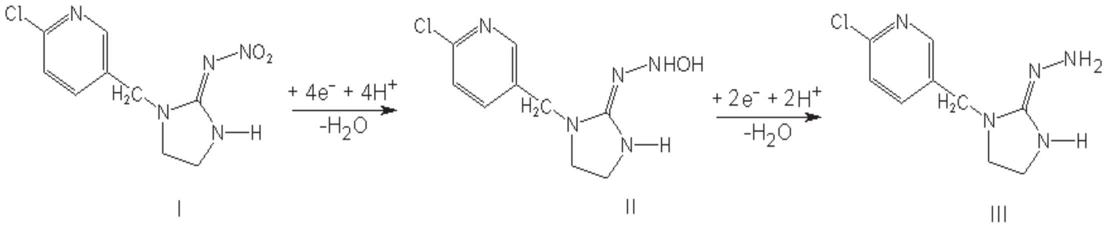
Regarding the neonicotinoid insecticides themselves, there is already a number of procedures employing various instrumental techniques and proposed for their detection and quantification in different samples. Often, such methods of choice are being based on high- and ultra-performance liquid chromatography (HPLC and UPLC) combined with the sensitive detection by a diode-array (Obana et al., 2002; Mandić et al., 2005; Watanabe et al., 2007), mass spectrometry (Obana et al., 2003; Kamel, 2010; Liu et al., 2010), thermal-lens spectrometry (Guzsvány et al., 2007a), amperometric detector (De Erenchun et al., 1997) or with an electrochemical detector and post column photochemical reactor (Rancan et al., 2006a,b). Furthermore, procedures based on photochemically induced fluorescence detection (Vilchez et al., 1998; Vilchez et al., 2001), micellar electrokinetic capillary chromatography (Carretero et al., 2003) and Fourier transform infrared spectrometry (Quintas et al., 2004), simple derivative spectrophotometry (Guzsvány, 2006; Guzsvány et al., 2009a) have also been used for the determination of imidacloprid or thiamethoxam. There are also studies related to bioassayes, the enzyme-linked immuno assay (ELISA) for identifying imidacloprid (Li et al., 2000; Lee et al., 2001; Kim et al., 2003; Watanabe et al., 2006), acetamiprid (Watanabe et al., 2006) and thiamethoxam (Kim et al., 2003; Kim et al., 2006). The above techniques are very convenient not just for the neonicotinoid residue analysis, or quality control of the commercial formulations, they are widely applied for the monitoring of the fate, stability and removal of these insecticides (Guzsvány, 2006; Guzsvány et al., 2008a,b; Guzsvány et al., 2009b; Guzsvány et al., 2010; Guzsvány et al., 2011b; Pena et al., 2011; Černigoj et al., 2008; Malato et al., 2001; Malato et al., 2002; Malato et al., 2003, and the references herein; Dell'Arciprete et al., 2010).

1.3 Electrochemistry and electroanalysis of insecticides

Electrochemical techniques, represent yet another alternative for the determination of various pollutants. Their main trump, compared to GC, HPLC, CE, CEC, and other sophisticated instrumentations, is a fairly low cost and wide flexibility, including relatively easy adaptation for field monitoring (Wang, 2002). Among the electrode systems available, various sensors and biosensors based on heterogeneous carbon materials have always attracted considerable attention, which is also the case of procedures proposed exclusively for analysis of organic pollutants (see e.g. Ulakhovich, 1993; and refs. therein).

Perhaps the most effective approaches to analyse insecticides electrochemically are represented by voltammetric techniques; namely, **cyclic voltammetry** (CV) for investigations/elucidation of the reaction mechanisms (Gosser, Jr., 1993) and the-so-called **stripping voltammetry** combined with preconcentration (accumulation) step for the trace level determination of target analytes. Regarding the potential ramp, most frequently used are the differential pulse voltammetry (DPV) for its reliable performance at low concentration levels (Kissinger and Heineman, 1996) and — still more often — square-wave voltammetry (SWV) for its insensitivity to dissolved oxygen (Lovric, 2005). Exceptionally, for sufficiently high concentration ranges, one can choose also classical polarography with the dropping mercury electrode (Barek et al., 2001).

As shown during fundamental polarographic investigations (see e.g. Navalón et al., 1999; Guziejewski et al., 2011a,b; Guzsvány et al., 2006; with other refs. therein), the determination of nitroguanidine neonicotinoids can be based on the irreversible reduction of the electroactive nitro group to hydroxylamine and amine. For instance, when reducing *Imidacloprid* at the mercury electrode, one has:



(1)

The whole reduction pathway (**1**) with schemes I-III (redrawn after Navalón et al., 1999) is complex, depending on experimental conditions, when the single wave or even more consecutive responses may be obtained. Besides the potential applied, the process strongly depends upon the pH, whose variations are reflected in the overall peak current intensity, as well as the respective peak potentials that are being shifted to more negative range with the increasing pH. In this respect, the neonicotionoids behave as many other electroactive organic compounds and their precise identification in more complex samples requires the corresponding standards (see below, in sections 2 and 3). Best developed and sufficiently separated peaks of the neonicotinoids were mostly observed in neutral and slightly alkaline solutions that had also represented the supporting media of choice for analytical purposes.

Regarding this specific group of insecticides, the individual methods proposed for their determination have employed the mercury-based working electrodes (Navalón et al., 1999; Guiberteau et al., 2001; Guzsvány, 2006; Guzsvány et al., 2006a with other refs. therein; Guziejewski et al., 2011a,b) or detection units incorporating various unmodified (Guzsvány et al., 2005; Guzsvány, 2006; Guzsvány et al., 2007a; Guzsvány et al., 2008a; Papp et al. 2009a,b; Papp et al., 2010; Papp, 2011; Papp et al., 2011) and bismuth particles modified carbon based electrodes (Guzsvány, 2006; Guzsvány et al., 2006c; Gaál et al., 2007; Guzsvány et al., 2008a,b; Guzsvány et al., 2011a) as well as on copper(II) phthalocyanine modified carbon ceramic electrode (Majidi et al., 2011) or the nanosilver Nafion®/nanoTiO$_2$ Nafion® composite modified glassy carbon electrode (Kumaravel and Chandrasekaran, 2011).

1.4 A little excursion into the electrochemistry with carbon paste-based electrodes

Intro. Apparently, the most popular heterogeneous carbon electrodes are the so-called **carbon paste electrodes**, (CPEs), invented and largely propagated by Adams a half a century ago (Adams, 1958; Švancara et al., 2009a; Švancara et al., 2011). Carbon paste electrodes are applied worldwide; primarily, because of their broad potential window (mainly at the anodic side), very low residual currents (background), unique surface characteristics, low cost, simple preparation (directly in labs), usually minimal toxicity, and mainly, thanks to almost countless possibilities of their chemical and biological modifications (Kalcher K., 1990; Kalcher et al., 1995; Kalcher et. al, 2006; Švancara et al., 2011).

Common carbon pastes and their modified variants. In brief, the **bare** (binary, unmodified) **carbon paste electrode, CPE**, is an assembly of a mixture of graphite (carbon) powder, suitable liquid (binder), which is − as a soft and incompact material − packed into a convenient electrode body (Adams, 1963). Both main components, as well as their mutual ratio then co-determine the physicochemical and electrochemical properties that can further be altered – and often purposely controlled – by adding a third constituent, when the substance of such a choice can be a modifier / stabilizer / catalyst / mediator, etc. In these cases, one obtains **chemically** or **biologically modified carbon paste electrodes**, **CMCPEs** (Kalcher, 1990) and **CP-biosensors** (Gorton, 1995), respectively. Largely, bare carbon paste mixtures are being made from highly pure spectroscopic graphites (with mesh *ca.* 5-20 μm) and mineral oil (Nujol) or silicone oils and greases; all serving as a binder. Whereas these mixtures are called **traditional carbon pastes** (Kalcher et al., 1995; Kalcher et al., 2006), there is also a wide spectrum of other types being classified as special carbon pastes.

Special Carbon Pastes. Such mixtures with their basic characterisation have been of particular interest in some latest reviews - see *e.g.* Švancara et al., 2009b; Švancara et al., 2011 - showing that the pastes preparable from the alternate carbon paste constituents represent a long line of possible candidates. Thus, instead of graphite, one can e.g use glassy carbon globules, carbon fibres, carbon nanotubes, nanohorns, and fullerenes, as well as (pyrolysis-produced) carbon and acetylene black, template carbon, purified coal or even powdered (and specially doped) diamond. The proper replacement for traditional oily binders can then be some liquid organic esters, higher hydrocarbons, halogenated aromates, or room-temperature ionic liquids (RTILs); the latter being especially popular in the recent years.

Tricresyl phosphate-based carbon paste electrode (TCP-CPE). One of such special carbon pastes is also a mixture made of graphite and liquid tricresyl phoshate (TCP), introduced into the electrochemistry with CPEs in the early 1990s (Srey, 1992; Švancara and Vytřas, 1993). The making of the TCP-CPE was inspired by the research work by Kalcher who had used related substances as special liquid modifiers with distinct ion-exchange properties (Kalcher, 1985a,b; Kalcher et al., 1987), as well as its previous use as plasticizer of liquid membranes for ion-selective electrodes (Vytřas, 1985). The TCP-CPE is a typical representative of CPEs with electrochemically active binder, where the molecules of organophoshate can readily be protonated (Švancara et al., 1998a):

$$(C_7H_7O)_3P{=}O \;+\; H^+ \;\longrightarrow\; [(C_7H_7O)_3P{=}OH]^+ \qquad (2a)$$

and, in this form, acting in numerous ion-exchange / ion-pairing processes; e.g.:

$$[(C_7H_7O)_3P{=}OH]^+ + Y^- \longrightarrow \{[(C_7H_7O)_3P{=}OH]^+ \,;\, [Y]^-\} \qquad (2b)$$

giving rise to the corresponding product – relatively stable and electroactive ion-associate.

Since then on, the TCP-CPE had successfully been employed in a number of electrochemical methods, utilising the above principles, given above in schemes (**2a**) and (**2b**) in combination with either voltammetric detection or potentiometric indication. More specifically, the TCP-CPE was the electrode of choice serving for the determination of gold in the form of $[AuCl_4]^-$ (Švancara and Vytřas, 1993; Vytřas et al., 1993), silver ions down to the picomolar level (Švancara et al., 1996b), bismuth as $[BiI_4]^-$ (Švancara and Vytřas, 1993), thallium via $[TlCl_4]^-$ (Konvalina and Vytřas, 1999), or numerous anions like BF_4^-, ClO_4^-, $HAsO_4^{2-}$, $[P(Mo_3O_{10})_4]^-$ (see Vytřas and Švancara, 2007 and refs. therein), and mainly for iodide (as I^- or I_3^- resp.; see e.g. Švancara et al., 1998a; Švancara et al., 2002). Moreover, the TCP-CPE could also be used for some theoretically oriented studies, which is the case of the microscopic study on the surface morfology of different carbon pastes (Švancara et al., 1996a), or the evaluation of stability constants for aurate(III) halides of the $[AuX4]^-$ type (where "X" is F, Cl, Br, SCN, and CN). Regarding organic substances and biologically important compounds, the tricresyl phosphate-based CPEs had thus far been tested in (preliminary) assays with polyaromatic nitrocompounds, PANs (Švancara et al., 1998b) and (unsuccessful) accumulation studies with 6-benzylaminopurine (a plant hormone; Švancara et al., 2001b). Thus, recent investigations on the applicability of the TCP-CPE in analysis of neonicotinoids, being in focus herein, represent just another of the few attempts to employ this rather unusual CPE in analysis of organic compounds and pollutants.

Bismuth-modified carbon paste electrodes. As mentioned above, the most appreciated feature of the CP-based electrode material is, without doubts, the fact that its electrochemical and electroanalytical value can immeasurably be enhanced by proper chemical (or biological) modification (Kalcher K., 1990; Kalcher et al., 1995; Kalcher et. al, 2006; Švancara et al., 2011). In the just-passed decade, one of the most intensively studied modification of CPEs and CMCPEs was their conversion into the **bismuth-**based **electrodes** and **sensors**, representing a new type of environmentally friendly detection system and, hand in hand, a principal step of modern electroanalysis into the realm of momentarily so popular »green chemistry« (Wang et al., 2000; Wang, 2002; Švancara et al., 2010).

Within the rapidly growing area of **non-mercury metallic electrodes**, the carbon paste as a special substrate offers a number of different variants, when one can choose amongst bismuth-film plated bare carbon pastes (BiF-CPEs), Bi(III)-solid compound containing carbon pastes (e.g., Bi_2O_3-CPE and BiF_3-CPE), or bismuth powder dispersed in bare carbon pastes (Bi-CPEs), including some of these variants being made from spedial carbon pastes of new generation, or being combined with the already modified carbon paste; e.g. BiF/Ze/CPE, where the modifier is zeolite (a natural clay bringing to the bare paste mixture better adhesive properties). All these configurations have certain advantages and drawbacks; nevertheless, their detailed characterisation is beyond the scope of this article and can be found elsewhere (*e.g.* Švancara et al., 2010).

In association with the previous survey of bismuth-versus-carbon-paste variants, it is interesting to notice that the spectrum of CP-based materials as the substrates for bismuth electrodes was relatively narrow being orientated on traditional (mineral and silicone oil-based) carbon paste mixtures. But the TCP-CPE, introduced above as the (bare) carbon paste electrode of choice for neonicotinoids is also applicable in the metallic film configuration. The first attempt of a kind has been made nearly twenty years ago (Švancara et al., 1993), when the TCP-CPE had been combined with a mercury film and - as the MF/TCP-CPE configuration - successfully used in stripping voltammetry of some not readily reducible ions like Mn^{2+} or Zn^{2+}. Analogously, a coupling with a gold film; *i.e.*, the AuF/TCP-CPE configuration, had been tested as the working electrode for stripping voltammetry of As(III); but the ultimate choice being another gold plated-CPE (Chadim, 1999). When considering bismuth and its deposition onto the TCP-CPE, this combination has for the first time been examined for analysis of the neonicotinoids and therefore, it deserves a special attention being discussed below – in section **3**.

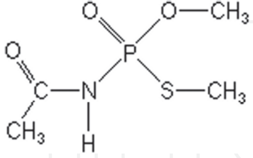
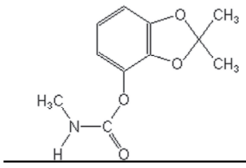
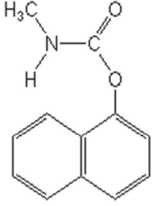
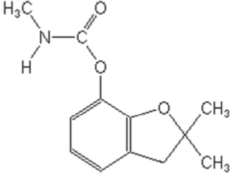
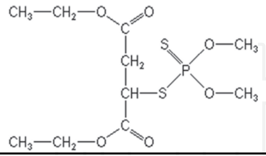
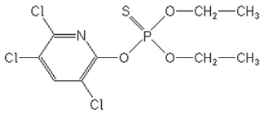
Carbon paste-based electrodes in retrospective reviews. The very first text of a kind on CPEs had been published by the inventor himself in the mid-1960s (Adams, 1963). Another related elaborate came a quarter of a century later; being focused predominantly on CMCPEs (Kalcher, 1990) and soon followed by two similar installments (Kalcher et al., 1995; Švancara et al., 2001a). In the recent years, the widespread area of carbon paste-based electrodes has been reviewed in a series of exclusive articles, including hitherto the most detailed chapter in an *Encyclopedia* (Kalcher et al., 2006) or the newest entry – the very first monograph on CPEs (Švancara et al., 2011). In all reviews cited, the reader can find almost complete information, with all newest achievements in the area which is further discussed in association with the key topic of this overview – with the electrochemistry and electroanalysis of neonicotinoid insecticides.

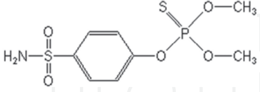
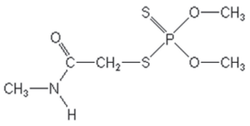
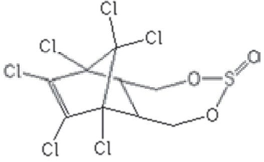
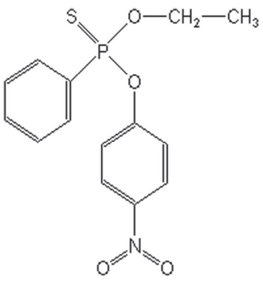
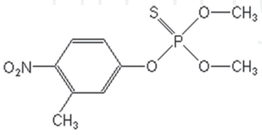
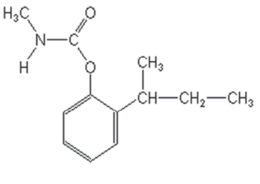
1.5 Carbon paste electrodes in analysis of insecticides

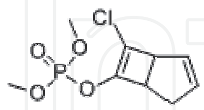
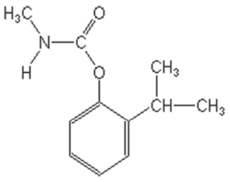
In contemporary literature (Kalcher et al., 2006; Zima et al., 2009a,b; Švancara et al., 2011), the individual methods for the determination of insecticides at CPEs, CMCPEs, and CP-biosensors have always been included within a group of the so-called **organic pollutants**; namely, together with other pesticides or animal poisons, with polyaromatic amines, nitro- and nitroso-derivatives, or various industrial products like dyes, catalysts, and food additives. The reason for such a grouping is that the respective electroanalytical procedures share usually some general features that correspond also to the main rules and recommendations for routine organic electrochemistry highlighted in the “fresh” review literature (see Zima et al., 2009a,b, Kalcher et al, 2009).

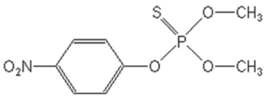
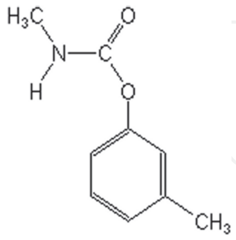
Regarding the insecticides as such, there is about three tens of different synthetic compounds that have already been analysed with the aid of carbon paste-based electrodes. Their (probably) complete survey is given in **Table 2**, specifying also the particular type of a CPE or a CMCPE, the technique of choice, a selection of typical experimental and instrumental parameters, as well as the basic electroanalytical characterisation via the linearity range or the limits of detection. Finally, the table also gathers the data on the individual samples, confirming that analyses of environmental specimens and commercial formulations had dominated. Herein, it should be quoted that the methods for the determination of the remaining pesticides (i.e., herbicides, fungicides, algaecides, rodenticides, molluscicides, acaricides, bactericides, and virucides) have also been reviewed and gathered in similar tables in two recent literature sources (Kalcher at al., 2006; Švancara et al., 2011)

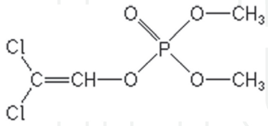
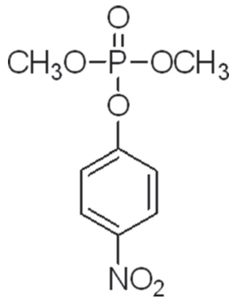
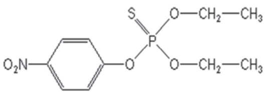
In the following sections, possibilities and limitations of **voltammetric measurements with carbon paste electrodes** are of interest, focused on the **neonicotinoid insecticides** and the authors' research with **tricresyl phosphate-based CPEs** used either in **the bare configuration** or as further chemically modified via electrolytic plating the electrode surface

Analyte (form / alter.n.)	**Chem. specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Acephate 	methoxy-sulfanyl-phosphoacetamide	CNTPE (+ Ru(bpy)$_3^{2+}$) [EH-µD]	CE-ECL	EH: electrically heated electrochemiluminescence detection; lin.r.: µM level; simult. detn. with *Dimethoate*	comm. forms	(Chen et al., 2007)
Bendiocarb 	dimethyl-benzo-di-oxo-ethylcarbamate	C/Nj (+ "C-18")	CV, DPV	modif.: ionex resin (50% in CP); o.c., MEx, BR-B (pH 5); LOD: 0.7 µg·mL^{-1}	model solns., soils	(P. Hernandez et al., 1993)
Carbaryl 	1-naphthyl-methyl-carbamate	C/PO (+ polyamide) [ft-D]	CZE-AD	hydrolysis to phenolic ders. and detn.; simult. detn. with *Fenobucarb*, *Isoprocarb* & *Metolcarb*; LODs: 3-6×10^{-8} M	environmental specimens	(Cheng et al., 2007)
Carbofuran 	subst. benzofuran methylcarbamate	C/PO (+ FePC) [CP-bio with enzymes]	AD (stat.)	inhibition effect of analyte; two diff. enzymes; LOD: 1×10^{-10} M;	model solns.	(Ciucu et al., 2003)
Carbophos 	di-MeO-phosphino-thio-butanoic acid e.	C/PO (Co^{II}-2,2'-dipy)	DPAdSV	studies on accum. mechanism, adsopt. pH-effect, interfs.; LOD: 1.2×10^{-9} M	model solns.	(Ulakhovicet al., 1998)
Chlorpyrifos 	diethyl-trichloro-py-phosphorothiolate	C/PO (+ *Zeolite Y*)	DPAdSV	study on ion-pairing accum. and effect of pH, modif.: nat. clay; lin.: 0.0001 - 2 ppm (t$_{acc}$ = 80 s); interf. Studies	enviromental specimens	(Sirisha et al., 2007)
Clothianidin (see Table 1)	neonicotinoid	C/SO (unm.), C/TCP (unm.)	DPV (dir.)	s.e.: BR-B (pH 7.0), lin.r.: 2-25 mg·L^{-1}	model solns.	(Papp et al., 2009a)

Analyte (form / alter.n.)	**Chem. specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Cythioate 	organo-S-phosphate	C/PO (crown-ethers)	CV, DPV	studies on accum., re-oxidn. processes; lin.r.: 4×10^{-9}-9×10^{-8} M; RSD < 4%	model solns.	(Shaidarova et al., 1998)
Dimethoate 	dimethyl-amino-2-oxo-dithiophoshate	CNTPE (+ $Ru(bpy)_3^{2+}$) [EH-µD]	CE-ECL	EH: electrically heated electrochemiluminescence detection; lin.r.: µM level; simult. detn. with *Acephate*	comm. forms.	(Chen, 2007)
Endosulfan 	subst. hexachloro-bis benzo-oxa-thiepine	C/PO (+ ionex "C-18") [trad. CPE + Cu^{2+}, in situ]	DPV	indirect detn. based on interaction of electroinactive EDS with Cu(II) / via the peak decrease; LOD: 40 ng·L^{-1}	model solns.	(El Bakouri et al., 2005)
EPN 	ethyl-O-nitro-Ph-Ph-phosphonothioate	a) CNTPEs (+ MeF, DNA) [µEs: needle type] b) C/PO (+ *Pseumonas putida* sp.+ OPH-enzyme)	a) ASV (trad. & *in vivo*) b) AD (stat.)	a) study with a series of w. electrodes, incl. GCE,AuE), MeF-: mercury film, 0.1M $NH_4H_2PO_4$; lin.r.: 10-210 ng·L^{-1}; b) CP-bio with modif. as bio-degrader, LOD: 1.6 ppb; detn. with *Fenitrothion*	a) orange, apple, and skin tissues b) lake water	a) (Ly et al., 2008) b) (Lei et al., 2007)
Fenitrothion 	diMeO-4-nitro-PhO -thioxo-phosphorane	C/PO (+ *Pseumonas sp.* + OPH-enzyme) [CP-bio + Co^{2+}, *in situ*]	AD (stat.)	modif: microbial cells (as biodegrader) 0.05M PhB (pH 7.5), E_w = 0.6 V / ref.; LOD: 1.4 ppb; simult. detn. with *EPN*	lake water	(Lei et al., 2007)
Fenobucarb 	2-butan-yl-2-phenyl methyl-carbamate	C/PO (+ polyamide) [ft-D]	CZE-AD	hydrolysis to phenolic ders. and detn.; simult.detn. with *Carbaryl*, *Isoprocarb* and *Metolcarb*; LODs: $3\text{-}6\times10^{-8}$ M	environmental specimens	(Cheng, 2007)

Analyte (form / alter.n.)	**Chem.** **specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Hostaquick 	chloro-bicyclo-di-methyl phosphate	C/Nj + m. (enzyme + Co-PC)	AD, HA	detn. based on analyte inhibition / bio-enzymatic effect; PC: phthalocyanine LOD: 3×10^{-4}- 0.1 g·L^{-1}	model solns.	(Skladal, 1991)
Imidacloprid (see Table 1)	neonicotinoid	a) C/SO, C/nTD, C/TCP b) C/SO, C/TCP [all CPEs as unm.] c) Bi powder bulk modified C/TCP	a,b,c) DPV (dir.)	a) comp. of three diff. CPEs (made of SO, tetradecane & tricresyl phosphate) s.e.: BR-B (pH 7.0), lin.r.: 1.7-30 mg L^{-1} b) comp. of two diff. CPEs (made of SO & tricresyl phosphate) s.e.: BR-B (pH 7.0), lin.r.: 2-25 mg L^{-1} c) Bi powder bulk modified CPE based on tricresyl phosphate, s.e.: BR-B (pH 7.0), lin.r.: 1.6-47.6 mg L^{-1}	a) river water, comm. preps. b) model solns.	a) (Papp et al., 2009, b) b) (Papp et al., 2009, a) c) Guzsvány et al., 2011)
Isoprocarb 	iso-propan-2-phenyl methyl-carbamate	C/PO (+ polyamide) [ft-D]	CZE-AD	hydrolysis to phenolic ders. and detn.; simult. detn. with *Carbaryl, Fenobucarb, Metolcarb*; LODs: 3-6 × 10^{-8} M	environmental specimens	(Cheng, 2007)

Analyte (form / alter.n.)	**Chem. specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Methyl parathion 	(subst. p-nitro-phen-oxy-organophoshate	a) C/PO (+ FePC) [CP-bio with enzymes] b) C/Nj (+ "C-18") c) C/MO (+ enzyme) d) CNT-IL (BMIMPF$_6$) [CP-film at the GCE] e) C/PO (MBD + OPH) f) C/PO (unm.) g) C/PO (+ mep-ZrO$_2$) h) C/PO (+ nano-ZrO$_2$)	a) AD (stat.) b,d) DPV c) FIA-EC e) LSV, AD (stat.) f) SWAdSV g) DPASV h) SWASV	a) nal. inhibition / bioenzymatic effect; b) interfs. studies; LOD: 7.9 ng mL^{-1}; c) catalysed hydrolysis; 0.2-1.0 µM; d) catalytic effect of both CNTs & IL, o.c. accum., PhB (pH 7), LOD: 1 nM e) modif: microbial cells (degrader) + enzyme; LODs: 0.3-5.3 ppb, simult. detn. with *Paraoxon* and *Parathion;* f) accum by adsorpt., LOD: 0.05 µM; g,h) o.c. accum. with strong affinity of P=O to mdf., DLs: a) 5 nM, b) 5 µgL^{-1}	a) model solns. b) lake water c) well water (spiked) d) nat. water, soil e) soil extracts f) model mixts. g) apple tissue h) diff. water specimens	a) (Skladal, 1991) b) (L. Hernandez et al., 1993) c) (Mulchandani et al., 2001, a) (Mulchandani et al., 2001, b) d) (Fan et al., 2008) e) (Lei et al., 2004; Lei et al., 2005) f) (Liu & Lin, 2005) g) (Tan et al., 2010) h) (Parham & Rahbar, 2010)
Metolcarb 	methyl-hydroxy-2-Ph-methylcarbamate	C/PO (+ polyamide) [ft-D]	CZE-AD	hydrolysis to phenolic ders. and detn.; simult.detn. with *Carbaryl, Fenobucarb, Isoprocarb* LODs: 3-6 ×10^{-8} M	environmental specimens	(Cheng, 2007)
Nitenpyram (see Table 1)	neonicotinoid	C/SO, C/TCP [both CPEs as unm.]	DPV (dir.)	s.e.: BR-B (pH 7.0), lin.r.: 2-25 mg L^{-1}; detn.with *Clothianidin* & *Imidacloprid* electrolytic activation of CPEs tested	model solns.	(Papp et al., 2009a)

Analyte (form / alter.n.)	**Chem. specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Dichlorvos 	dimethyl-2,2-dichlo-rovinyl phosphate	C/PO (+ Co-PC) [CP-bio with enzymes]	AD (stat.)	detn. based on analyte inhibition / bio-enzymatic effect; PC: phthalocyanine, LOD: 2×10^{-4}- 0.1 $g{\cdot}L^{-1}$; RSD < ±3 %	model solns.	(Skladal, 1991)
Paraoxon-methyl 	subst. p-nitro-phen-oxy-organophoshate	a) C/PO (+ OPH-enzyme) b) C/PO (FePC + m-ezs) c) C/PO [+ *Arthrobacter* sp. + OPH-enzyme (m)] d) C/PO [+ *Pseudomonas putida JS444* sp + OPH]	a) FIA-EC b) AD (stat.) c) AD (stat.) d) LSV	OPH: phosphorus-hydroxylase; add. membrane + 2 enzymes; a,b) PhB, (pH 7-8), c) PhB + Na-citrate (pH 7.5) LODs: a) 0.1 μM, b) 1×10^{-10} M, c) 2.8 ppb; c) detn. with *Methylparathion* d) mdf: microbial degrader + enzyme, detn. with *Parathion, Methylparathion*	a) well water (spiked) b) model solns. c) soil extracts d) model solns.	a) (Mulchandani et al., 2001, a) (Mulchandani et al., 2001, b) b) (Ciucu, 2003) c) (Lei et al., 2004) d) (Lei et al., 2005)
Parathion 	subst. p-nitro-phen-oxy-organophoshate	a) C/PO [+ *Pseudomonas putida JS444* sp + OPH] b) C/PO (+ MIP)	a) LSV b) CV, DPV	a) mdf: microbial degrader + enzyme; detn. with *Paraoxon, Methylparathion* b) mdf.: molecularly imprinted polymer (sel. recogn. / extr. effect), l: 2-900 nM.	a) model solns. b) ground water, vegetables	a) (Lei et al., 2005) b) (Alizadeh, 2009)

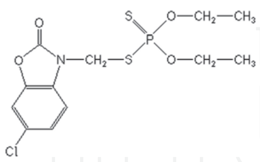
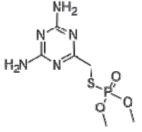
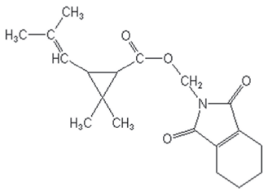
Analyte (form / alter.n.)	**Chem. specification**	**Type of CPE (modifier) [configuration]**	**Technique (mode)**	**Selected experimental conditions and analytical parameters; notes**	**Sample(s)**	**Ref (s)**
Phosalon 	chloro-diethoxy-thio phosphin-benzoxazol	C/PO (+ Co^{II}-2,2'-dipy)	DPAdSV	studies on pH-effect, adsorpt. & accum mechanism, interfs.; LOD: 5.5×10^{-9} M	model solns.	(Ulakhovic, 1998)
Saiphos 	(subst. diamino-phos-phino-thioyl-triazine	C/PO (+ crown-ethers)	CV, DPV	studies on accum. & reoxidn. process; lin.r.: 5×10^{-9}-1×10^{-7} M	model solns.	(Shaidarova et al., 1998)
Tetramethrin 	subst. cyano-phen-oxy-benzylalcohol	C/PO (+ *Sepiolite*)	DPV	studies on pH, accum. process, interfs. o.c., MEx, pH 5.3 + 12, LoD: 45 μg L^{-1}	water samples, soils	(Hernandez, 1989)
Thiamethoxam (see Table 1)	neonicotinoid	C/TCP (unm.)	DPV (dir.)	detn. without accum., s.e.: BRB (pH 7) lin.r.: a) 3.7-41.5 μg·mL^{-1}, RSD = ± 1.3%	river water, comm. prep. (*Actara 25-WG*)	(Papp et al., 2010)

Table 2. Determination of insecticides at carbon paste-based electrodes, sensors, and detectors. Survey of methods and selected studies.

with a relatively compact structure of metallic bismuth; i.e., as the **Bi(F)-TCP-CPE** or **bulk modified, $Bi_{5\%}$-TCP-CPE**, detection systems. By discussion the results and observations from the previous investigations, it is shown that all types of the TCP-CPE may offer a very fine electroanalytical performance in analysis of typical representatives of the neonicotinoid insecticides.

2. Choice and characterization of carbon paste electrodes for analysis of the neonicotinoids

2.1 Voltammetric behaviour of the neonicotinoids at CPEs and the effect of pasting liquid

As found out (Guzsvány et al., 2005; Guzsvány, 2006; Gaál et al., 2007; Papp et al., 2009b; Papp et al., 2010; Papp et al., 2011; Guzsvány et al., 2011), the voltammetric analysis of nitroguanidine and nitrometylene neonicotinoids at carbon-based working electrode revealed only the first reduction step, giving rise to the single analytical signal, which is similar to the previous experiments with the mercury electrode; see scheme (**1**) above.

Typical behaviour of the neonicotinoids at carbon paste-based electrodes is then depicted in **Fig. 1**, illustrating the initial testing (Papp et al., 2009b) in the same solution of *Imidacloprid* by using different types of CPEs, but with the same surface diameter of 2 mm. The respective CPEs had been prepared from three different liquid binders: **1**) silicone oil (the electrode denoted as "SO-CPE"), **2**) n-tetradecane ("C14-CPE"), and **3**) tricresyl phosphate ("TCP-CPE"). Moreover, in order to compare the individual reduction signals with traditional type of carbon electrode, identical voltammetric measurements were made also with **4**) the glassy carbon electrode (GCE, with the same diameter).

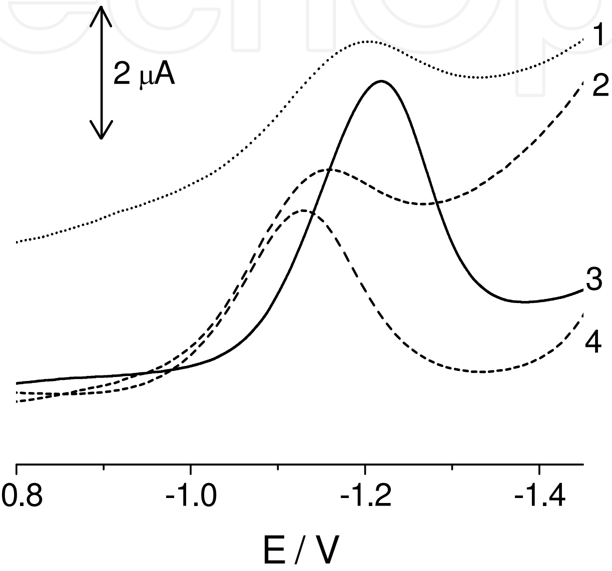


Fig. 1. Comparison of the DPV signals obtained at different working electrodes: SO-CPE (1), C14-CPE (2), TCP-CPE (3) and GCE (4) in the same solution of *Imidacloprid*. Experimental parameters: 25 mV s^{-1}, pulse amplitude 50 mV, pulse width 50 ms, c= 33.3 μg mL^{-1}, pH 7.0.

In all cases, one reduction peak was observed, but the reduction signals are different. The voltammogram recorded at the TCP-CPE (curve 3) is best developed, with most satisfactory signal-to-noise characteristics compared to the remaining signals at SO-CPE, C14-CPE, as well as GCE (curves 1, 2, and 4). As discussed in the original papers such behavior of the TCP-CPE was likely due to its polarity (Švancara and Vytřas, 1993; Papp et al., 2009b), facilitating the contact of polar neonicotinoid molecules with the electrode surface. Also, it can be noticed that the maximum of reduction peak of model compound is of about 0.1 V more negative at the TCP-CPE compared to both C14-CPE and the GCE. In conclusion, it was demonstrated that among the investigated binding liquids (i.e., silicone oil, *n*-tetradecane and tricresyl phosphate (TCP), the latter had offered the best electroanalytical performance for analytical applications (Papp et al., 2009b) and, naturally, the TCP-CPE is of continuing interest in our further investigations.

Thus, the same electrode has also undergone a special characterization by means of microscopic imaging using scanning electron microscopy (SEM). More specifically, the graphite powder (type "CR5"), one of the two basic component of the electrode, and the resultant TCP-CPE were observed and their microstructure is shown in **Fig. 2**. As reported earlier (Švancara and Vytřas, 1993 and Papp et al., 2009b), two different morfologies of the SEM sample can be observed. Characteristic particles of CR5 graphite with distinct sharp edges are well recognizable on the carbon powder surface (A), while in the case of the TCP-based paste, the surface looks notably smoother and more uniform. At some images (e.g. those reported in Švancara et al., 1996; Papp et al., 2009b; Papp et al., 2011), this texture had moreover manifested a notable tendency to form very compact aggregates, making thus the TCP-paste quite unique in comparison with the other common mixtures. Although the exact reflection of this feature into the behaviour of the TCP-CPE has not been yet fully explained, this unique microstructure is undoubtedly behind some specifics of this unusual CPE (Švancara et al., 2011).

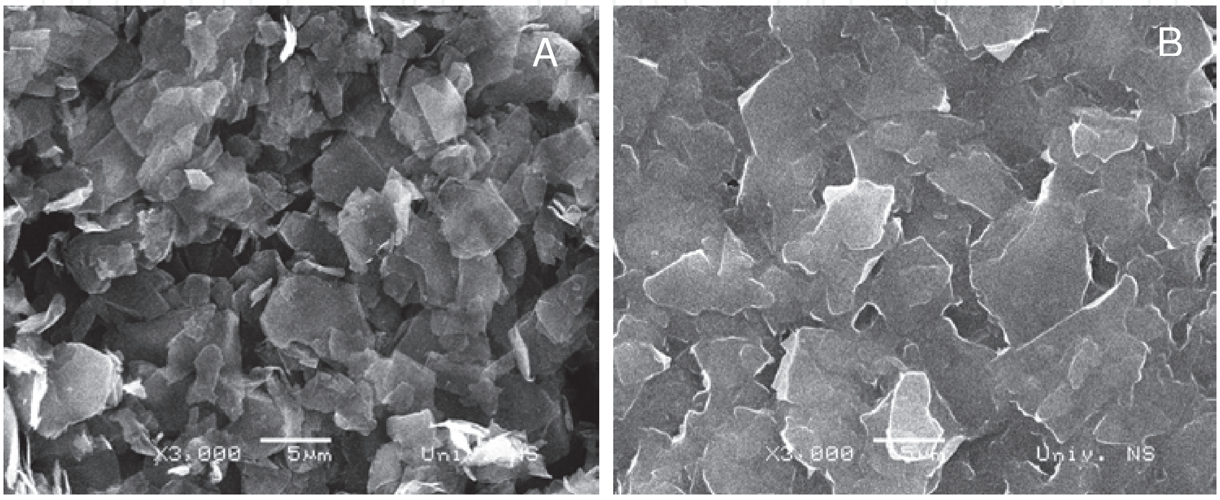


Fig. 2. SEM image of the CR5 graphite powder (A) and TCP-CPE (B).

Herein, one can quote two most distinct abnormalities of the TCP-CPE compared to common CPEs, as well as other carbonaceous electrodes. At first, it is unusually high signal-to-noise ratio and its overall magnitude, when - in some cases - the respective values may reach even a ten-fold intensity of that being typical for Nujol oil (Švancara et al., 2002) - or silicone oil-based CPEs (Švancara et al., 2002.; Papp et al., 2009b). Secondly, it is a shorter lifetime of the TCP-CPE given by higher volatility of tricresyl phoshate compared to traditional oily binders (Švancara and Vytřas, 1993; Papp, 2011; Papp et al. 2011). According to purely empirical observations, an average lifetime of a TCP-CPE is about two weeks only; afterwards, the paste becomes desiccated and unavoidably disintegrates, losing quickly all typical properties. This can be clearly documented in **Fig. 3**, visualising the recent experiment on the ageing of the TCP-CPE. As can be seen, the "old" paste has lost totally its sensitivity to the model analyte, exhibiting also notably higher background. (Both phenomena indicate the loss of the binder, as well as the increased content of graphite in the desiccated mixture.) Newly (Papp et al., 2011), it was shown that this drawback of the TCP-CPE can be minimised by enveloping the tip of the electrode with Parafilm® and storage in the fridge (at ca. 4 °C) - in other words, by preventing the evaporation of tricresyl phoshate - and the overall lifetime can thus be extended up to several months of use (!)

2.2 Development and optimisation of the method for the determination of neonicotinoids at the bare TCP-CPE

Our previous investigations with the bare TCP-CPE gathered in the respective reports (Papp et al., 2009a, 2009b, 2011) have finally resulted in a simple procedure, allowing us also quantitative analysis of selected neonicotinoids, as well as sensitive monitoring during their

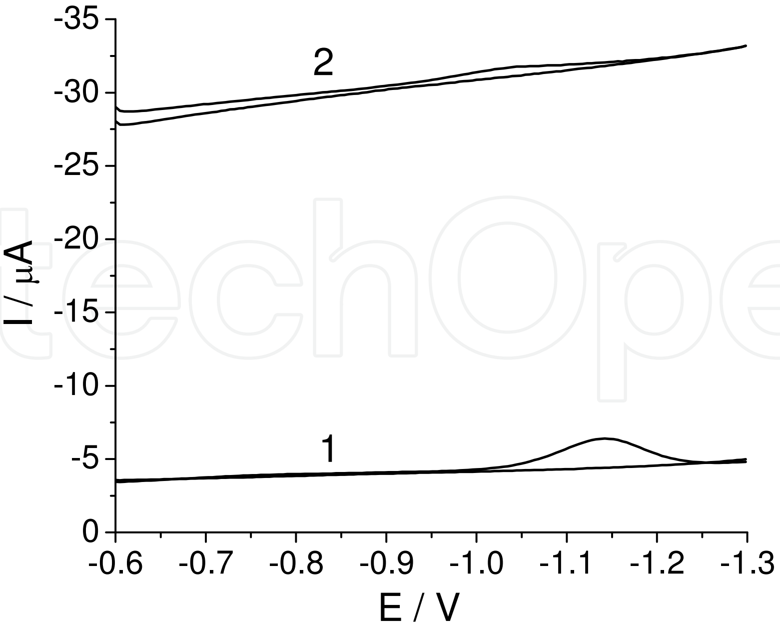


Fig. 3. Comparison of DPV signals obtained for Imidacloprid with the TCP-CPE: 1) one day after preparation, 2) ten days after preparation in solution with the same concentration of model substance (c = 33.3 µg mL^{-1}). Note: below are shown the corresponding baselines (blank solution).

degradibility in the course of time. All the principal features of these measurements are briefly summarised in the following sections.

In the first phase, elaboration of the proper procedure (Papp et al., 2009a, 2009b, 2010) required to investigate / optimise several key parameters; namely, the effect of dissolved oxygen (see **Fig. 4**), electrode conditioning (**Fig. 5**), acidity of the supporting electrolyte (not shown), or accumulation capabilities of model neonicotinoids (**Fig. 6**); again, when keeping in mind specific signal-to-noise characteristics of the TCP-CPE.

Effect of Oxygen and Electrode Conditiong. It was shown that the purging of the sample solutions with inert gas (**Fig. 4**, curve 2) was necessary to suppress the effect of the dissolved oxygen (curve 1). In the case of the neonicotionoids, this step had been found inevitable despite the previous observation that the TCP-CPE would have exhibited generally lowered signal of oxygen reduction (Švancara et al., 1993; Kalcher et al., 2006). Further, as mentioned earlier (Papp et al., 2009b) and shown in Fig. 5, electrochemical conditioning of the TCP-CPE by potential cycling was found beneficial in the potential range of interest, resulting in effective lowering of the background and more stable voltammetric signals.

Accumulation Study. A possible adsorptibility of the neonicotinoids as a way of potentially effective pre-concentration at the TCP-CPE surface was tested with *Imidacloprid*, when setting the respective time periods within an interval of 1-20 min. The whole experiment is given in Fig. 6, where curve 1 represents the initial stage, *i.e.,* the DP-voltammogram No. 1 (obtained by reducing the model substance). Afterwards, the electrode was left in the same solution (with pH 8.0) for 20 min without potential applied; the subsequent DPV record being No. 2. As seen, there is almost no difference between both records, suggesting us that *Imidacloprid* have had no tendencies to be adsorbed onto the TCP-CPE surface.

Reproducibility Studies. At the TCP-CPE, the signals for the four investigated compounds were checked as the corresponding replicates for a model concentration of each neonicotinoid. This assay had been included to reveal again whether or not the system studied would exhibit some accumulation capabilities, such as sorption affinity. **Fig. 7** showing a nonet of replicates confirming good reproducibility for a signal of 3.72 μg mL^{-1} *Thiamethoxam*, within the time interval of approx. 30 min, with no evidence for a spontaneous accumulation and with the RSD being less than 2.5% rel. Nearly the same results has then been obtained also for the remaining three neonicotinoids (Papp, 2011).

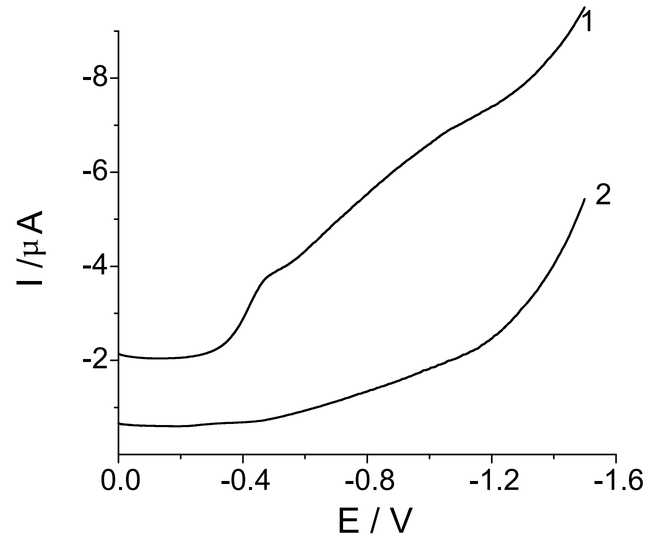


Fig. 4. Effect of presence (1) and absence (2) of dissolved oxygen on the baseline of DPV signals at pH 7.0 (after Papp et al., 2009a).

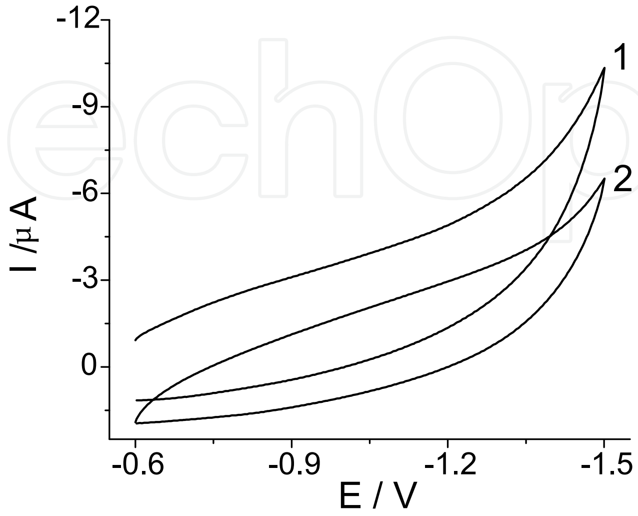


Fig. 5. Potential cycling of TCP-CPE. Exp. parameters: pH 7.0; v = 100 mV/s^{-1} (1: 1st cycle; 2: 10th cycle) (after Papp et al., 20011).

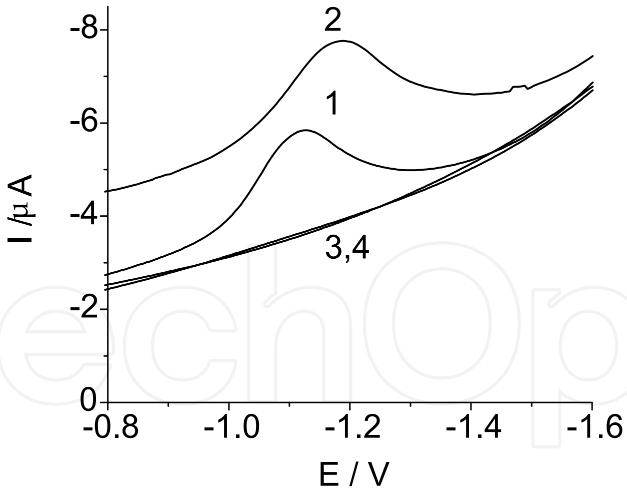


Fig. 6. An assay on potentially adsorptive behavior of *Imidacloprid* at the TCP-CPE: 1) DPV reduction, 2) DPV reduction after 20 min. of accumulating under open-circuit conditions, and 3,4) base-lines before and after 1st measurement. Other experimental parameters: pH 8.0, c(IMI) = 33.3 μg mL^{-1}; scan rate, 25 mV s^{-1}, pulse amplitude, +50 mV, pulse width 50 ms

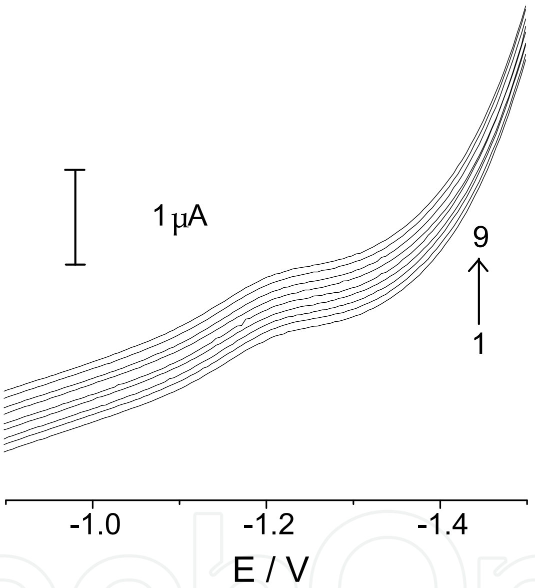


Fig. 7. The reproducibility of the analytical signal for *Thiamethoxam* at the TCP-CPE. Model concentration, c(TH) = 3.7 μg mL^{-1} measured in an time interval of 30 min (Papp, 2011).

Comparison of two different TCP-CPEs. After the checking the reproducibility of the analytical signals and their stability in time, the next step was to compare the electroanalytical performance of two individual TCP-CPEs in analysis of the same sample solution. This assay was assembled for an eventuality if a series of identical working electrodes would be needed for routine analysis; for example, in the field monitoring at different locations. For this purpose, *Clothianidin* was selected as the substance of choice being determined at two identical TCP-CPEs that had been prepared from the same batch of carbon paste (see **Fig. 8**). In both cases, the electrodes tested showed almost the same performance, confirming the applicability of the TCP-CPE to the decentralized determination; i.e., at more sites in one time. Herein, however, it should be emphasised that any joint (absolute) calibration is not feasible and each electrode has to be prepared for quantitative analysis individually. (This is given by the specific character of the carbon paste electrode material, when every respective electrode under actual use represents a unique item with its own characteristics – for other details, see Švancara and Schachl, 1999).

Other practical notes and hints. The ultimate method for the determination of *Imidacloprid* and *Thiamethoxam* at the TCP-CPE in model solutions, as well as real samples (various commercial formulations), has already been elaborated into detail a couple of years ago (Papp et al., 2009a; 2009b; 2010), including the assesment of the individual instrumental options and experimental parameters for the determination of *Clotianidin* and *Nitenpyram*. In brief, both neonicotninoids of interest could be determined at the low ppm level from 1 or 2 $\mu g\ mL^{-1}$, respectively, up to 35 and 45 $\mu g\ mL^{-1}$ with the RSD lower than 2.4% rel.

As discussed therein, the voltammetric characteristics of the two compounds had depended strongly upon the pH of the sample solution; for each the optimum being at pH 7.0. Finally, limits of quantitation (LOQs) estimated in a conventional way (3s) were found to be at the low $\mu g\ mL^{-1}$ level for all the neonicotinoids included in the study – i.e., for *Imidacloprid, Thiamethoxam, Clothianidin*, and *Nitenpyram*, too.

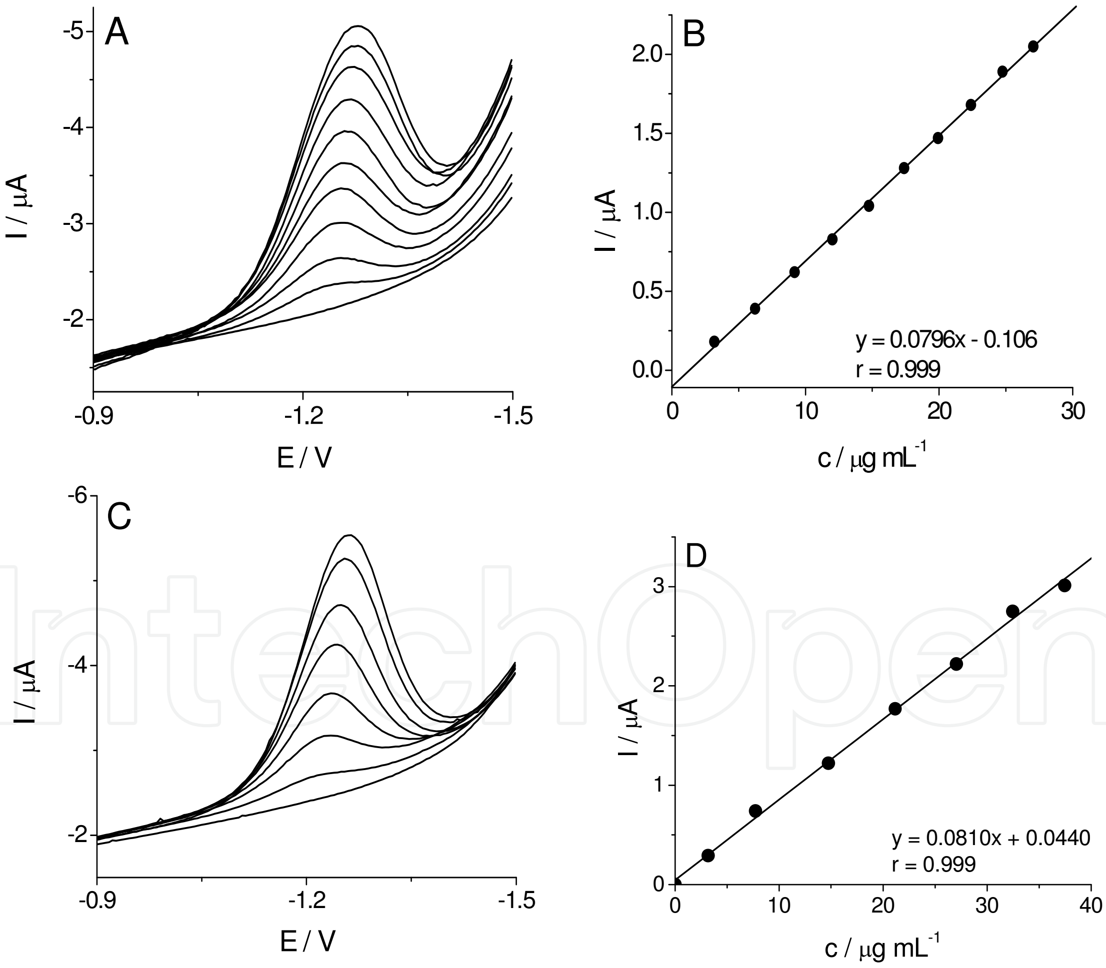


Fig. 8. Differential pulse voltammograms of clothianidin recorded at different concentrations of two TCP-CPE identical composition. A) TCP-CPE-1 and C) TCP-CPE-2; B) and D) the corresponding calibration curves (Papp, 2011).

Concerning the real analysis, the method for the determination of neonicotinoids at the TCP-CPE (Papp et al., 2009a; Papp et al., 2009b; Papp et al., 2010; Papp et al., 2011; Papp, 2011) in combination with DPV was applied to identify and quantify *Imidacloprid* and *Thiamethoxam* in samples of river water and some commercial formulations; namely: "Macho 200 SL" (for the respective analysis, **Fig. 9**), "Confidor 200 SL" and "Actara 25 WG"), when using the standard addition method with multiple injection of the standard (in aliquots).

It can be stated that all the tests performed had shown a very good correlation between the determined and the nominal (added) amounts of each. And, in all cases, the results of electrochemical analyses had been compared to the reference method employing HPLC/DAD, showing good agreement for each sample.

Finally, the TCP-CPE was also examined in the monitoring of photolytic and photocatalytic degradation of *Thiamethoxam* (for the latter, with TiO_2 particles as the photocatalyst, Degussa 25) under natural insolation (see **Fig. 10**), as well as in the dark regime (Fig. 11, lines 3, 4). It was shown that, under insolation in the autumn period (September, 2009), the photolytic processes followed the first-order reaction kinetics, while the photocatalytic process followed a kinetics of the pseudo-first order. As the DPV method and the reference HPLC/DAD had given very similar kinetic data, the voltammetric method with TCP-CPE could thus be evaluated as fully applicable to obtain the fast (orientation) information about the concentration of the neonicotinoids during their photodegradation (Papp, 2011).

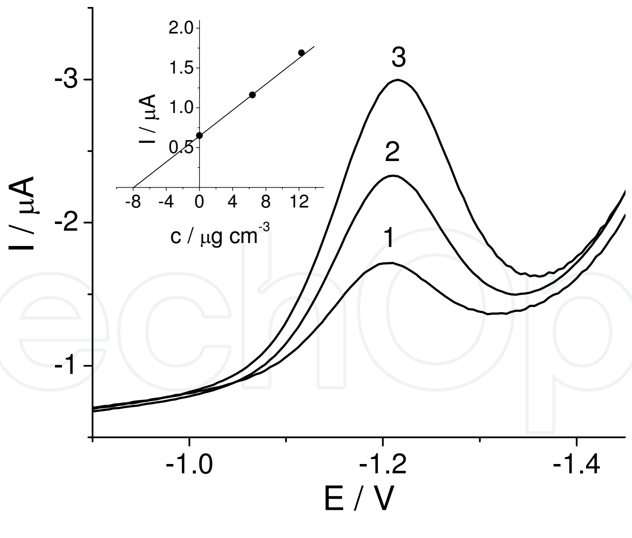


Fig. 9. Determination of *Imidacloprid* in commercial formulation "Macho 200 SL". 1) sample and 2,3) two successive additions of standard solutions of *Imidacloprid*.

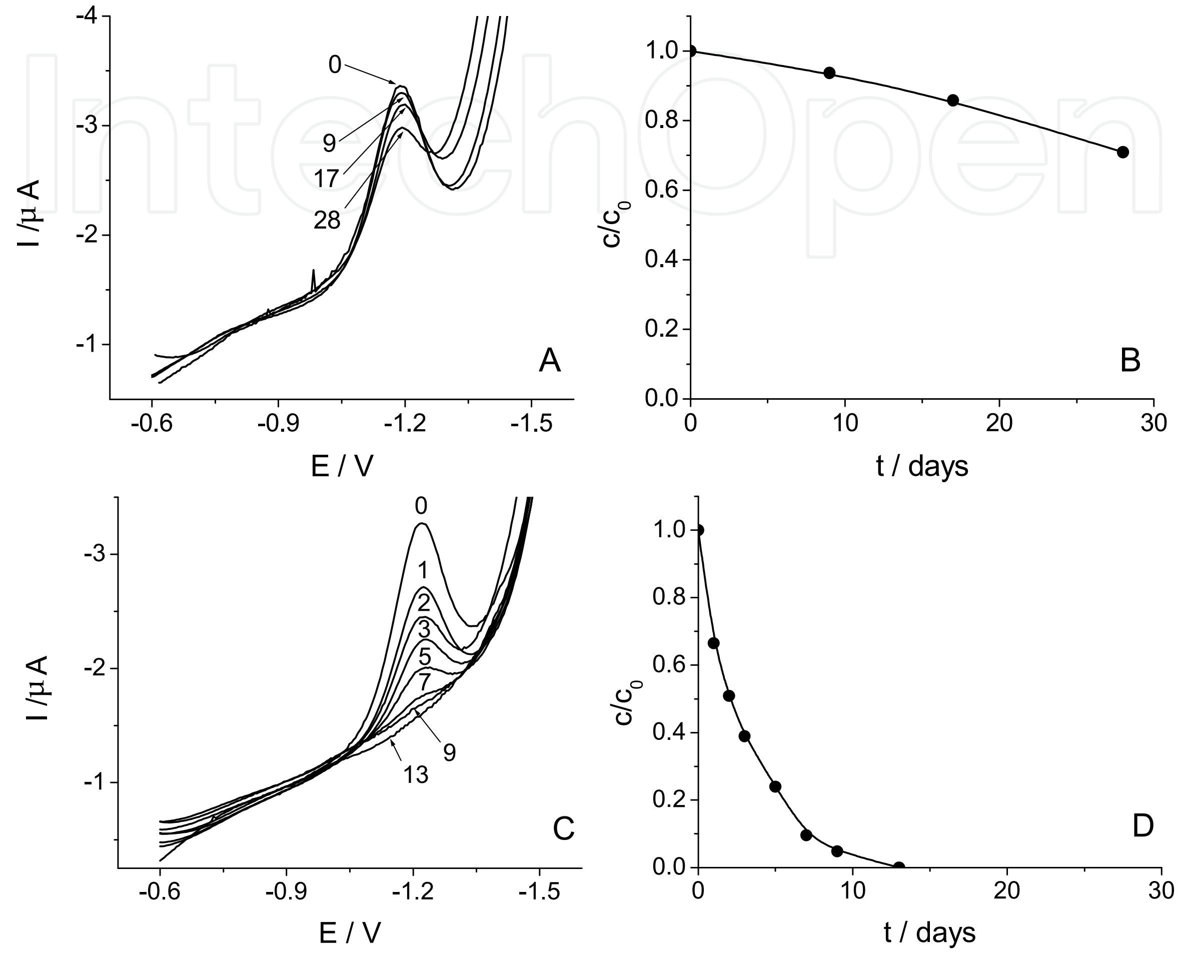


Fig. 10. Differential pulse voltammograms recorded with TCP-CPE during photolytic (A) and photocatalytic (C) degradation of *Thiamethoxam* solution under natural insolation, as well as the corresponding kinetic curves (B and D). The initial concentration of the insecticide was 116.7 µg mL^{-1}. The sample aliquots were diluted with adequate Britton – Robinson buffer solutions pH 7.0. Numbers on DPV curves indicate the days of sampling (Papp, 2011).

In contrast to the results obtained under natural insolation, the dark-regime measurements with *Thiamethoxam* had not reveated any significant changes in the presence and absence of the photocatalyst as can be seen in **Fig. 11** overleaf. Under natural insolation promoted by the presence of TiO_2, the half-life time of the nitroguanidine electroactive site in the *Thiametoxam* molecule had been ascertained to be about just 2 days. The fast removal of *Thiamethoxam* in this case could be attributed to the presence and specific functioning of the rutile form of TiO_2 (Abramović et al. 2007; Guzsvány et al., 2010).

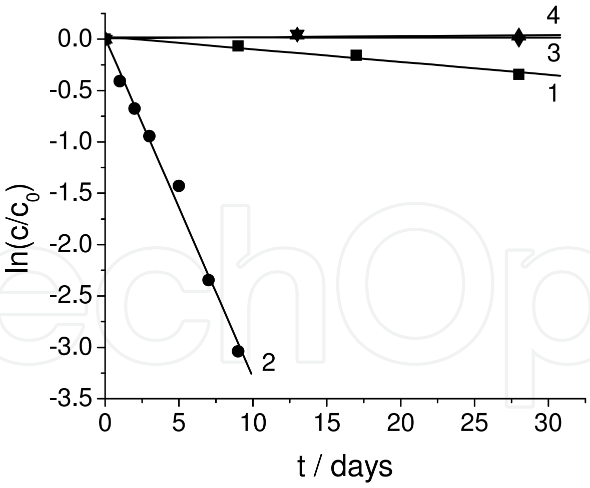


Fig. 11. Comparison of the kinetics of the photolytic (1) and photocatalytic (2) degradation of *Thiamethoxam* monitored by DPV with TCP-CPE. The lines for the monitoring of the stability of *Thiamethoxam* in dark in absence (3) and presence (4) of TiO_2 are also presented. The initial concentration of the insecticide was 116.7 μg mL^{-1}.

In general, the developed procedure could then be recommended as a convenient tool for the determination of *Thiamethoxam* during the photodegradation without a sample clean-up, which may further lower overall expenses. Though the chromatographic technique has been found to provide more detailed information about the system monitored, voltammetry with TCP-CPE that utilises fine electroactivity of all typical neonicotinoids represent, in our opinion, an attractive and low-cost alternative for environmental screening, being also capable of gaining information about the actual pollution with the insecticide and its eventual concentration changes during the photolytic and photocatalytic degradation.

3. Bismuth modified TCP-CPEs in analysis of selected neonicotinoids

3.1 Bismuth-film plated TCP-CPE for the determination of *Imidacloprid*

As mentioned above, the bismuth-film plated tricresyl phosphate-based carbon paste electrode; i.e., the BiF/TCP-CPE configuration has firstly been tested and used for the determination of some neonicotinoids. Similarly like other bismuth-film plated glassy carbon electrodes (Hutton et al., 2004; Guzsvány, 2006; Guzsvány et al., 2006c; Gaál et al., 2007; Guzsvány et al., 2008b; Claux and Vittori, 2007; Moreno et al., 2009; Nigović et al., 2009; Li et al., 2010; de Figueiredo-Filho et al., 2010 and the references herein), also this variant has undergone the thorough characterization. The individual studies included also the comparison of TCP-CPE with Nujol oil and silicone oil-containing carbon pastes ("Nj-CPE" and "SO-CPE", respectively) in their electroanalytical performance for model solutions of *Imidacloprid*. In the case of the TCP-CPE and SO-CPE, the plating was carried out *ex situ* in (quiet) solution consisting of 0.02 M $Bi(NO_3)_3$, 1 M HCl, and 0.5 M KBr in an analogy to the previous procedure for the bismuth deposition onto the glassy carbon substrate electrode - GCE (Guzsvány et al., 2006c; Gaál et al., 2007; Guzsvány et al., 2008b). The choice of the deposition potential within this study for the respective bismuth-film electrodes is illustrated in **Fig. 12** (A and B): the maximum of the bismuth reduction peak is the most convenient plating potential. On the other hand, images "C" and "D" demonstrate the differences in sensitivity for both BiF/TCP-CPE and BiF/SO-CPE with respect to *Imidacloprid*. In contrast to the sharp reduction peak obtained at the BiF/TCP-CPE, the reduction signal obtained at both bare TCP-CPE and SO-CPE are much lesser, which is also the case - rather surprisingly - of the BiF/SO-CPE responding with ca. 5x less intensity compared to the TCP counterpart. Furthermore, in contrast to measurements with the bare TCP-CPE that need to remove dissolved oxygen (see par. **2.1**), the presence of bismuth film at the surface had allowed to run the voltammetric scans even in the presence of oxygen, which is widely appreciable benefit of using bismuth-film based electrodes in cathodic measurements (Wang, 2005).

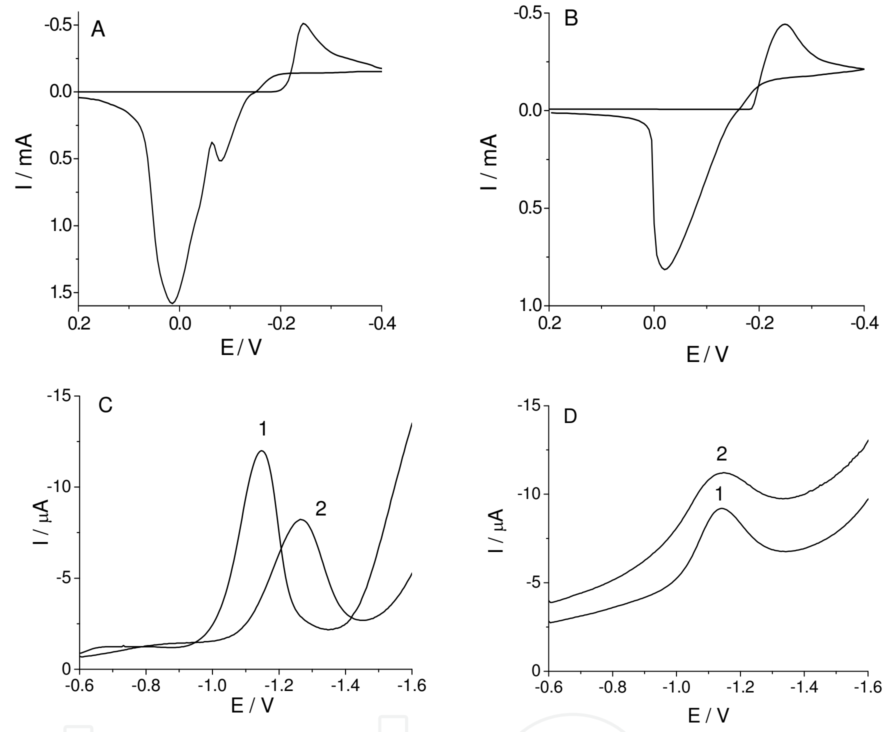


Fig. 12. Cyclic voltammogram recorded with two types of TCP in the solution consisting of 0.02 M Bi(NO$_3$)$_3$, 1 M HCl and 0.5 M KBr, (v =25 mV s^{-1}): A) TCP-CPE and B) SO-CPE and comparison of DPV signals obtained at two different bare and surface modified substrate working electrodes: C) BiF/TCP-CPE (1) and TCP-CPE (2) and D) BiF/SO-CPE (1) and SO-CPE (2) in the same *Imidacloprid* solution while c= 33.34 μg mL^{-1} and pH 7.0.

3.2 Bismuth bulk-modified TCP-CPE for analysis of *Imidacloprid* and *Nitenpyram*

The tricresyl phosphate-based CPE in the role of substrate for bismuth has also been tested in the alternative configuration – with a fine bismuth powder mechanically embedded and thus dispersed into the TCP-CP mixture. This "pseudo"-film arrangement functioning almost identically like common bismuth-film configurations (Hočevar et al., 2005; Švancara et al., 2006) seemed to be particularly convenient in combination with polar molecules of TCP, allowing us to accomplish the sensitive determination of selected neonicotinoid insecticides

(Papp et al., 2009a; Papp et al., 2009b; Papp et al., 2010; Papp et al., 2011) if the powdered bismuth is incorporated into the TCP-CPE at the appropriate amount (Guzsvány et al., 2011).

The scanning electron microscopic (SEM) imaging of the surface microstructure of the TCP-CPE containing 5% (w/w) bismuth ("$\text{Bi}_{5\%}$/TCP-CPE") has shown that the binary carbon paste matrix contains a rather homogenous solid phase with randomly distributed irregularities that are, in fact, the aggregates of tiny Bi particles (see **Fig. 13**). This was confirmed by energy dispersive spectrometric measurements (EDS; **Fig. 14**) performed on two different sites of the actual $\text{Bi}_{5\%}$/TCP-CPE surface, selected so that both of them contains the mentioned Bi-aggregates dispersed in the TCP-CPE matrix (Guzsvány et al., 2011).

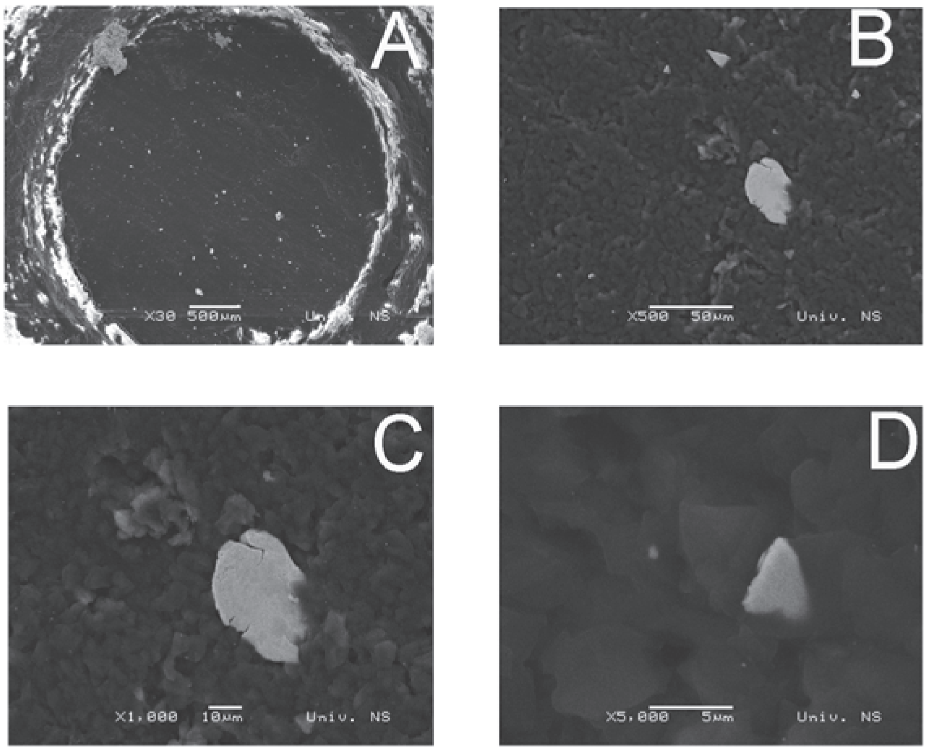


Fig. 13. Scanning electron micrographs of $\text{Bi}_{5\%}$/TCP-CPE obtained at different magnification.

The applicability of the bare (unmodified) TCP-CPE and of the $\text{Bi}_{5\%}$/TCP-CPE as two different working electrodes to determine the model compound, *Imidacloprid*, has been examined by comparing at the same experimental conditions (Guzsvány et al., 2011). In the case of both electrodes, the reduction peak was observed at ca. −1.2 V vs. ref., but the reduction signals were somewhat different. In comparison with TCP-CPE, a potential shift of about 50 mV towards the less negative potentials could be observed for the Bi5%/TCP-CPE, resulting in better insensitivity of this electrode to the presence of oxygen so that there was no need to purge the solution with inert gas (Guzsvány et al., 2011). Similar observations with both TCP-CPE and $\text{Bi}_{5\%}$/TCP-CPE have also been made for analysis of *Nitenpyram* as documented in **Fig 15**. The whole study also permitted to estimate the limit of quantification (LOQ); the respective values being down to 1.9 μg mL^{-1} and 1.6 μg mL^{-1} *Nitenpyram* for TCP-CPE and $\text{Bi}_{5\%}$-TCP-CPE, respectively. Also, the reproducibility studies swith both electrodes were performed, when six replicates with each and in the model solution of 15.4 μg mL^{-1} *Nitenpyram* gave the RSD typically less than ±2.5%

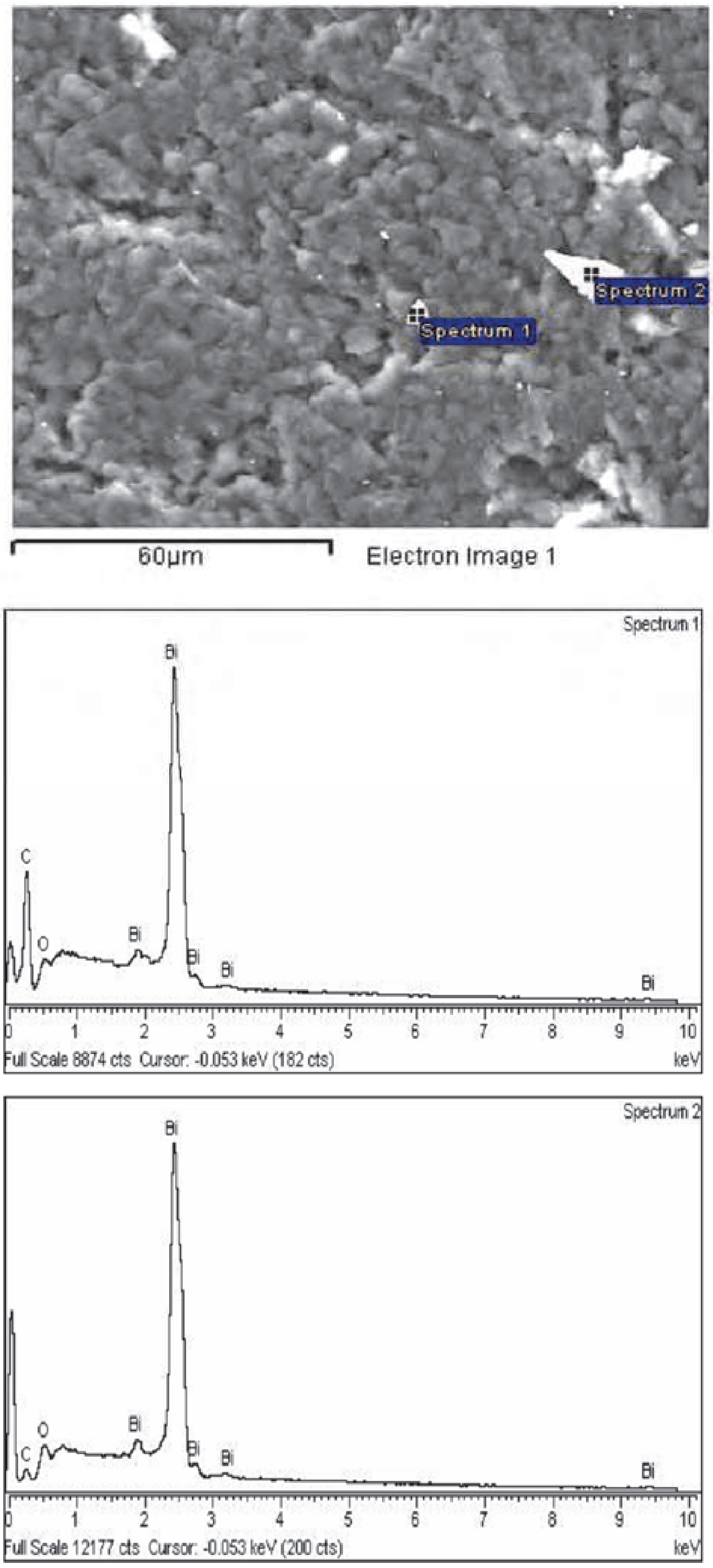


Fig. 14. Representative part of the $Bi_{5\%}$/TCP-CPE surface and EDS microanalysis spectra of the bismuth particles inside the actual surface area.

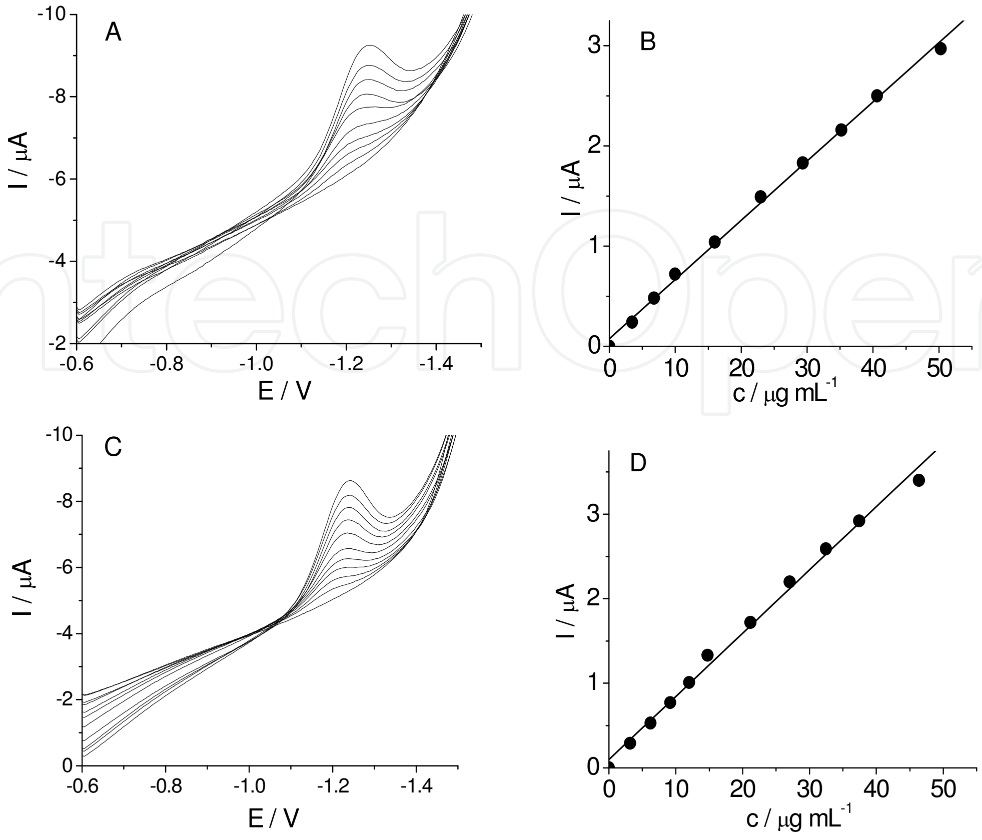


Fig. 15. Differential pulse voltammograms of *Nitenpyram* recorded at different concentrations of the compound at $Bi_{5\%}$/TCP-CPE (**A**) and TCP-CPE (**C**) with the corresponding calibration curves (**B** and **D**).

All these results have shown that there were no significant differences in the overall electroanalytical performance in direct cathodic determinations and, in fact, both TCP-CPE and $Bi_{5\%}$/TCP-CPE could be used in similar way and with comparable results. But, there was one distinct difference between, when the latter had not required the removal of oxygen prior to measurement. Thus, the most time-consuming subroutine with bubbling can be eliminated and the whole procedure significantly shortened. In addition, the necessity to purge the solution would require the permanent source of inert gas, which could complicate eventual field (outdoor) monitoring, which, in the case of the Bi/TCP-CPE, becomes irrelevant.

4. Conclusion

In this article, electroanalysis of some neoniciotinoids has been reviewed, for the first time, in exclusive combination with carbon paste-based electrodes. As shown, the electrode of choice can be the TCP-CPE; a special type of carbon paste electrode with tricresyl phosphate as the pasting liquid. Alternatively, one can employ the same electrode as the substrate (support) for either being plated with a bismuth film (with the aid of controlled electrolysis); i.e., the BiF/TCP-CPE configuration, or its related variant prepared again from the bare TCP-CPE when admixing a fine bismuth powder into the bulk; the resultant configuration being $Bi_{5\%}$/TCP-CPE.

The proper determination with both TCP-CPE and Bi(F)/TCP-CPE surprisingly does not involve any accumulation step since the compounds of interest - herein: *Imidacloprid, Nitenpyram*, *Clothianidin* and *Thiamethoxam* - have not exhibited any notable affinity to be spontaneously pre-concentrated at the CP-surface. Despite this rather unusual feature, the determination of the target compounds can be accomplished with good sensitivity, allowing one to detect the analyte(s) of interest down to the low ppm (μg mL^{-1}) level.

One of the main goals of this article was to demonstrate that often underestimated electroanalysis can also be a powerful tool for the determination of some organic pollutants, with its overall performance fully comparable to separation and optical techniques, but applicable at much lower investment and operational costs. Moreover, electroanalytical procedures, including those reviewed herein, have great potential for being used in the field monitoring and in *on-line* analysis of insecticides, including the neonicotinoids.

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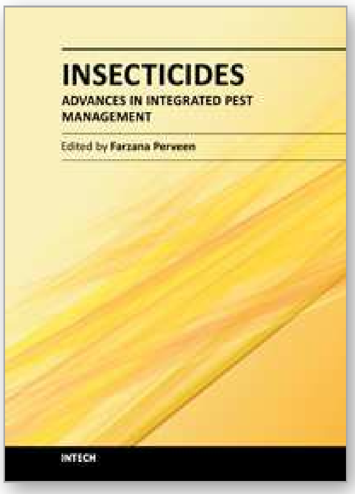

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This book contains 30 Chapters divided into 5 Sections. Section A covers integrated pest management, alternative insect control strategies, ecological impact of insecticides as well as pesticides and drugs of forensic interest. Section B is dedicated to chemical control and health risks, applications for insecticides, metabolism of pesticides by human cytochrome p450, etc. Section C provides biochemical analyses of action of chlorfluazuron, pest control effects on seed yield, chemical ecology, quality control, development of ideal insecticide, insecticide resistance, etc. Section D reviews current analytical methods, electroanalysis of insecticides, insecticide activity and secondary metabolites. Section E provides data contributing to better understanding of biological control through Bacillus sphaericus and B. thuringiensis, entomopathogenic nematodes insecticides, vector-borne disease, etc. The subject matter in this book should attract the reader's concern to support rational decisions regarding the use of pesticides.

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