Sensing
in Electroanalysis

Vol. 7 (K. Kalcher, R. Metelka, I. Švancara, K. Vytřas; Eds.), pp. 265–281.
© 2012 University Press Centre, Pardubice, Czech Republic.
ISBN 978-80-7395-563-2 (printed); 978-80-7395-564-9 (on-line)

Bismuth-Modified and the Native Tricresyl Phosphate-Based Carbon Paste Electrode for the Determination of Two Different Pesticides

Jelena Đorđević[1], **Marko Rodić**[2], **Amir Ashrafi**[3], **Zsigmond Papp**[2], **Valéria Guzsvány**[2*], **Tatjana Trtić-Petrović**[1], **Ivan Švancara**[3], and **Karel Vytřas**[3]

[1] *Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia,*

[2] *Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, RS-21000 Novi Sad, Republic of Serbia,*

[3] *Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ-532 10 Pardubice, Czech Republic.*

Abstract: In this article, the voltammetric responses of the bismuth powder bulk-modified tricresyl phosphate-based carbon paste electrode ($Bi_{5\%}$-C/TCP, where 5% is the content of pulverized metal), surface-modified, bismuth film-plated BiF-C/TCP), and the unmodified carbon paste electrode of the C/TCP type were studied and subsequently optimized for the cathodic determination of *Imidacloprid* (IMI), an insecticide reducible in a fairly negative potential range. The individual comparisons have shown that the determination of IMI is more efficient with the $Bi_{5\%}$-C/TCP or $Bi_{20\%}$-C/TCP, respectively, by the direct cathodic differential pulse voltammetry (DPV). Concerning the determination of *Carbendazim* (CBZ), a fungicide oxidizable at the positive potentials, the unmodified C/TCP was applied to the determination in the differential pulse anodic stripping voltammetric mode. The respective LODs were at the low μg mL^{-1} level for IMI or even down to the ng mL^{-1} for a more sensitive determination of CBZ.

Keywords: Tricresyl phosphate-based carbon paste; two bismuth-modified variants, unmodifed form; voltammetric determination, *Imidacloprid (IMI)*, *Carbendazim (CBZ)*.

---

*) Author to whom correspondence should be addressed. E-mail: valeria.guzsvany@dh.uns.ac.rs

Introduction

The increasing use of pesticides; namely, herbicides, insecticides, and fungicides in agriculture, forestry, and domestic activities (to control pests) causes pollution of the water resources, environment, as well as of many foodstuffs.

Today, one particular group of neonicotinoids represents the fastest-growing class of insecticides available on the market since the commercialization of pyrethroids [1,2]. *Imidacloprid* (IMI), i.e., (*EZ*)-1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidene-amine, (see Fig. 1a) represents the most required product of the seven commercialized neonicotinoids. First synthesized in its active form by Bayer HealthCare (in Japan, 1986), it was developed to control a variety of insects in agriculture and veterinary practice.

Carbendazim (CBZ), methyl-1H-benzo-[d]-imidazol-2-yl-carbamate, (Fig. 1b), is the most typical broad-spectrum benzimidazole fungicide, playing an important role as the systemic in plant disease control [3]. Its function is the inhibition of the fungi growth; probably by interfering with the spindle formation at mitosis (cell division) [4]. CBZ has extensive applications worldwide, with the global market over $200 million, equivalent to over 12,000 tons active ingredient [5].

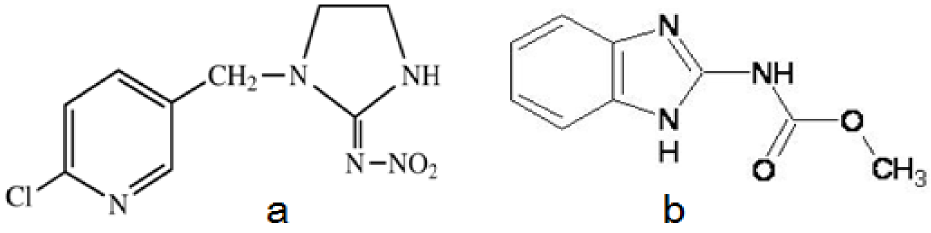

Fig. 1: *Structural formulas of Imidacloprid* (**a**) *and Carbendazim* (**b**)

A wide spectrum of analytical methods has been used to analyze different types of pesticides; most of them being based on chromatographic separations. Benzimidazole fungicides and neonicotinoid insecticides cannot be analyzed directly by gas chromatography because of their polar and thermolabile nature. Therefore, HPLC is used instead; often, with the diode array detector unit [6-10].

Other detection systems, such as electrochemical detector [11] or mass spectrometer [12-15] are also feasible and applicable to these compounds. However, the HPLC separation is both instrumentally and financially demanding, and the respective analysis may become less attractive due to the time-consuming procedure.

Nowadays, modern voltammetric methods in combination with a large variety of electrodes / detection systems, represent simple, inexpensive, and sufficiently sensitive / selective approaches applicable to a large-scale monitoring of electrochemically active environmental pollutants [16,17]. Often, the crucial point of the corresponding procedures is the proper choice of the working electrode operated with high sensitivity, satisfactory reproducibility of the signal, within a wide potential window and, if possible, insensitive to dissolved oxygen. This is also the case of the so-called *carbon paste electrodes* (CPEs [18,19]), one of the most popular types of simple sensors made in laboratories and applicable in the whole spectrum of electrochemical and electroanalytical measurements. There are also some special CPEs with electroactive binder; typical example being the tricresyl phoshate-based carbon paste electrode (TCP-CPE or C/TCP, respectively), introduced in the early 1990s [20]. Especially this electrode has proved itself to be a very convenient tool for analysis of insecticides as elaborated earlier [21-25] and already reviewed in a book chapter by our group [26].

Among others, the C/TCP can serve as the supporting electrode for metallic films or dispersions, including bismuth-based variants, representing one of the “hottest topics” in electroanalysis since the commencement of the new millennium [27-30]. Although the dominant area of the bismuth-based electrodes, BiEs, is still trace analysis of heavy metals (see [27] and refs. therein), the determination of organic pollutants comes also to the fore (*e.g.* 4-amino-3-nitrophenol [31], *Nitenpyram* or *Imidacloprid* [32,33]; the latter two representing one of the very first examples of employment of the C/TCP in analysis of neonicotinoid insecticides, to date as preliminary tests on their determination. Moreover, as far as the oxidizable pesticides are concerned, the phenylurea-based herbicides, *Linuron* and CBZ are also measurable with the C/TCP; best, when employing its unmodifed (native) form [34-36].

In this article, some continuing experiments with two above-mentioned pesticides are presented, herein with two bismuth-modified tricresyl phosphate-based carbon paste electrodes (namely: Bi-C/TCP and BiF-C/TCP configurations) for the determination of *Imidacloprid* (IMI), and with the original (bare) C/TCP to determine *Carbendazim* (CBZ), a benzimidazole fungicide that can readily be oxidized at the positive potentials.

Experimental

Chemicals, Reagents, Stock, and Standard Solutions

All chemicals used were of analytical reagent grade, and all the solutions were prepared in doubly distilled water. Analytical standard of IMI (*Sigma-Aldrich*, PESTANAL®) was of 99.9% purity. The concentration of the IMI stock solution was 6.5 x 10^{-4} mol L^{-1} (≈ 176.0 µg mL^{-1}), being diluted as required. CBZ (with 99% purity) was obtained from *Fitofarmacija* (Zemun, Serbia). The concentration of the CBZ stock solution was 0.01 mol L^{-1} (≈ 200 µg mL^{-1}), it was made by its dissolving in DMFA (*Sigma-Aldrich*) and kept in dark at –4 °C. The Britton-Robinson buffer (BRB) solutions with different acidity (varying from pH 2.0 to 8.0) and serving as the model supporting electrolytes were prepared by mixing solutions of 0.04 mol L^{-1} H_3PO_4, 0.04 mol L^{-1} H_3BO_3, and 0.04 mol L^{-1} CH_3COOH (all acids purchased from *Merck*), and adjusting the pH by the appropriate amount of 0.2 mol L^{-1} NaOH (*Merck*).

Apparatus

In all voltammetric measurements, an electrochemical system AUTOLAB PGSTAT12 (*Eco Chemie*; The Netherlands) was used in combination with GPES software (the same manufacturer). The cell stand included a three-electrode system with a TCP-CPE, Bi-TCP-CPE or BiF-TCP-CPE as working, a saturated calomel electrode (SCE) (*Amel*, Italy) as reference, and a platinum (*Amel*) auxiliary electrode. All potentials are referred versus the SCE.

Preparation of CPE and its Modification with Bismuth

C/TCP. The unmodified carbon paste electrode was prepared by hand-mixing of 0.25 g graphite powder (*Graphite Týn,* Czech Republic) with 0.1 mL tricresyl phosphate (mixture of isomers, *Sigma-Aldrich*); the detailed procedure of the electrode preparation being described earlier [37]. The prepared paste was packed into the piston-driven holder [38,39] with the surface diameter of 2 mm. Whenever needed, the CPE surface was renewed mechanically – by wiping off the used CP-layer, when extruding and smoothing the new one.

$Bi_{n\%}$-C/TCP, where "n" ... 0.5, 1.5, 5, 10, 15, and 20 % Bi (w/w). The bismuth powder-bulk modified pastes were prepared by replacing of the respective amount of carbon powder with bismuth powder (purity: 99.99%, 100 mesh, *Aldrich*) [32,33], whereas the mixing procedure was otherwise identical to that for the native carbon paste as well as the way of surface renewal [37]. For proper experimentation, the electrodes with 5% and 20% Bi were finally selected to represent two particular mixtures with the lowest and highest suitable content of the modifying metal.

BiF-C/TCP. The bismuth-film modified TCP-CPE was prepared *via* the bismuth film deposition at a potential of −0.22 V vs Ag/AgCl by using the already described procedure [40,41]. The plating procedure was carried out *ex situ* in a solution of 1.0 mol L^{-1} HCl + 0.5 mol L^{-1} KBr containing 0.02 mol L^{-1} $Bi(NO_3)_3$, by electrolysing for 60 s [40], or 0.5 mol L^{-1} KCl, for 60 s, without stirring. Following this, the BiF-GCE was rinsed lightly with 1 mol L^{-1} HCl. Before the film deposition, the potential of the polished TCP-CPE was cycled (10 cycles) in the plating solution from 0.00 V to −0.60 V vs. ref.

Voltammetric Measurements

IMI was measured in 5.00 mL of the solution of different concentration, to which 5.00 mL of BRB pH 7.0 was added. The potential range in the cyclic voltammetry (CV) was from 0.1 to -1.5 V, at the scan rate, v_{CV} = 100 mV s^{-1}, whereas the operational parameters in the differential pulse voltammetry (DPV) were as follows: the pulse amplitude, ΔE = 50 mV, pulse width, w = 50 ms, and the scan rate, v_{DPV} = 25 mV s^{-1} [32].

CBZ was measured in 5 mL of the solution of different concentration, to which 5 mL of the BRB pH 4.0 was added. The CV characterization experiments were performed in the potential range from −0.1 to +1.2 V at a scan rate, v_{CV} = 100 mV s^{-1}. The differential pulse adsorptive stripping voltammetric (DPAdSV) characterization of CBZ was performed using the TCP-CPE in the BRB solutions in the range of pH from 2.0 to 8.0. The optimized experimental conditions for the determination of CBZ were as follows: start potential -0.10 V, end potential 1.30 V, accumulation potential, E_{acc} = -0.35 V, accumulation time, t_{acc} = 120 s and v = 100 mV s^{-1} [35,36].

Results and Discussion

Comparison of the TCP-CPE and Bismuth-Modified TCP-CPEs for Direct Cathodic Determinations of IMI

Our previous experiments have shown that TCP is a convenient binder because it converts the originally hydrophobic character of carbon paste to a more polar one, allowing us the sensitive determination of neonicotinoids [21-26] in a direct voltammetric regime (i.e., without accumulation step) in the cathodic range; especially, if the neonicotinoid of interest consists of a nitroguanidine group (*Imidacloprid, Thiamethoxam*, and *Clothianidin*) or the nitromethylene structure (*Nitenpyram*); all being reducible at fairly negative potentials.

In comparison with traditional CPEs containing non-polar liquids such as paraffin or silicon oils, the TCP-based CPE offer a somewhat better performance; mainly, wider potential window and lower residual currents [22].

Furthermore, the purging of the solutions with nitrogen (for 10 min) leads to a lower background current and better reproducibility of determination for the target compounds in the negative region of potential. By the electrochemical activation of TCP-CPE surface via the potential cycling from −0.60 to −1.60 V (in 10 cycles) results then in the baseline stabilization [21,22]. It is also worth mentioning that no adsorption of neonicotinoids was observed under simple immersing of the TCP-CPE in the solution with the analyte. The influence of bismuth as a bulk or surface modifier of TCP-CPE has been confirmed in relation with the determination of IMI and *Nitenpyram* [32,33]. It is expected that the continuing studies on these effects may give new applications of these electrodes.

In order to compare the responses of the Bi-modified and unmodified TCP-CPEs the cyclic voltammograms (see Fig. 2 overleaf) were recorded for a solution with 1 10^{-4} mol L^{-1} IMI in the BRB solution (pH 7.0), when using the TCP-CPE (curves **a**), $Bi_{5\%}$-C/TCP (curves **b**) and $Bi_{20\%}$-CP/TCP (curves **c**). Because of the presence of dissolved oxygen and the electroactive nature of tricresyl phosphate, the cyclic voltammogram obtained at the C/TCP is characterized by a complex irreversible reduction peak in the potential range from -0.5 to -1.1 V vs. ref. Obviously, this peak then defines the proper applicability of the electrode. It was found that the bubbling with nitrogen had reduced the content of dissolved oxygen in the solution, which had quite favorable effect on the overall performance of the C/TCP for cathodic reductions.

In the case of the different amounts of bismuth present in the bulk of the CPE, there appear certain differences in the peak at -0.75 V [32, 33], which is more pronounced in the case of the electrode with 20% of Bi. As was also described previously [31-33], at the higher bismuth content it is possible to observe the more pronounced random spiky noise signals. This is probably a consequence of the poor contact between the carbon paste and bismuth particles. As can be seen from Fig. 2, the voltammetric reduction peak of IMI, observed at about -1.2 V vs. ref., is well separated from the peak appearing on the baseline recorded with all three types of electrodes.

The DPV curves recorded for the blank using the $Bi_{5\%}$-C/TCP is characterized by a complex reduction peak with a pronounced maximum at -0.75 V (see Fig. 3a, curve **2**). This peak is probably a combined signal of the binding component and the bismuth. However, the potential of the signal is such that it does not significantly affect the reduction peak of the target analyte, in this case, of IMI.

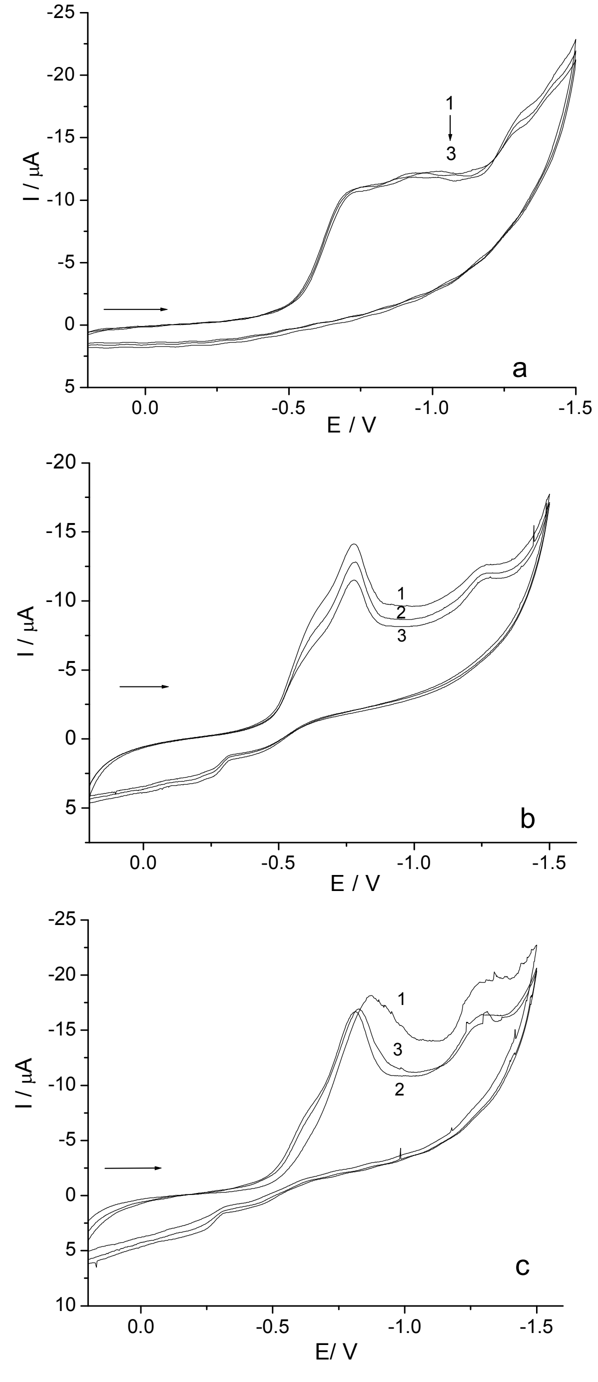

Fig. 2*: Cyclic voltammograms of IMI obtained with the bare C/TCP (**a**), $Bi_{5\%}$-C/TCP (**b**) and $Bi_{20\%}$-C/TCP (**c**). Model solution: BRB (pH 7.0), scan rate v = 100 mV s^{-1}.*

In the case of the $Bi_{20\%}$-C/TCP, the baseline has also a reduction peak at -0.75 V (Fig. 3a, curve **1**), which is much more pronounced than the corresponding peak on the voltammogram obtained with the $Bi_{5\%}$-C/TCP, indicating that the amount of bismuth present in the electrode bulk influences the intensity of this signal. Although the reduction peak for IMI at -1.2 V recorded with this electrode is stronger than the one recorded with the $Bi_{5\%}$-C/TCP, it was eliminated from the further investigations because of the unfavorable signal-to-noise ratio arising from the presence of random spiky noise signals.

It should also be pointed out that the procedure for the electrochemical activation of the C/TCP and $Bi_{5\%}$-C/TCP surfaces should be preceded by the removal of the electrode surface layer with wet filter paper. The subsequent electrochemical conditioning involves the potential cycling (10 cycles) of the electrodes in the BRB solution (pH 7.0), which results in a wider potential window in the cathodic range, lower background currents and a more stable base-line. The combined pretreatment of the electrodes means cleaning of the electrode surface and regeneration of the principal functional groups in the system.

The linearity of the calibration graph obtained with the $Bi_{5\%}$-C/TCP was checked in the range of the IMI concentration of 1.6–60 $\mu g\ mL^{-1}$, and the calculated value of the limit of detection (LOD) (3σ) was 0.52 $\mu g\ mL^{-1}$. On the other hand, it was previously reported [22] that the corresponding value obtained with the C/TCP was 1.7-30 $\mu g\ mL^{-1}$; *i.e.*, both electrodes are applicable at the $\mu g\ mL^{-1}$ concentration level.

Fig. 3 also shows the reproducibility of the signal of interest for 9.96 $\mu g\ mL^{-1}$ IMI at $Bi_{5\%}$-C/TCP (curves **b**) and at C/TCP (curves **c**) recorded in the time interval of 30 min. Although the signals obtained with $Bi_{5\%}$-C/TCP contain a marked oscillation, the reproducibility of the measurement is better compared to that obtained with the unmodified C/TCP. Further, the signals obtained at these two electrodes are of similar intensity.

A comparison of the data obtained with the $Bi_{5\%}$-C/TCP in the presence of oxygen with the data obtained with unmodified C/TCP after oxygen removal shows that they are similar, indicating that the bismuth-powder modified electrode is more suitable for the practical analysis of IMI, since it can be carried out without the removal of the oxygen from the solution. The BiF-C/TCP with a bismuth film electrodeposited *ex situ* on the C/TCP substrate electrode is also suitable for the voltammetric determination of IMI. Based on the DPV signals recorded for IMI, it can be concluded that the sensor surface states are different.

The DPV curves shown in Fig. 4 represent the responses of the electrode films prepared using different plating electrolytes. Namely, the curves shown in Fig. 4a were recorded using the Bi film deposited from the solution containing KCl, and those in Fig. 4b with the BiF-C/TCP prepared from the solution that contained KBr. For the comparison, the figure also shows the voltammograms recorded with the unmodified C/TCP (curves **c**).

When the bismuth-modified configurations used in this study are concerned, it can be concluded that the electrochemical properties of the substrate, *i.e.* of the C-TCP itself, are being significantly reflected on the behavior of the resulting $Bi_{5\%}$-C/TCP and BiF-C/TCP electrodes, giving them favorable polarization / depolarization characteristics [32,33].

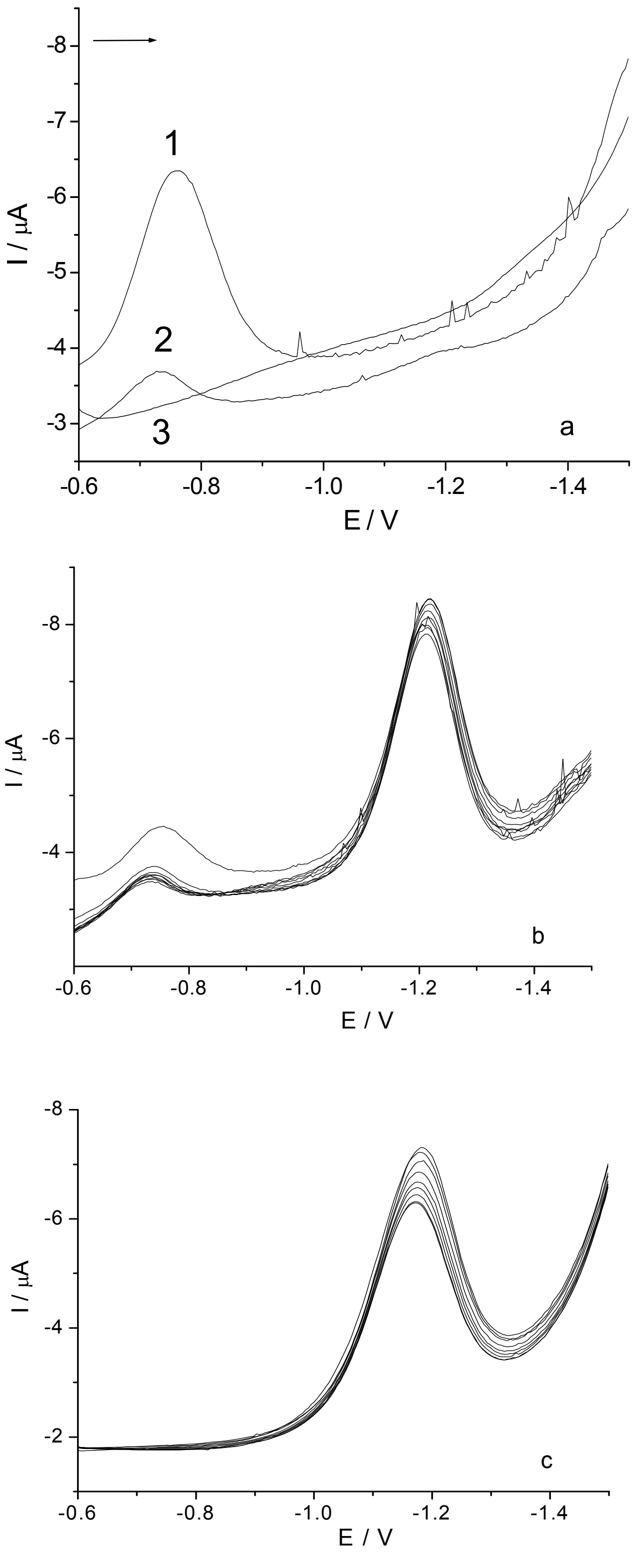

Fig. 3: *DPV signals of:* ***a)*** *baseline obtained with* $Bi_{20\%}$*-C/TCP* ***(1)****,* $Bi_{5\%}$*-C/TCP* ***(2)*** *and bare C/TCP* ***(3)****. Reproducibility of the DPV signal for IMI reduction recorded with* $Bi_{5\%}$*-C/TCP* ***(b)*** *and bare C/TCP (c) (****b*** *+* ***c****;* $c_{IMI} = 30\ \mu g\ mL^{-1}$ *). BRB (pH 7.0).*

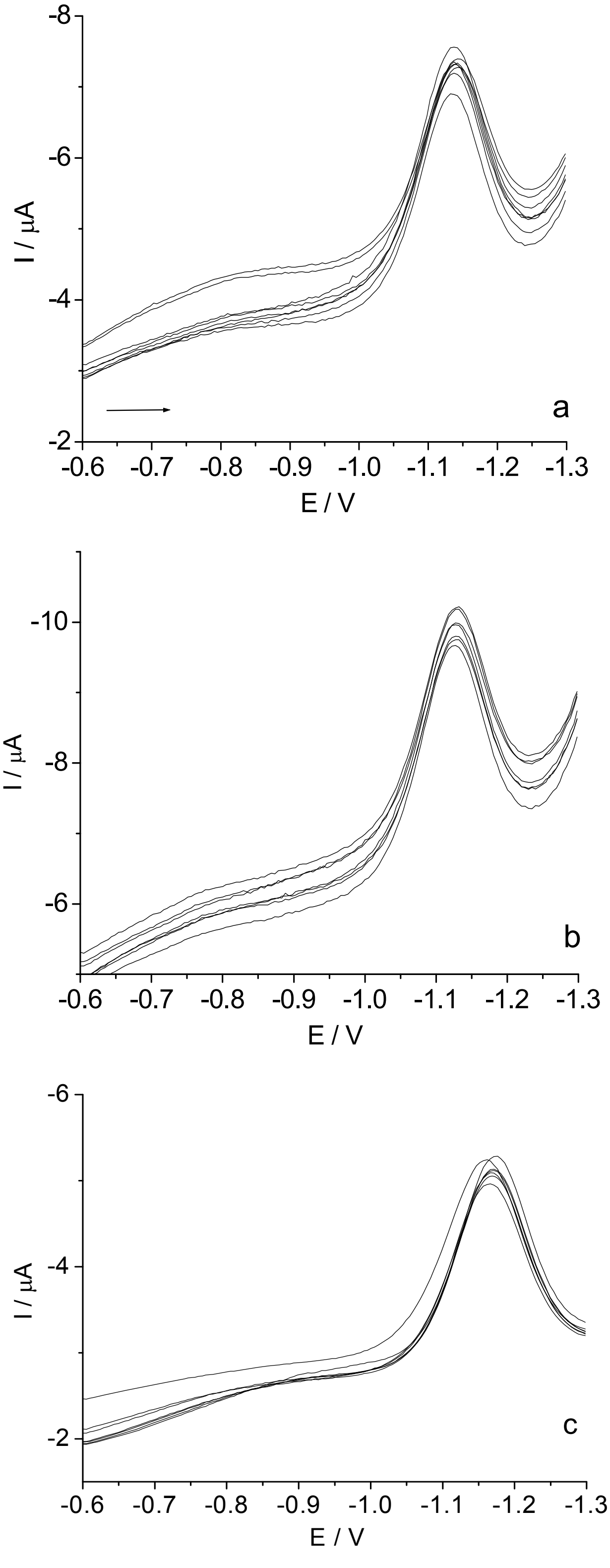

Fig**. 4**: *Reproducibility of the DPV reduction signals of Imidacloprid (23 µg mL^{-1} IMI) at BiF-C/TCP electrodeposited in solution of KCl (**a**), BiF-C/TCP in KBr (**b**) and the bare C/TCP (**c**); all in eight replicates. BRB (pH 7.0).*

The presence of oxygen did not affect the signal intensities obtained with the Bi-C/TCP containing dispersed metal in the bulk. The signal-to-noise ratio is favorable in the case of 5% (w/w) bismuth. Here, it can be concluded that the BiF-C/TCP seem also promising for the further investigations concerning their characterization and application.

Anodic Adsorptive Stripping Voltammetric Determination of CBZ

Based on the previous investigations, the bare C/TCP is also applicable for the anodic type of voltammetric measurements, for the trace-level determination of herbicide *Linuron* [34,36], and fungicide CBZ [35,36], as they have electrooxidizable groups in their structures. As mentioned in the previous work, the appearance of the oxidation signal of CBZ depends on the pH of the medium (see Fig. 5), recorded for a 3.0 10^{-6} mol L^{-1} solution of CBZ.

The effect of the potential cycling on the shape of oxidation peak of CBZ (5.2 10^{-4} mol L^{-1}) and its counterpart in the BRB pH 4.0 obtained with the conditioned C/TCP are shown in Fig. 6. The decrease of the intensity of the signal in the second sweep can be explained by the presence of a chemical reaction following the electrochemical process, which was elaborated in our previous paper [35].

For the determination of CBZ at the trace level, the DPAdSV mode was selected. As was pointed out earlier [35,36], the two key parameters which are to be optimized in order to elaborate sufficiently sensitive method are the accumulation potential E_{acc}, and accumulation time t_{acc}. The E_{acc} was optimized in the range from +0.15 to -0.55 V vs. ref.. As can be seen from Fig. 7, the peak current increased to a potential of -0.35 V and then started to decrease; the optimal value being -0.35 V vs. ref.

The curves recorded to optimize the choice of the accumulation time are illustrated in Fig. 8. It is evident that the oxidation signal increased with the prolonged deposition time up to 120 s, whereas the deposition time of 300 s did not bring any further enhancement of the peak. Hence, the time of 120 s was selected as the optimum accumulation time.

The dependence of the I_{pa} on the concentration of CBZ is presented in Fig. 9a, and the linearity can be observed in the range from 0.9 to 12.0 ng mL^{-1}, which is evident from the calibration graph shown in Fig. 9b. As seen, the method can be used for the determination of CBZ down to the ng mL^{-1} level. Further experiments are planned to test the method for the determination of CBZ in different real samples.

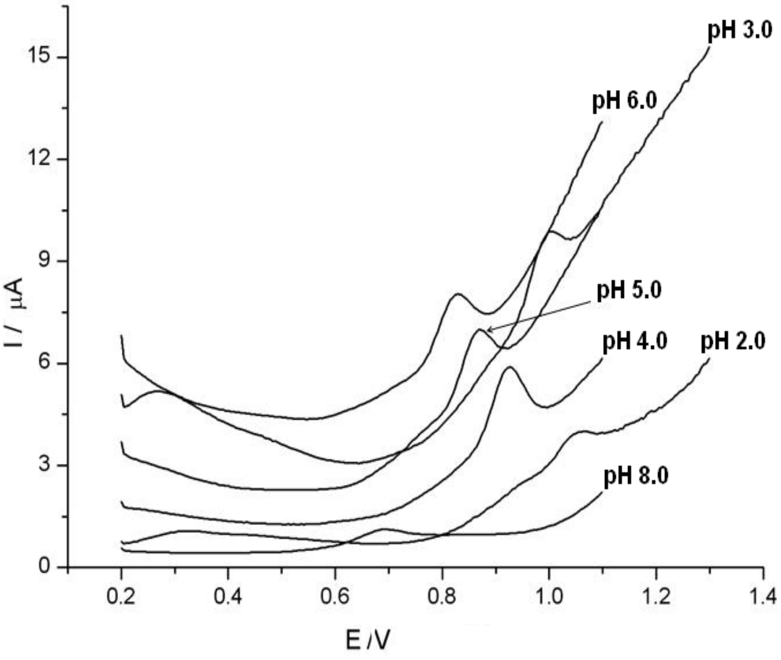

Fig. 5: *Influence of pH on DPAdSV signals of CBZ (the pH values of the solutions are indicated at curves). Exp. parameters:* $v = 100$ *mV* s^{-1}, $E_{acc} = -0.35$ *V,* $t_{acc} = 120$ *s,* $c = 3\ 10^{-6}$ *mol* L^{-1}.

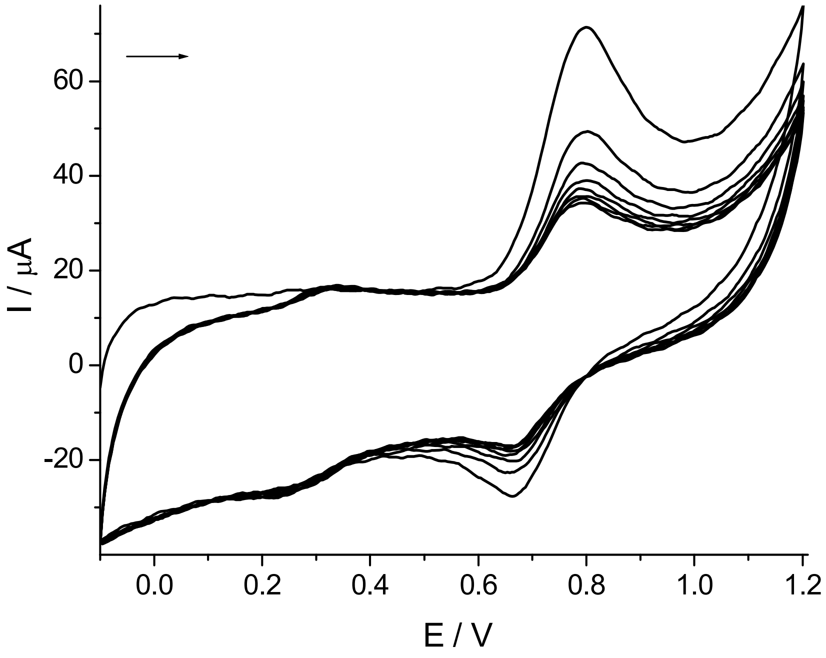

Fig. 6: *Effect of the potential cycling on the shape of oxidation peak of CBZ (5.2* 10^{-4} *mol* L^{-1}*) and its counterpart in the BRB pH 4.0 obtained with the conditioned TCP-CPE.*

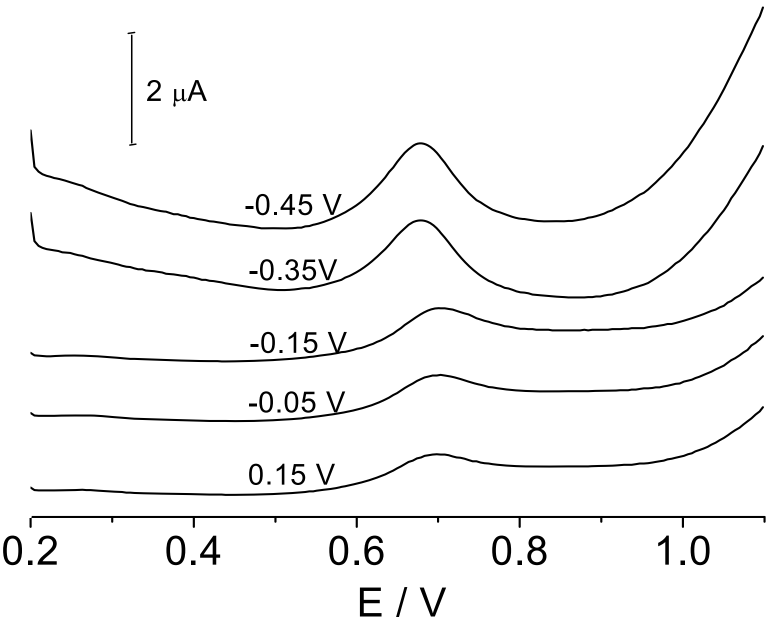

Fig. 7: *Influence of E_{acc} on the DPAdSV signal for CBZ (3 10^{-6} mol L^{-1}). BRB (pH 4.0), t_{acc} = 120 s.*

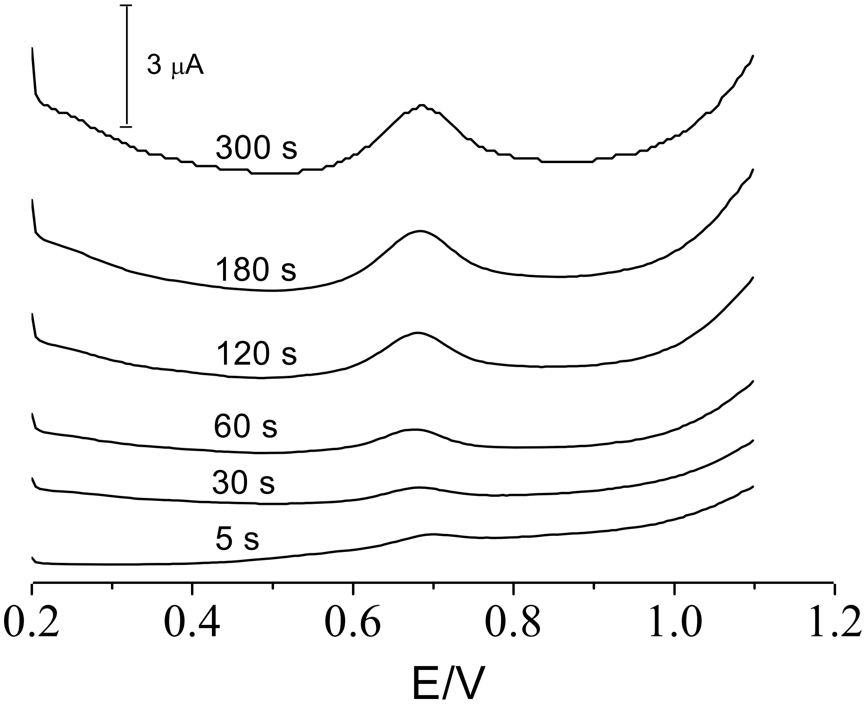

Fig. 8: *Influence of accumulation time, t_{acc}, on the DPAdSV signal for CBZ (3 10^{-6} mol L^{-1}). BRB (pH 4.0), E_{acc} =-0.35 V.*

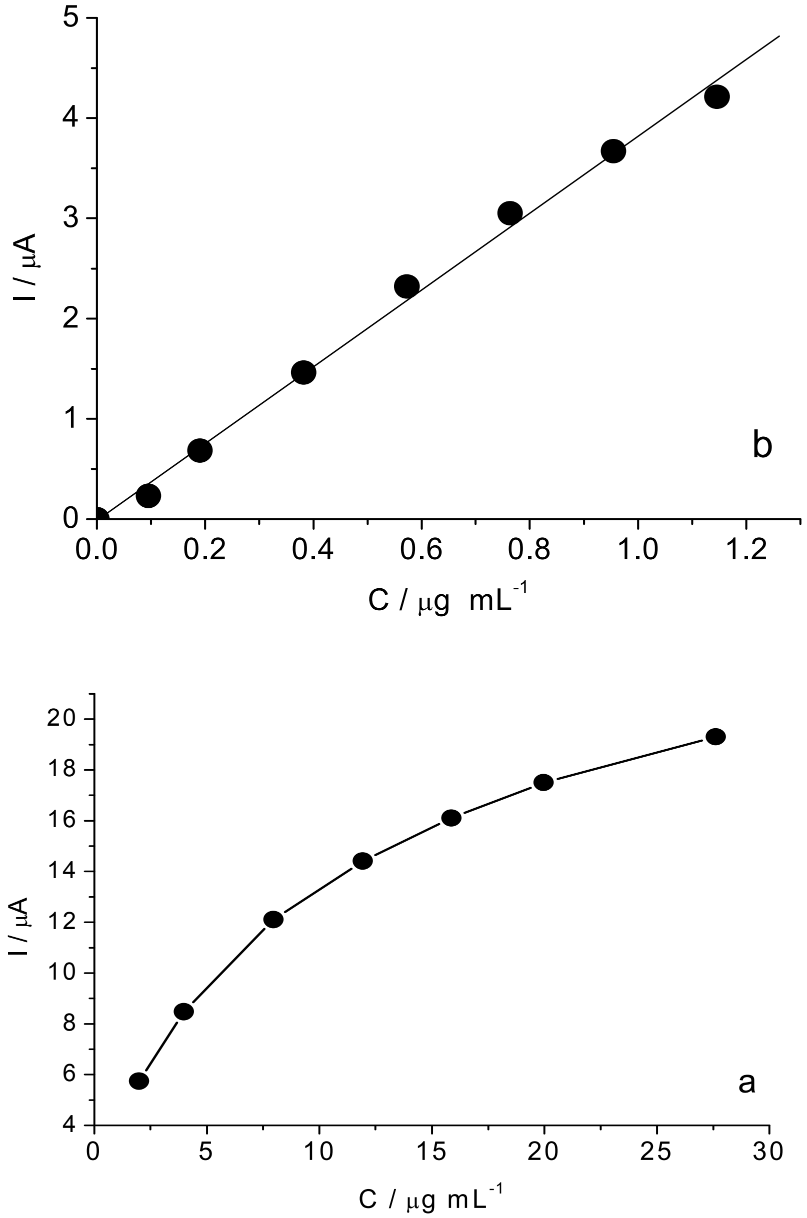

Fig. 9: *The dependence of the intensity of* I_{pa} *on the CBZ concentration in a wide concentration range* (a) *and the calibration graph* (b).

Conclusions

This paper can be considered as another contribution to the hitherto knowledge concerning the functioning and application of unmodified and bismuth-modified carbon paste electrodes in analysis of neonicotionid insecticides.

It has been demonstrated that the modification of the tricresyl phosphate-based carbon paste electrode (C/TCP or TCP-CPE, resp. [20,26]) with bismuth can be performed in two different ways: (**i**) by the partial replacement of the carbon powder moiety with pulverized bismuth (bulk modification *via* a bismuth dispersion) or with the aid of (**ii**) depositing the metallic film onto the CPE.

All three types of electrodes (unmodified, bulk-modified and surface-modified) have been shown to be suitable for a sensitive cathodic determination of the *Imidacloprid* insecticide in the differential pulse voltammetric mode (in direct regime, without accumulation). The bulk-modified electrode with 5% (w/w) Bi and the surface modified ones appeared to be superior to the remaining electrodes under testing because of wholly better and less noisy response and due to the possibility to use this type of electrode in the presence of oxygen dissolved in the solution to be analyzed.

Finally, it has also been proved that the unmodified (native) C/TCP can be used for anodic oxidation of the *Carbendazim* fungicide; in this case, in the differential pulse adsorptive stripping voltammetric mode. Consensually, further experiments are still needed to verify the applicability of the individual electrodes in analysis of real samples.

Acknowledgements

The authors would like to acknowledge financial supports of the Ministry of Education, Science and Technological Development (Project No. 172012, 172059 and III 45006). The Czech authors are thankful to the Ministry of Education, Youth, and Sports for the support from the following projects: LC 06035 and MSM0021627502. The CEEPUS II (CII-CZ-0212-04-1011) and CEEPUS III programs are also gratefully acknowledged. Finally, the results in this report have also partially been obtained by utilizing financial donation from the Project HUSRB 1002/214/188 – MATCROSS ("Development of new materials for application in environmentally friendly technologies for the cost-effective remediation of contaminated sites threatening cross-border regions").

References:

1. P. Jeschke, R. Nauen, M. Schindler, A. Elbert: *J. Agric. Food Chem.* ***59*** (2011) 2897.
2. P. Jeschke, R. Nauen: *Pest Manag. Sci.* ***64*** (2008) 1084.
3. The European Union On-Line, Official Documents, E.U., 2000; http://europa.eu.int.
4. Official Report; WHO/FAO Joint Meeting on Pesticides Residues (JMPR), Carbendazim (072), Carb3, 1994.

5. IPCS International Programme on Chemical Safety Health and Safety Guide No. 82.
6. S. Seccia, P. Fidente, D. Montesano, P. Morrica: *J. Chromatogr. A* ***1214*** (2008) 115.
7. A. Mandić, S. Lazić, S.N. Ökrész, F. Gaál: *J. Anal. Chem.* ***12*** (2005) 1134.
8. H. Obana, M. Okihashi, K. Akutsu, Y. Kitagawa, S. Hori: *J. Agric. Food Chem.* ***50*** (2002) 4464.
9. R.P. Mathur, S. Sharma, R. Bhushan*:* *J. Liquid Chromatogr.* ***11*** (1988) 2621.
10. H.X. Kong, H. Yun, N.X. Qiu: *Chin. J. Anal. Lab.* ***26*** (2007) 65.
11. N.R. de Erenchun, Z.G. de Balugera, M.A Goicolea, R.J. Barrio: *Anal. Chim. Acta* ***349*** (1997) 199.
12. H. Obana, M. Okihashi, K. Akutsu, Y. Kitagawa, S. Hori: *J. Agric. Food Chem.* ***51*** (2003) 2501.
13. S. Seccia, P. Fidente, D.A Barbini, P. Moricca: *Anal. Chim. Acta* ***553*** (2005**)** 21.
14. B.A. Vega, G.A. Frenich, M.L.J. Vidal: *Anal. Chim. Acta*, ***538*** (2005) 117.
15. P. Cheng, H.M. Tang, S.X. Yang, L. Wang: *Modern Agrochemicals* ***3*** (2009) 36.
16. J. Barek, J. Fischer, T. Navrátil, K. Pecková, B. Yosypchuk, J. Zima: *Electroanalysis* ***19*** (2007) 2003.
17. J. Wang: *Analytical Electrochemistry*, 3rd Ed.; Wiley-VCH: Hoboken, New Jersey, USA, 2006.
18. I. Švancara, K. Vytřas, K. Kalcher, A. Walcarius, J. Wang: *Electroanalysis* ***21*** (2009) 7.
19. I. Švancara, K. Kalcher, A. Walcarius, K. Vytřas: *Electroanalysis with Carbon Paste Electrodes*. CRC Press, Boca Raton (FL, USA), 2012.
20. I. Švancara, K. Vytřas: *Anal. Chim. Acta* ***273*** (1993) 195.
21. Zs. Papp: "Voltammetric Characterization and Determination of Selected Neonicotinoids Using Different Carbon-Based Electrodes". *PhD Thesis* (in Serbian), Univ. Novi Sad, Novi Sad (Serbia), 2011.
22. Zs. Papp, I. Švancara, V. Guzsvány, K. Vytřas, F. Gaál: *Microchim. Acta* ***166*** (2009) 169.
23. Zs. Papp, V. Guzsvány, Sz. Kubiak, A. Bobrowski, L. Bjelica: *J. Serb. Chem. Soc.* ***75*** (2010) 681.
24. Zs. Papp, V. Guzsvány, I. Švancara, K. Vytřas, F. Gaál, L. Bjelica, B. Abramović; in: *Sensing in Electroanalysis, Vol. 4* (K. Vytřas, K. Kalcher, I. Švancara; Eds.), pp. 47-58. Univ. Pardubice Press Centre, Pardubice (Czech Rep.), 2009.
25. Zs. Papp, V. Guzsvány, I. Švancara, K. Vytřas: *Int. J. Electrochem. Sci.* ***6*** (2011) 5161.
26. V. Guzsvány, Zs. Papp, I. Švancara, K. Vytřas; in: *Insecticides / Book 3* (F. Perveen, Ed.), pp. 541-578. InTech, Rijeka (Croatia), 2012.
27. I. Švancara, C. Prior, S.B. Hočevar, J. Wang: *Electroanalysis* ***22*** (2010) 1405.

28. J. Wang, J.-M. Lu, S. B. Hočevar, P. A. M. Farias, B. Ogorevc: *Anal. Chem.* ***72*** (2000) 3218.

29. A. Królicka, R. Pauliukaitė, I. Švancara, R. Metelka, E. Norkus, A. Bobrowski, K. Kalcher, K. Vytřas: *Electrochem. Commun.* ***4*** (2002) 193.

30. S. Hočevar, I. Švancara, K. Vytřas, B. Ogorevc: *Electrochim. Acta* ***51*** (2005) 706.

31. H. Dejmková, J. Zima, J. Barek; in: *Sensing in Electroanalysis, Vol. 3* (K. Vytřas, K. Kalcher, I. Švancara; Eds.), p. 83. Univ. Pardubice Press, Pardubice (Czech Rep.), 2008.

32. V. Guzsvány, Zs. Papp, J. Zbiljić, O. Vajdle, M. Rodić: *Molecules* ***16*** (2011) 4451.

33. V. Guzsvány, Zs. Papp, I. Švancara, K. Vytřas, in: *Sensing in Electroanalysis, Vol. 6* (K. Kalcher, R. Metelka, I. Švancara, K. Vytřas; Eds.), pp. 231-246. Univ. Pardubice Press Centre, Pardubice (Czech Rep.), 2011.

34. J. Đorđević, Zs. Papp, V. Guzsvány, I. Švancara, T. Trtić-Petrović, M. Purenović, K.Vytřas: *Sensors* (Basel) ***12*** (2012) 148.

35. A.M. Ashrafi, J. Đorđević, V. Guzsvány, I. Švancara, T. Trtić-Petrović, M. Purenović, K. Vytřas: *Int. J. Electrochem. Sci.* ***6*** (2012) 9717.

36. J. Đorđević: "Membrane extraction of pesticide: Application for quantitative analysis in natural waters and their removal from industrial water", *PhD Thesis* (in Serbian); Fac. Sci. and Mathem., Univ. Niš, Niš (Serbia), 2012.

37. I. Švancara, K Schachl: Chem. Listy **93** (1999) 490.

38. I. Švancara, R. Metelka, K. Vytřas; in: *Sensing in Electroanalysis* (K. Vytřas, K. Kalcher, Eds.), pp. 7-18. Univ. Pardubice, Pardubice (Czech Rep.), 2005.

39. Univ. Pardubice; I. Švancara, R. Metelka, K. Vytřas: *CZ Patent*, Czech Industrial Property Office. № 301714, 2010.

40. V. Guzsvány, M. Kádár, F. Gaál, L. Bjelica, K.Tóth: *Electroanalysis* ***18*** (2006) 1363.

41. F.F. Gaál, V. J. Guzsvány, L.J. Bjelica: *J. Serb. Chem. Soc.*, *72* (2007) 1465.