Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.yu • www.shd.org.yu/JSCS

J. Serb. Chem. Soc. 72 (12) 1465–1475 (2007)
JSCS–3676

UDC 543:615.285+615.45:541.135.5–039.26
Original scientific paper

Determination of various insecticides and pharmaceuticals using differently modified glassy carbon electrodes

FERENC F. GAÁL[1,2*#], VALÉRIA J. GUZSVÁNY[1#] and LUKA J. BJELICA[1#]

[1]*Faculty of Sciences, Department of Chemistry, Trg D. Obradovića 3, 21000 Novi Sad and* [2]*Academy of Sciences and Arts of Vojvodina, Dunavska 37, 21000 Novi Sad, Serbia*

(Received 31 July 2007)

Abstract: The applicability of differently modified glassy carbon (GC) electrodes for direct or indirect determinations of various physiologically active compounds (insecticides and pharmaceuticals) in different formulations and some real samples was investigated. Samples of selected insecticides from the group of neonicotinoids with nitroguanidine (thiamethoxam and imidacloprid), cyanoimine (acetamiprid) and nitromethilene (nitenpyram) fragments, prepared in an appropriate manner, were determined by voltammetry on bare and surface-modified GC electrodes, while in the case of pharmaceuticals such as Trodon and Akineton, the chloride anion titration was followed using bare GC and phosphorus doped (P–GC) electrodes. The P–GC was also used to monitor the chloride content in the photocatalytic degradation of the (4-chloro-2-methylphenoxy)acetic acid herbicide. It was found that apart from the nature of the electrode material, the analyte and supporting electrolyte, as well as the pretreatment of the electrode surface essentially influences the applicability of the employed sensors.

Keywords: bismuth film electrode, tetradecane film electrode, phosphorus-doped glassy carbon, insecticides, pharmaceuticals, electroanalytical determinations.

INTRODUCTION

Of various electrode materials, glassy carbon (GC) is particularly useful because of its high electrical conductivity, impermeability to gases, high chemical resistance, reasonable mechanical and dimensional stability and widest potential range of all carbonaceous electrodes.[1] Although GC serves as a very good electrode material, many attempts have been made to improve its electrochemical properties by chemical modification. Surface modification comprises several methodologies, including 1) the addition of a variety of molecular catalysts and mediators to the electrode surface by adsorption, 2) covalent bonding of electroactive catalysts, 3) entrapment of metals within an affixed polymer film and 4) va-

* Corresponding author. E-mail: gaal@ih.ns.ac.yu
# Serbian Chemical Society member.
doi: 10.2298/JSC0712465G

por or electrodeposition of metals directly onto the electrode.[1,2] It is well known that GC is a convenient material for surface modification with metals, *e.g.*, mercury[3] and bismuth.[4] Although bulk bismuth electrodes were used in amperometric titration several decades ago,[5] this electrode has recently experienced its renaissance in voltammetric determinations.[6] Namely, apart from bulk bismuth electrodes, use is often made of its film, primarily aimed at replacing toxic Hg film.[7,8] Such films have been used in different types of anodic stripping analysis for trace level determination of a wide assortment of metal ions.[7–11] On the other hand, the application of bismuth and bismuth film electrodes (BiFEs) have been much less studied for the determination of organic compounds.[12,13]

Another approach, yielding homogeneously modified materials, involves the introduction of heteroatoms in the carbon precursor.[2,14–16] Such a homogeneous modification of GC is highly desirable because of the expectation that an electrode modified at the atomic level would exhibit efficient catalysis, high stability, and comparatively simple renewability. Hitherto, a number of elements have been used for GC doping, *e.g.*, nitrogen,[2] chlorine,[14] fluorine,[14] platinum,[2] lithium,[15] boron,[16] phosphorus,[16] *etc*.

It is generally accepted that the microstructure of the carbon material, cleanliness of the electrode surface and surface functional groups are important determinants of electrode reactivity and suitability for surface modification. It is also known that bare solid electrodes suffer from memory effects and, due to the inability to achieve surface renewal, surface regeneration is frequently required.[1,17] The strategies for surface renewal include polishing,[18] electrochemical activetion,[17,19] ultrasonic activation,[20] laser activation,[21] *etc*.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) on bare or differently modified GC electrodes have proved to be suitable for the sensitive and selective determination of many pharmaceutical[22–24] and pesticide compounds.[25–27]

The aim of this work was to study the possibility of applying various GC-based electrodes, *i.e.*, two bare GC samples from different manufacturers, surface modified GC (bismuth film, BiFE, and tetradecan film, C14FE) and bulk-modified GC with phosphorus as dopant (P–GC) for direct or indirect determinations of various physiologically active compounds (insecticides and pharmaceuticals) in different formulations and some real samples.

EXPERIMENTAL

Reagents and solutions

All chemicals used were of the analytical reagent grade. The reference standards were: nitenpyram ($C_{11}H_{15}ClN_4O_2$), pestanal, purity 99.9 %, and (4-chloro-2-methylphenoxy)acetic acid, MCPA ($C_9H_9ClO_3$) (Riedel-de-Haën, Germany), purity 98.8 %, thiamethoxam ($C_8H_{10}ClN_5O_3S$), acetamiprid ($C_{10}H_{11}ClN_4$) and imidacloprid ($C_9H_{10}ClN_5O_2$) pestanals (Syngenta, Switzerland), purity > 99.7 %. The applied commercial formulation of acetamiprid was Volley (Nippon Soda, Japan). Primary stock solutions were prepared by dissolving each reference standard in doubly distilled wa-

ter or in buffer solutions at a concentration of 0.50 mg cm^{-3}. The contents of chloride were determined in the following pharmaceutical preparations: biperiden hydrochloride ($C_{21}H_{30}ClNO$) in Akineton tablets (Lek, Slovenia) and tramadol hydrochloride ($C_{16}H_{26}ClNO_2$) in Trodon capsules (Hemofarm, Serbia). Britton–Robinson buffer solutions were prepared from a 0.04 mol dm^{-3} stock solution of phosphoric (Merck, Germany), boric (Merck), and acetic (Merck) acids by adding 0.2 mol dm^{-3} sodium hydroxide (Merck) to the required pH.

Apparatus

Voltammetric measurements were performed on an Easyscan 5000 (Amel, Italy) instrument furnished with a software package for pulse techniques. The stand included a three-electrode system, a Radiometer saturated calomel electrode (SCE), a platinum ring auxiliary electrode and a GC (Sigri Electrographit, HTT 2400 °C, Sigri-GC and Amel, Amel-GC, HTT not stated), BiFE or C-14FE as working electrode.

The surface morphology of the bare GC and bismuth films was studied on a JEOL JSM-6460LV scanning electron microscope (SEM, Japan Electron Optics Laboratory, Japan). Energy dispersive spectroscopic (EDS) microanalysis was performed using an INCA microanalysis system (Oxford Instruments, United Kingdom).

The course of indirect controlled-current potentiometric titrations was monitored using P–GC and standard Sigri-GC electrodes. Both GC electrodes were in the form of rods (Ø 3 mm) and were mounted in Teflon holders. The P–GC was prepared by carbonizing a phenol–formaldehyde resin, containing 1 % w/w phosphorus added in the form of $(NH_4)_2HPO_4$, at 1000 °C.[28]

The microcomputer-aided[29] potentiometric (I = 1 μA) titrations were performed using a negatively polarized indicator electrode coupled to a Radiometer SCE *via* a double-junction salt bridge ([GC(–)|SCE(+)]). Comparative argentometric potentiometric titrations were performed with the aid of a silver wire electrode connected *via* a suitable SCE and an appropriate resistor, to ensure the zero-current regime. The titrant was added continuously by a Radiometer ABU 80 automatic piston burette at an optimum rate of 0.25 cm^3 min^{-1}.

Comparative high-performance liquid chromatography (HPLC) measurements were performed on an Agilent 1100 series liquid chromatograph (Agilent Technologies Inc., USA) using a Zorbax Eclipse XDB-C18 (4.6 mm×250 mm, 3.5 μm) column and a diode-array detector (DAD) for insecticide determination and a Shimadzu Class LC-10 chromatographic system with a Shimadzu, Japan UV/Vis, SPD-10A detector at 272 nm for Trodon analysis, according to the manufacturer's procedure.

All pH measurements were made on a digital pH meter (Radiometer, Netherlands) using a combined glass electrode (Metrohm, Switzerland).

Voltammetric investigations

The GC electrode, was polished with alumina powder (Buechler, USA) of different particle size (0.5 and 0.3 μm) suspended in doubly distilled water, using finally 0.3 μm grade on a polishing cloth, to attain a mirror fine finish. Afterwards, the GC electrode was washed in an ultrasonic bath with doubly distilled water to remove any residual polishing material. To attain a better functioning, the electrode was pretreated by *ex situ* potential cycling (10 cycles) with amplitude in the 0.4 to −1.9 V (*vs.* SCE) before each measurement. This was carried out in an aqueous solution of the same supporting electrolyte as in voltammetric experiments. In the case of the deposition of a bismuth film, the plating procedure was carried out *ex situ* in a still solution consisting of 0.02 M $Bi(NO_3)_3$, 1 M HCl and 0.5 M KBr[10] at −0.25 V for 60 s.[26] Subsequently, the BiFE was rinsed slightly with 1 M HCl. Before film deposition, the polished GC electrode was activated by *in situ* potential cycling in the plating solution from −0.40 to −1.2 V. To remove the film, a potential of 0.20 V was applied. The tetradecane film electrode was prepared by placing two drops of alkane

solution in hexane on a polished, ethanol-washed and dried Sigri-GC. The film was dried by manual rotation of the electrode. In all cases, the insecticides in the model systems and commercial formulations were measured in 10.0 cm^3 solution in the presence of Britton–Robinson buffer solution, after recording the baseline. For the real samples, the overall volume was 2.00 cm^3. All data were taken at ambient temperature.

Zero-current and controlled-current potentiometric titrations

An aliquot of the titrated solution was diluted with 5.00 cm^3 of doubly distilled water and the mixture was titrated with standard silver nitrate solution. The indicator electrode was P–GC or Sigri-GC. The titration end-point was determined using a computer program[29] for finding the intersection of the straight lines before and after the equivalence point in chloride determination. The procedure was the same in the zero-current regime with a silver indicator electrode. The titration end-point was determined using the mentioned computer program[29] for finding the maximum of the first derivative of the titration curves. In all cases the results were corrected for the blank (10^{-5} mol dm^{-3} solution of potassium nitrate). The procedures for comparative methods were as recommended by the manufacturer.

RESULTS AND DISCUSSION

Glassy carbon and surface-modified glassy carbon electrodes in insecticide analysis

As the nitroguanidine (imidacloprid and thiamethoxam), nitromethylene (nitenpyram) and cyanoimine (acetamiprid) neonicotinoid insecticides have functional groups reducible in a fairly negative potential range (from −0.5 to −2.0 V), *ex situ* potential cycling of the working electrode was employed to expand the potential window. It appeared that the electrochemically pretreated electrode had an about 150 mV more negative potential of hydrogen evolution than the polished electrode and the residual current was significantly higher in the case of the polished surface. The voltammograms recorded in the neonicotinoid model solutions with an *ex situ* pretreated electrode showed a two times more reproducible response (RSD between 2.5 and 3.1 %) than a wet-polished working electrode. The shape of obtained voltammograms was strongly dependent on pH, which can be explained by the significant role played by protons in the complex reduction mechanisms.[30] Since the Sigri-GC and Amel-GC electrodes had different residual currents in the range where the reduction peaks were observed, it appeared that the nature of the GC substrate influenced significantly the determination. By comparing the reduction signals of acetamiprid obtained with Amel-GC (Fig. 1A) and Sigri-GC (Fig. 1B), it can bee seen that the latter was two times more intensive, hence this electrode was used in its determination as the active component in the commercial formulation Volley by the standard addition method (Fig. 1C). The obtained results are in agreement with those of the manufacturer's declaration and the HPLC/DAD method. The advantage of the voltammetric method lies in the simplicity of the sample preparation and the speed of the determination of neonicotinoids (imidacloprid, thiamethoxam, nitenpyram and acetamiprid), although in a higher concentration range (from about 30 to 500 μg cm^{-3}).

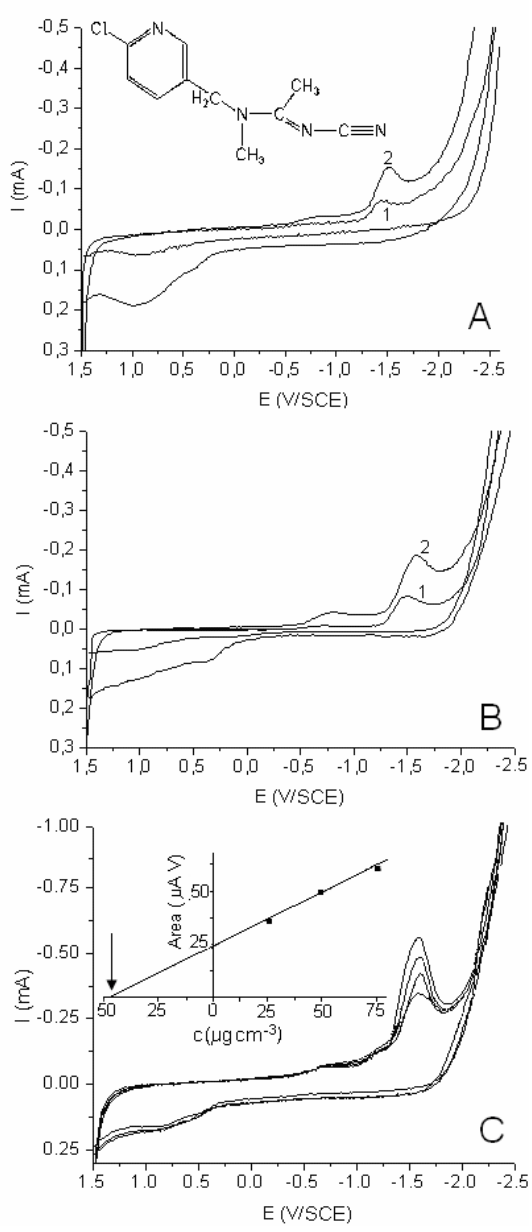

Fig. 1. Cyclic voltammograms of acetamiprid obtained with Amel-GC (A) and Sigri-GC (B) electrodes in Britton–Robinson buffer model solution pH 3.0 at a scan rate of: 1) 100 mV s^{-1} and 2) 500 mV s^{-1} and cyclic voltammograms of its commercial formulation Volley obtained by Sigri-GC (C) at pH 3.0 and 500 mV s^{-1}; the voltammograms recorded after standard addition of acetamiprid. The inset shows the corresponding calibration curve.

With the aim of improving the sensitivity and reproducibility of the determination, two different films, BiFE and C-14FE, were tested in the cathodic voltammetric analysis of thiamethoxam. In the case of an *ex situ* cathodic application, the BiFE should be removed from the plating solution, and, very often, immersed in a neutral or basic solution, which may passivate its surface. This ope-

ration yields a different distribution of the bismuth crystals, which certainly influences the nature of the sensing surface. In the present case, washing in 1 M HCl appeared to be a suitable procedure for the removal of the bismuth bromide complex without affecting the sensitivity of the surface. EDS analysis of the BiFE surface showed that, apart from 60 % of carbon and 20 % of bismuth, there was a significant amount of bromide, which was not observed after washing. After such a pretreatment, the electrode was subjected to electrochemical activation by potential cycling in the potential range from −0.40 V to −1.6 V in the supporting electrolyte. A comparison of the BiFE surfaces before and after potential cycling reveals a rearrangement of bismuth crystals (Fig. 2).

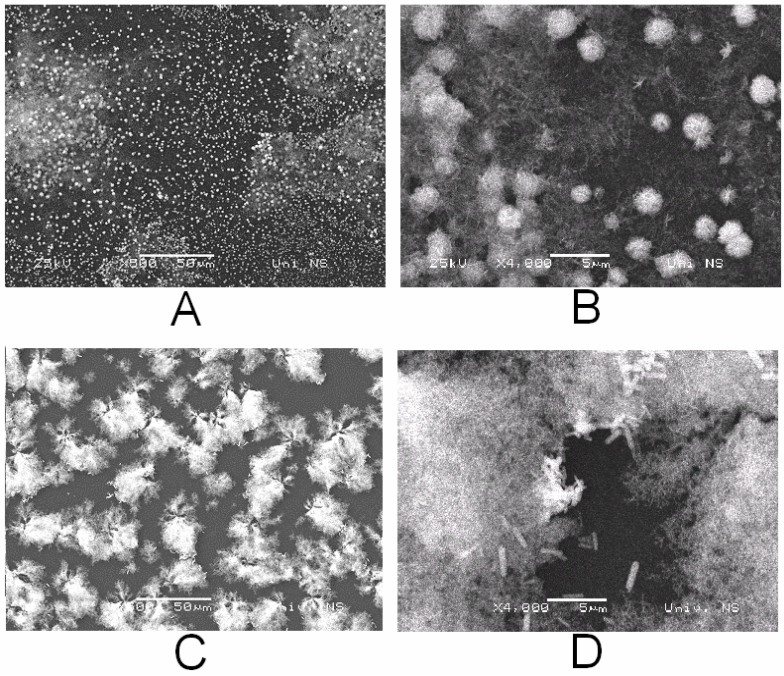

Fig. 2. SEM Morphology of the freshly electrodeposited (A, B) and electrochemically-conditioned BiFE (C, D) taken at two magnifications.

The cyclic volammograms obtained in the conditioning procedure also showed surface stabilization and a significant decrease of the background current after the first cycle (Fig. 3A), which is of a peculiar shape.[26] The electrode prepared in this manner, in combination with the highly sensitive DPV method under optimized conditions, appeared to be convenient for the determination of thiamethoxam in maize[26] and potato (Fig. 3B) samples.

In contrast to the BiFE, with the C-14FE potential cycling did not facilitate film adsorption. This may be explained by the fact that electrochemical conditioning yields a more hydrophilic GC electrode surface compared to the surface

prepared only by polishing. With *n*-alkane films, the hydrophobic interaction of the surface and the compound may favor film adsorption. A comparison of the cyclic voltammograms for thiamethoxam reduction on a C-14FE (Fig. 4, curve 1) and a bare Sigri-GC electrode (Fig. 4, curve 2) shows that the former electrode is advantageous over the latter one. Namely, the corresponding reduction peak is better defined and more symmetric, and the peak current is by 1.2 times higher. The application of the stripping step at 1.0 V and 60 s yielded an increase of the signal by 2.5 times, even at a thiamethoxam concentration of 0.08 mg cm^{-3}.

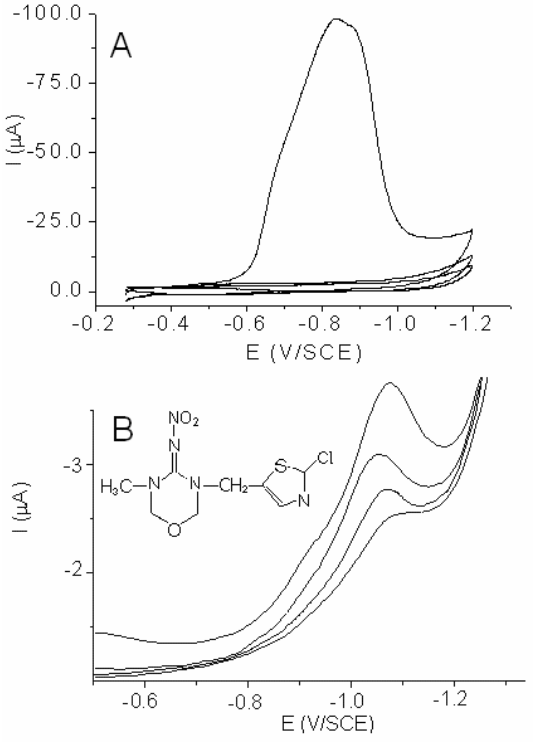

Fig. 3. Electrochemical conditioning of the BiFE surface by cyclic voltammetry (A) and the DPV determination of thiamethoxam on BiFE (B).

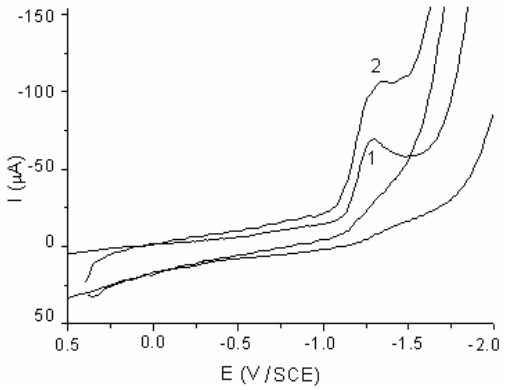

Figure 4. Cyclic voltammograms of thiamethoxam obtained on a C-14FE (1) and a bare Sigri-GC electrode (2).

On the basis of the above, it can be concluded that the different types of GC electrodes differed in their applicability for the determination of organic compounds with functional groups reducible in a fairly negative potential range. Furthermore, the above films in combination with a stripping step in the case of C-14FE and a pulse technique for BiFE lowered the limit of determination and improved the reproducibility.

Bulk-modified glassy carbon electrode in pharmaceutical analysis

In a previous study, it was shown that doping of GC with phosphorus yielded significant changes in the surface properties of the material in comparison to the undoped one and the Sigri-GC electrode. This material was applied as the sensor in the potentiometric argentometric controlled-current titrations of halides and compared with the performance of the Sigri-GC and Ag-wire electrodes. Generally, the P–GC electrode appeared to be suitable for the determination of halides in model systems, and also for the indirect determination of the active component of pharmaceutical preparations containing chlorine and bromine.[24,28] As can be seen from Fig. 5A, the shape of the curves recorded in the titration of chloride from Trodon capsules (curves 1 and 3) and the model solution of chloride (curves 2 and 4) was favorable in the case of using a P–GC electrode. Similar results were also obtained in the titration of chloride from Akineton tablets.

The experiments showed that the potentiometric response depended on the mode of polarization and nature of the analyte and supporting electrolyte. In addition, electrochemical conditioning of the P–GC surface also played an important role. Namely, it was observed that a negative polarization (1.0 V *vs.* SCE until the residual current decayed to about 5 μA) of GC in a 10^{-5} mol dm^{-3} potassium nitrate solution had a favorable effect on the shape of the titration curve. The starting potential of such an electrode was much more negative than in the case when the same electrode was pretreated by polishing. Such a treatment probably resulted in the reduction of oxygen functional groups, thus making the surface more sensitive to silver ions. This conditioning procedure was most favorable for functionalization of a P–GC electrode. It should be noticed that the negative polarization *in situ* did not result in any satisfactory results. Furthermore, the presence of acetate buffer (pH 4.5) in the model system improved the reproducibility even by three times (RSD 0.6 %). It can be supposed that similar buffer additives in the medicaments can have the same effect.

As can be seen from Fig. 5B, the method developed for the indirect determination of different pharmaceuticals was also applicable for monitoring of the chloride concentration during the photocatalytic degradation of the herbicide MCPA in the presence of TiO_2 catalyst. The obtained results are in agreement with literature data.[31] The advantage of a P–GC electrode over a silver electrode lies in the possibility of measuring 100 times lower concentrations of chloride, which is especially important with those systems where the solubility of the parent compound itself is low.

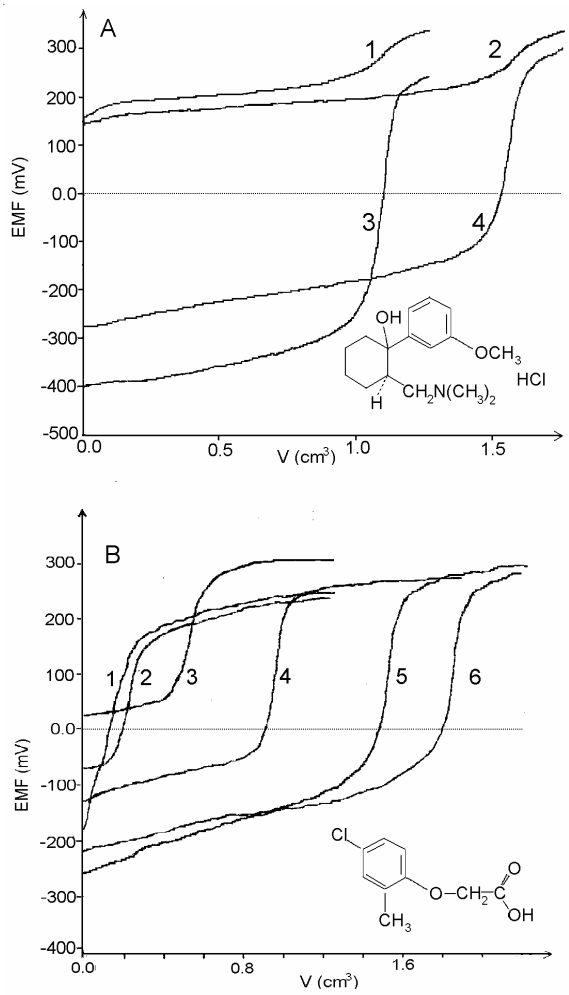

Fig. 5. Zero-current [Ag|SCE], (I = 0) (1,2) and controlled-current [P–GC(–)|SCE(+)], (I = 1 μA) potentiometric titration curves (3,4) of 4.65 mg of tramadol hydrochloride in Trodon capsules (A) and controlled-current [P–GC(–)|SCE(+)], (I = 1 μA) potentiometric titration curves of chloride with 1×10^{-2} mol dm^{-3} $AgNO_3$ obtained in the monitoring of the photocatalytic degradation of 2.7 mol m^{-3} MCPA in the presence of O_2/TiO_2 (B) in the following UV irradiation intervals: 1) 0; 2) 10; 3) 30; 4) 60; 5) 120 and 6) 180 min.

As can be seen from the above examples, various GC-based electrodes are applicable for the determination of different compounds. These methods do not require tedious pretreatment and involve a limited pre-separation procedure, which, consequently, reduces the cost of the analysis.

Acknowledgement. This study was supported by the Ministry of Science of the Republic of Serbia (Project: "Development of New and Improvement of the Existing Procedures for the Monitoring and Advancement of the Quality of the Environment", No. ON142029).

И З В О Д

ОДРЕЂИВАЊЕ РАЗНИХ ИНСЕКТИЦИДА И ФАРМАЦЕУТСКИХ ПРОИЗВОДА ПРИМЕНОМ РАЗЛИЧИТО МОДИФИКОВАНИХ ЕЛЕКТРОДА ОД СТАКЛАСТОГ УГЉЕНИКА

FERENC F. GAÁL[1,2], VALÉRIA J. GUZSVÁNY[1] И ЛУКА Ј. БЈЕЛИЦА[1]

[1]Природно–математички факултет, Департман за хемију, Трг Д. Обрадовића 3, 21000 Нови Сад и [2]Војвођанска академија наука и уметности, Дунавска 37, 21000 Нови Сад

Испитана је могућност примене различито модификованих електрода на бази стакластог угљеника за директно или индиректно одређивање физиолошки активних једињења (инсектицида и лекова) у различитим типовима узорака. Одабрани инсектициди из групе неоникотиноида са нитрогуанидинским (тиаметоксам и имидаклоприд), цијаноиминским (ацетамиприд) и нитрометиленским (нитенпирам) фрагментом су одређивани волтаметријски применом електрода на бази стакластог угљеника, које су биле са и без површинске модификације, док је у случају лекова (тродон и акинетон) титрација хлоридног анјона праћена електродама од стакластог угљеника (GC) и електродама допованим фосфором (P–GC). P–GC електрода је такође примењена за праћење садржаја хлорида у фотокаталитичкој деградацији хербицида (4-хлор-2-метилфенокси)сирћетне киселине. Нађено је да поред природе електродног материјала, аналита и основног електролита припрема електродне површине посебно утиче на применљивост коришћених сензора.

(Примљено 31. јула 2007)

REFERENCES

1. R. L. McCreery, in: *Electroanalytical Chemistry*, Dekker, New York, 1991, p. 221
2. N. L. Pocard, D. C. Alsmeyer, R. L. McCreery, T. X. Neenan, M. R. Callstrom, *J. Mater. Chem.* **2** (1992) 771
3. T. M. Florence, *Anal. Chim. Acta* **119** (1980) 217
4. J. Wang, J. Lu, S. B. Hočevar, P. A. M. Farias, B. Ogorevc, *Anal. Chem.* **72** (2000) 3218
5. M. S. Jovanović, F. F. Gaál, L. J. Bjelica, *Z. Anal. Chem.* **255** (1971) 277
6. M. Bučková, P. Gründler, U. G. Flechsig, *Electroanalysis* **17** (2005) 440
7. J. Wang, *Electroanalysis* **17** (2005) 1341
8. A. Economou, *Trends Anal. Chem.* **24** (2005) 334
9. K. Vytřas, I. Švancara, R. Metelka, *Electroanalysis* **14** (2002) 1359
10. A. Królicka, A. Bobrowski, *Electrochem. Commun.* **6** (2004) 99
11. S. B. Hočevar, B. Ogorevc, J. Wang, B. Pihlar, *Electroanalysis* **14** (2002) 1707
12. E. A. Hutton, B. Ogorevc, S. B. Hočevar, F. Weldon, M. R. Smyth, J. Wang, *Electrochem. Commun.* **3** (2001) 707
13. E. A. Hutton, B. Ogorevc, M. R. Smyth, *Electroanalysis* **16** (2004) 1616
14. H. D. Hutton, W. Huang, D. C. Alsmeyer, J. Kometani, R. L. McCreery, T. X. Neenan, M. R. Callstrom, *Chem. Mater*. **5** (1993) 1110
15. H. Maleki, C. D. Cojocaru, C. M. A. Brett, G. M. Jenkins, J. R. Selman, *J. Electrochem. Soc*. **145** (1998) 721
16. T. Đurkić, A. Perić, M. Laušević, A. Dekanski, O. Nešković, M. Veljković, Z. Laušević, *Carbon* **35** (1997) 1567
17. L. J. Bjelica, R. Parsons, R. M. Reeves, in: *Electrode Processes*, S. Bruckenstein, J. D. E. McIntyre, B. Miller, E. Yeager, Eds., The Electrochemical Society, Princeton, NJ, 1980, p. 190
18. G. N. Kamau, W. S. Willis, J. F. Rusling, *Anal. Chem*. **57** (1985) 545

19. T. Nagaoka, T. Fukunaga, T. Yoshino, I. Watanabe, T. Nakayama, S. Okazaki, *Anal. Chem*. **60** (1988) 2766
20. Q. Fulian, R. G. Compton, *Anal. Chem.* **72** (2000) 1830
21. P. Chen, R. L. McCreery, *Anal. Chem.* **68** (1996) 3958
22. B. Uslu, B. Doğan, S. A. Özkan, *Anal. Chim. Acta* **537** (2005) 307
23. M. R. Majidi, A. Jouyban, K. Asadpour–Zeynal, *J. Electroanal. Chem*. **589** (2006) 32
24. B. F. Abramović, V. J. Guzsvány, F. F. Gaál, *J. Pharm. Biomed. Anal*. **37** (2005) 265
25. V. J. Guzsvány, F. F. Gaál, L. J. Bjelica, Sz. N. Ökrész, *J. Serb. Chem. Soc*. **70** (2005) 735
26. V. Guzsvány, M. Kádár, F. Gaál, L. Bjelica, K. Tóth, *Electroanalysis* **18** (2006) 1363
27. D. C. Coomber, D. J. Tucker, A. M. Bond, *J. Electroanal Chem.* **452** (1998) 5
28. B. F. Abramović, L. J. Bjelica, F. F. Gaál, V. J. Guzsvány, Lj. S. Jovanović, *Electroanalysis* **15** (2003) 878
29. B. F. Abramović, S. D. Tepavčević, B. K. Abramović, F. F. Gaál, *Analyst* **121** (1996) 425
30. V. Guzsvány, M. Kádár, F. Gaál, K. Tóth, L. Bjelica, *Microchim. Acta* **154** (2006) 321
31. A. Topalov, B. Abramović, D. Molnár-Gábor, J. Csanádi, O. Arcson, *J. Photochem. Photobiol. A* **140** (2001) 249.