

NEW APPROACHES TO LARGE SCALE MONITORING OF VARIOUS BIOLOGICALLY ACTIVE ORGANIC COMPOUNDS USING BARE AND MODIFIED ELECTRODES BASED ON NON-TRADITIONAL ELECTRODE MATERIALS

Jiri Barek

Charles University, Faculty of Science
Department of Analytical Chemistry
UNESCO Laboratory of Environmental Electrochemistry
Albertov 6, CZ 12843 Prague 2, Czech Republic

The aim of this contribution is to demonstrate that in many cases modern voltammetric and amperometric methods can successfully compete with fascinating possibilities of modern spectrometric and separation methods. The main problem with the practical application of voltammetric and/or amperometric methods for the determination of submicromolar concentrations of electrochemically active organic compounds in complex biological and/or environmental matrices is connected with the passivation of the working electrode. It will be shown that this problem can be in many cases eliminated by using non-traditional electrode materials, the surface of which can be successfully renewed mechanically, chemically, or electrochemically. Moreover, their chemical and/or biological modification can further increase both selectivity and sensitivity of appropriate electroanalytical methods. This approach will be demonstrated on methods recently developed in our UNESCO Laboratory of Environmental Electrochemistry for the determination of various chemical carcinogens, pesticides, phenols, and nitro phenols and other biologically active organic compounds in various environmental matrices, and of various biomarkers (of illness, exposition, or treatment) in biological fluids.

In the first part, attention will be paid to the use of novel electrodes based on non-toxic solid or paste mercury amalgams [1], bismuth electrodes [2], and antimony electrodes [3] suitable for voltammetric and/or amperometric determination of electrochemically reducible organic compounds

(e.g. carcinogenic nitrated polycyclic aromatic hydrocarbons, electrochemically reducible pesticides, anticancer drugs derived from anthraquinone, some cancer biomarkers, and food dyes).

Second part will be devoted to the use of novel versions of carbon paste electrodes [4], boron doped diamond film electrodes [5], carbon film electrodes [6], and nanostructured sputtered electrodes [7] on either conductive or non-conductive substrate, and their application for the determination of electrochemically oxidisable organic compounds (e.g. carcinogenic amino derivatives of polycyclic aromatic hydrocarbons, hydroxyl derivatives of polycyclic aromatic hydrocarbons as markers of exposure to parent hydrocarbons, various pesticides, cancer biomarkers, etc.).

Third part will be focused on electrode miniaturization [8–12] and on their application both in batch analysis and in flowing systems [13–15] and their combination with a preliminary separation and preconcentration (solid phase extraction, membrane separation, hollow fibre micro extraction, etc.).

Fourth part will be devoted to the possibilities and limitations of 3D printing in this field together with the use of smart sensors based on DNA modified electrodes [16], electrodes modified with molecularly imprinted polymers and electrodes modified with various nanoparticles.

Some practical applications of the above mentioned methods for monitoring of tumour biomarkers [17], saccharides [18], derivatized DNA [19] and cholesterol [20, 21] will be given

References

1. T. Navratil, K. Novakova, J. Barek, V. Vyskocil, J. Chylkova, *The Use of the Silver Solid Amalgam Electrode for Voltammetric Determination of 9-nitroanthracene*. *Anal. Lett.*, 2016.– 49.– 37–48.
2. V. Prchal, V. Vyskocil, J. Barek, *Determination of 2,4,6-Trinitrophenol by Differential Pulse Voltammetry at a Bismuth Bulk Working Electrode*. *J. Electrochem. Soc.*, 2017.– 164.– H316–H320.
3. J. Gajdar, J. Barek, J. Fischer, *Antimony film electrodes for voltammetric determination of pesticide trifluralin*. *J. Electroanal. Chem.*, 2016.– 778.– 1–6.
4. H. Dejmkova, H. Adamkova, J. Barek, J. Zima, *Voltammetric and amperometric determination*

- of selected catecholamine metabolites using glassy carbon paste electrode. *Monatsh. Chem.*, 2017.– 148.– 511–515.
5. K. Schwarzova-Peckova, J. Vosahlova, J. Barek, I. Sloufova, E. Pavlova, V. Petrak, J. Zavazalova, Influence of boron content on the morphological, spectral, and electroanalytical characteristics of anodically oxidized boron-doped diamond electrodes. *Electrochim. Acta*, 2017.– 243.– 170–182.
 6. T. Rumlova, I. Jiranek, V. Vyskocil, J. Barek, Electrochemical study of 5-nitroquinoline using carbon film electrode and its determination in model samples of drinking and river water. *Monatsh. Chem.*, 2016.– 147.– 153–158.
 7. M. Libansky, J. Zima, J. Barek, A. Reznickova, V. Svorcik, H. Dejmekova, Basic electrochemical properties of sputtered gold film electrodes. *Electrochim. Acta*, 2017.– 251.– 452–460.
 8. Š. Skalova, L.M. Goncalves, T. Navratil, J. Barek, J.A. Rodrigues, V. Vyskocil, Miniaturized voltammetric cell for cathodic voltammetry making use of an agar membrane. *J. Electroanal. Chem.*, 2017, submitted.
 9. J. Gajdar, J. Barek, M. Fojta, J. Fischer, Micro volume voltammetric determination of 4-nitrophenol in dimethyl sulfoxide at a glassy carbon electrode. *Monatsh. Chem.*, 2017.– 148.– 1639–1644.
 10. J. Gajdar, T. Gonec, J. Jampilek, M. Brazdova, Z. Babkova, M. Fojta, J. Barek, J. Fischer, Voltammetry of a Novel Antimycobacterial Agent 1-Hydroxy-N-(4-nitro-phenyl)naphthalene-2-carboxamide in a Single Drop of a Solution. *Electroanalysis*, 2017.– in press. DOI: 10.1002/elan.201700547.
 11. A. Hajkova, V. Vyskocil, B. Josypcuk, J. Barek, A miniaturized electrode system for voltammetric determination of electrochemically reducible environmental pollutants. *Sensors and Actuators B-Chemical*, 2016.– 227.– 263–270.
 12. M. Libansky, J. Zima, J. Barek, H. Dejmekova, Voltammetric determination of homovanillic acid and vanillylmandelic acid on a disposable electrochemical measuring cell system with integrated carbon composite film electrodes. *Monatsh. Chem.*, 2016.– 147.– 89–96.
 13. D. Baval, H. Dejmekova, M. Scampicchio, J. Zima, J. Barek, Combination of Flow Injection Analysis and Fast Scan Differential Pulse Voltammetry for the Determination of Antioxidants. *Electroanalysis*, 2017.– 29.– 182–187.
 14. H. Dejmekova, M. Baroch, M. Krejcova, J. Barek, J. Zima, Coulometric detector based on carbon felt. *Applied Materials Today*, 2017.– 9.– 482–486.
 15. O. Josypcuk, J. Barek, B. Josypcuk, Electrochemical Biosensors Based on Enzymatic Reactors Filled by Various Types of Silica and Amalgam Powders for Measurements in Flow Systems. *Electroanalysis*, 2016.– 28.– 3028–3038.
 16. A. Hajkova, J. Barek, V. Vyskocil, Electrochemical DNA biosensor for detection of DNA damage induced by hydroxyl radicals. *Bioelectrochemistry*, 2017.– 116.– 1–9.
 17. A. Makrlikova, E. Ktena, A. Economou, J. Fischer, T. Navratil, J. Barek, V. Vyskocil, Voltammetric Determination of Tumor Biomarkers for Neuroblastoma (Homovanillic Acid, Vanillylmandelic Acid, and 5-Hydroxyindole-3-acetic Acid) at Screen-printed Carbon Electrodes. *Electroanalysis*, 2017.– 29.– 146–153.
 18. T.V. Shishkanova, P. Fitl, V. Kral, J. Barek, Nanoparticles functionalized with phenylboronic acid for the potentiometric detection of saccharides. *J. Electroanal. Chem.*, 2016.– 761.– 106–111.
 19. A. Danhel, Z. Trosanova, J. Balintova, L. Havran, M. Hocek, J. Barek, M. Fojta, Voltammetric analysis of 5-(4-Azidophenyl)-2'-deoxycytidine nucleoside and azidophenyl-labelled single- and double-stranded DNAs. *Electrochim. Acta*, 2016.– 215.– 72–83.
 20. J. Klouda, J. Barek, K. Nesmerak, K. Schwarzova-Peckova, Non-Enzymatic Electrochemistry in Characterization and Analysis of Steroid Compounds. *Crit. Rev. Anal. Chem.*, 2017.– 47.– 384–404.
 21. J. Klouda, J. Barek, P. Kocovsky, T. Herl, F.-M. Matysik, K. Nesmerak, K. Schwarzova-Peckova, Bile acids: Electrochemical oxidation on bare electrodes after acid-induced dehydration. *Electrochem. Commun.*, 2017.– in press. doi:10.1016/j.elecom.2017.11.024.