

# Application of Modern Electrochemical Techniques and Electrode Materials in Determination of Trace Elements in Environment

TOMÁŠ NAVRÁTIL and IVANA ŠESTÁKOVÁ  
 Department of Biophysical Chemistry  
 J. Heyrovský Institute of Physical Chemistry AS CR, v.v.i.  
 Dolejškova 3, 182 23 Prague 8  
 CZECH REPUBLIC  
 tomas.navratil@jh-inst.cas.cz <http://www.jh-inst.cas.cz>

*Abstract:* Voltammetry (polarography) belongs to the group of traditional electroanalytical methods, which has been successfully used for almost ninety years in (not only) environmental analysis. This technique has achieved many pronounced successes in determination of trace elements due to high sensitivity, preciseness, simple managing and ability of speciation. However, number of voltammetrical devices has decreased in course of last decades. We tried to reveal some reasons, which can be considered as causes of it: stage of instrumentation (therefrom arising low labor productivity) and the use of mercury as traditional electrode material. In this contribution are described two modern types of electrode materials (solid amalgam and composite electrode materials), which can successfully replace the traditionally used electrodes containing liquid mercury. Increase of labor productivity can be achieved by introducing a multichannel device for sequential autonomous measurements developed in our laboratory, which is able to analyze a set (the testing prototype up to 8) of samples in a chosen sequence, where each sample can be analyzed using different method, different parameters, etc.

*Key-Words:* Environment; Trace elements; Electrochemistry; Voltammetry; Polarography; Mercury; Solid amalgam electrodes; Solid composite electrodes; 8-channel device for sequential autonomous measurements; Automation.

## 1 Introduction

In studying environmental problems (soil, air, drinking water, waste-waters), of biological samples (human or animal tissues, body fluids as blood, urine), in health service, in water industry, in metallurgy, in education, in food industry, in agriculture, etc., as well as in environmental control, simple, precise, sufficiently highly sensitive methods, which can be easily automated and which can be applied in field measurements, are necessary. From this point of view, electrochemical methods, especially voltammetry and potentiometric stripping analysis (PSA), or electrochemical detection used in separation methods, are very well suited. Wide range of applications belongs to their advantages as well. These techniques are advantageous due to their possibility to be utilized in analysis of trace elements, their complexes, various inorganic and organic compounds in aqueous as well as nonaqueous solution systems [1, 2]. A high sensitivity and/or improvement in the signal-to-noise ratio can be attained by electrochemical preconcentration of the analyte and by application of non-stationary measuring techniques in voltammetry [3]. Computer control of the voltammetric measurement then enables complete automation of the measurement itself and of the handling of the evaluation of analyses.

The modern voltammetric methods have been derived from polarographic ones (polarography was introduced by Jaroslav Heyrovský in 1922 - awarded by Nobel Prize in 1959 for Polarography as analytical method). This method has proved to be very useful not only in analytical chemistry, but in many other branches of physical chemistry and other scientific branches as well. The development of polarography as an analytical method has been a long process. In the sixties of 20<sup>th</sup> century it was extensively replaced by new optical methods, especially atomic-absorption spectrometry (AAS) and ICP. The basic polarographic technique, DC polarography, can be used to determine electroactive substances down to concentrations of  $10^{-5}$  M and thus could not compete with these methods. The situation was changed by the introduction of hanging mercury drop electrode (HMDE) and of new voltammetric methods introduced in consequence of development in electronics (pulse techniques, as differential pulse voltammetry (DPV), stripping techniques etc.) [2].

The main field of analytical applications of voltammetry is in determination of trace elements. Here can be mentioned one of its main advantages: possibility of speciation. It is very important to understand the long term physicochemical behavior of trace elements and to check that legislation related to the discharge of these elements is respected [4]. Even in low concentrations,

heavy metals may present a severe hazard to normal functioning of aquatic ecosystem as they are not biodegradable but involved in biogeochemical cycles and then distributed under different physicochemical forms (i.e., simple inorganic species, organic complexes and metal ions adsorbed onto a variety of colloidal particles) [4]. The proportion of these different forms may vary continuously with space and time due to concurrently occurring physical, chemical and biological processes [4]. Any variation in the speciation of an element will affect its bioavailability, its rate of transport to the sediment and its overall mobility in the aquatic system. Thus, not only total metal concentration, but also metal speciation measurements (realizable by voltammetric techniques) are required to understand and predict the role and the fate of trace metals in environmental systems [5].

This contribution aims to analyze, how the problems (many times imaginary complications) connected with application of voltammetric (electroanalytical) methods, can be removed and how these can be reintroduced into common laboratories.

## 2 Main barriers in application of voltammetric techniques

The main limitations or better to say complications in reintroducing voltammetric techniques into common laboratories can be found in: a) stage of instrumentation and arising therefrom low productivity of labor (and demand on labor force); b) the use of mercury as traditional electrode material and c) pure incorporation of these techniques into legislative system.

### 2.1 Electrode materials

Modern voltammetric devices utilize one small drop of mercury for the complete measurement and the electrodes with about 1 mL reservoir (HMDE) can work for many weeks. Nevertheless, although not well-scientifically founded, we witness increasing fears of toxicity of liquid mercury in the last decades (from the toxicological point of view, the liquid mercury is practically non toxic; dangerous are its vapors, soluble inorganic and organic compounds only!), which resulted in almost "mercury-phobia", nowadays even embedded in resolutions of European parliament [6]. Strict ecological and safety rules introduced in the world as well as popular prejudices, fears and faults essentially complicate the use of mercury or liquid mercury containing electrodes (including HMDE). Paradoxically, some people replaced the HMDE by mercury film electrodes, which are prepared from solution of highly toxic Hg(II)-ions. In consequence of this situation, the

attention has been recently devoted to the development of solid electrodes, containing no liquid mercury. Some of these solid electrodes have been used for many decades (gold, silver copper etc.). However, there are some new types of them, which have been successfully utilized in analysis of trace elements in environment. We can mention a few highly interesting new trends in their development, e.g., solid amalgam, composite (or their combinations), carbon paste, boron doped diamond film, or bismuth electrodes (e.g., [7]). Let us describe the first two mentioned types of successfully applied electrode materials more in detail in the following paragraphs.

#### 2.1.1 Solid amalgam electrodes

Solid amalgam electrodes (SAEs) as environmentally friendly alternatives to mercury electrodes are suitable both for batch analysis and for HPLC with electrochemical detection (HPLC-ED) or flow injection analysis with electrochemical detection (FIA-ED) of electrochemically active substances with limit of quantitation (LOQ) down to  $10^{-7}$  mol.L<sup>-1</sup>. They can be easily prepared in any laboratory and their simple electrochemical pretreatment in many cases eliminates problems with their passivation. They are described in other place of this book in detail [8]. These electrodes proved to be very suitable in many fields of electroanalysis, e.g., of trace elements (Cd, Pb, Cu, Tl, Zn etc.), of amino acids, of environmentally important organic compounds (nitrobenzene, nitrophenols, Doxorubicin, Ostazine Orange etc.), of phytochelatin, of metallothioneins, of nucleic bases, of DNA [9-26]. There are several types of MeSAE (Me means the metal, from which is the dental amalgam formed): polished – liquid mercury free solid amalgam electrode (p-MeSAE); mercury film – polished MeSAE covered by mercury film (MF-MeSAE); mercury meniscus – polished MeSAE covered by mercury meniscus (m-MeSAE); paste – based on a fine solid amalgam powder and liquid oil (or other suitable liquid part of the paste; MeSAPE); composite – based on a fine solid amalgam powder and a solid polymer (MeSACE). Working electrodes (WE) from solid amalgams containing metal which is electrochemically less active than mercury (e.g., AgSAE, AuSAE, IrSAE) have their main properties similar to HMDE. SAEs including metal more active than mercury (e.g., CuSAE, BiSAE, CdAgSAE) can be applied for specific purposes when an analyte interacts just with this metal [20]. Their stability and possibility of adoption to the required form enable their utilization in flow-through analysis or in field applications as well as in the form of screen printed electrodes.

### 2.1.2 Solid composite electrodes

Solid composite electrodes belong to the group of composite electrodes with randomly distributed two or more compounds, which after their mixing exhibit solid consistency. They are composed of at least one conductor phase and at least one insulator phase, particles of which are mutually mixed [27, 28]. Electrode materials, mentioned in this contribution, belong to the group of composite electrodes-random ensembles-dispersed-solid electrodes. Insulator phase is usually represented by polymeric (acrylic polymer, epoxy resin, polyvinyl chloride (PVC), teflon, vinylacetate, polyester, polyethylene, etc.) or monomeric material. Conductor phase can be formed by a metal (silver, gold, etc.) or by other nonmetallic conducting material (e.g., graphite powder). Some other components can be added into bulk of the electrode materials to achieve desired properties, e.g., cobalt phthalocyanine,  $\text{Cu}_2\text{O}$ , Ni/Cu, hexacyanoferrate, manganese, methylene blue,  $\text{Ru}[(\text{tpy})(\text{bpy})\text{Cl}]\text{PF}_6$ , or their mixtures. Surface of these electrodes can be also modified, e.g., by Nafion or by a catalyst (e.g., enzymes (e.g., tyrosinase), Au-Pd,  $\text{RuO}_2$ , silica gel) [7, 27-35]. There are many other variants of composite electrode materials with various applications in environmental analysis. Similarly as the SAEs, due to their stability, possibility of adoption to the required form, easy preparation and contacting etc., they can be utilized in flow-through analysis or in field applications as well as in the form of screen printed electrodes.

Electrodes constructed on basis of the above mentioned materials can be utilized for classical electroanalytical purposes as well as for scientific studies of some interesting effects, e.g., underpotential deposition effect (UPD) (where in dependence on electrode material, analyte and its concentration more than one peak is registered during the scan), which can be later applied in analysis again [29, 30, 32-40].

Analytical applications of solid composite electrodes are very wide. They can be used as amperometric sensors in voltammetry, in PSA, in HPLC-ED, in FIA-ED, in luminescence techniques or in CZE-ED; in aqueous as well in non-aqueous solutions. They can be applied in determination of metals (Pb, Cd, Tl, etc.), inorganic (e.g., chlorides, iodides, nitrates) as well as organic compounds (e.g., phenylglyoxylic acid, alizarin chrome black PT, adenine, guanine, ascorbic acid, metallothionein) (e.g., [7, 29, 30, 32-41]).

To advantages of composite electrodes belongs a relatively wide potential window, which can reach more than 4 V (e.g., graphite composite electrode (30 % of graphite), in 0.05 M borax buffer pH 9.2) ([34, 35, 38-40]).

## 2.2 Automation of Electrochemical Experiments

There are some effects, which are limiting the wider utilization of voltammetric and other methods derived from polarography (e.g., chronoamperometry, potentiometric stripping analysis), not only in research, but also in industrial laboratories: higher demand on operator qualification in comparison with spectral methods, and relatively low productivity of measurements. Modern trends of development of instrumentation of electrochemical methods, mostly connected with application of computer technique, enable to reduce essentially the mentioned disadvantages.

Many attempts have been made in the history of electrochemistry to increase the productivity of measurements. Probably to the first ones belong the attempts about 80 years ago [42] to construct something like carousel with active and resting electrodes. Further development of the automation process was enabled by introduction of computer technique in the nineties of the last century. Some attempts were performed to connect and to control more than one polarographic device using only one controlling computer [43]. However, the suggested solutions were not optimal. The other variant, suggested in [43], to send parallel signal to all stands connected to the interface card, and sequential processing of outputting signals using a multiplexer, seems to be hardly realizable in fast measurements.

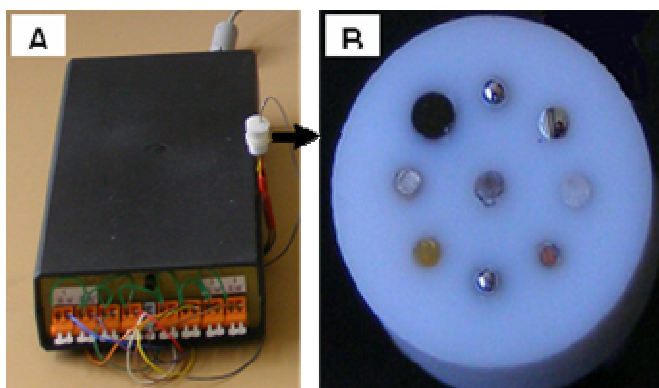
Relatively wide spread and on the market commonly available is the handheld electrochemical sensor interface Palmsens (Palm Instruments, The Netherlands). This instrument is used for sensors or cells with 2 or 3 electrodes and allows application of micro- as well as macroelectrodes [44]. It can be extended with an optional 8-channel multiplexer. However, the parameters applied to all sensors must be identical.

A computer-controlled instrument, based on scanning electrochemical microscope technology, was employed in the miniaturized combinatorial electrosynthesis of localized compound collections [45, 46]. Other automated system utilized for submersible voltammetric continuous in-situ monitoring was described in [4].

The multichannel device for sequential autonomous measurements for laboratory as well as field in-situ realized analysis was recently developed and constructed in our laboratory [47, 48]. This device is composed of computer (PC or notebook), interface card, control box (including the multiplexer) and set of sensors. The prototype of the instrument (Fig. 1) is able to analyze up to 8 samples in a chosen sequence, where each sample can be analyzed using a different method, different parameters, in 2- or 3- electrode mode, etc. Generally, the analyzer enables to apply the following techniques: direct current (DC) voltammetry, DP voltammetry, potentiometric stripping analysis, differential

potentiometric stripping analysis, chronoamperometry, and coulometry. Nevertheless, the actually applied method can be designed, using software "MultiElchem Design Utility", according to requirements of the user (e.g., DC scan for electrode surface renovation, or for sample pretreatment, and the determination can be realized using DPV or PSA). The software includes a software unit for processing of registered curves by Elimination Voltammetry with Linear Scan [23, 35, 49, 50].

The device was tested in connection with multisensor with 8 different sensors (Fig. 1) (5 different solid amalgam electrodes, platinum, gold and glassy carbon electrodes), designed for small volumes (5-200  $\mu\text{L}$ ). This multisensor ( $\text{\O} 0.8 \text{ mm}$ ) was composed of an array of small sensors - 8 working electrodes: m-AgSAE ( $\text{\O} 0.8 \text{ mm}$ ), MF-AgSAE ( $\text{\O} 0.8 \text{ mm}$ ), p-AgSAE ( $\text{\O} 0.8 \text{ mm}$ ), copper (CuE;  $\text{\O} 0.6 \text{ mm}$ ), m-CuSAE ( $\text{\O} 0.8 \text{ mm}$ ), gold (AuE;  $\text{\O} 0.4 \text{ mm}$ ), platinum (PtE;  $\text{\O} 0.6 \text{ mm}$ ) and glassy carbon (GCE;  $\text{\O} 2.0 \text{ mm}$ ), and one platinum auxiliary electrode ( $\text{\O} 0.8 \text{ mm}$ ) (Fig. 1) (where "SAE"-means solid amalgam electrode, "m-" means modified, "p-" polished, MF-mercury film). The working electrodes were situated on the circumference of a disc, the platinum electrode, used as a common auxiliary electrode for the working electrodes, was placed in the centre of the disc (see Fig. 1). Calomel reference electrode based on silver solid amalgam was prepared in a disc shape, complementary to the above described sensor disc [19].



**Fig 1.** A) 8-channel polarographic/voltammetric/potentiometric computer-controlled device; B) the array of sensors containing Pt auxiliary electrode (in the centre) and 8 working electrodes (clockwise): m-AgSAE, MF-AgSAE, p-AgSAE, CuE, m-CuSAE, AuE, PtE and GCE.

The described device was successfully used for optimization of determinations of various organic and inorganic compounds as guanine (Gua), adenine (Ade), DNA, ascorbic acid, ferrocene, citric acid, iodates, heavy metals (e.g., Cd, Pb, Tl, Cu), etc.

### 3 Conclusion

Some disadvantages, weak points (e.g., low labor productivity) and alleged dangers (the use liquid mercury as electrode material) of the use of voltammetric techniques in electroanalysis can be easily removed. This aim can be fulfilled e.g. by introduction of new computer controlled devices, which are able to analyze sequentially number of sets of samples applying identical or different parameters of analysis, or to analyze one sample using a set of various electrodes. Miniaturized (in comparison with most of common devices), computer controlled, 8-channel electrochemical system, especially aimed at analysis of DNA, was designed and tested. This device enables to set up a different measurement method for each sensor (DCP, DCV, CV, DPV, PSA, DPSA, chronoamperometry etc.), 2- or 3-electrode mode, different parameters of measurement and parameters of electrochemical regeneration of each working electrode before every scan for each channel, independently of others. Each working electrode can utilize its own reference electrode or one common reference electrode can be used for all channels (advantageous e.g. in DNA analysis).

The liquid mercury in electrodes can be successfully replaced by new modern electrode materials, as in this contribution described solid amalgams (polished or by film layer or by meniscus modified surfaces) or solid composite materials (composed at least from one conducting and one insulating material).

We believe that each modern analytical laboratory can be equipped by voltammetric devices, which are of high-quality, low cost and the obtained results of analysis of environmental samples (including trace metal determination) are fully comparable with those achieved using other techniques.

#### Acknowledgements

Financial support of this work was provided by the GA  $\text{\C}R$  (projects No. 521/06/0496 and No. 203/07/1195) and by the MPO  $\text{\C}R$  (project No. 1H-PK/42).

#### References:

- [1] M. Kopanica and I. Sestakova, Electroanalysis in Environmental Control, in *Electrochemistry for Environmental Protection* Eds: K. Stulik and R. Kalvoda), UNESCO ROSTE, Venice 1996, pp. 165-172.
- [2] M. Kopanica, Modern Polarographic Methods in Chemical Analysis, in *Advanced Instrumental Methods of Chemical Analysis* (Ed: J. Churacek), Academia, Praha 1993, pp. 75-94.
- [3] R. Kalvoda, *Electroanalytical Methods in Chemical and Environmental Analysis*, Plenum Press, New

- York 1987.
- [4] M. L. Tercier, J. Buffle, and F. Graziottin, Novel voltammetric in-situ profiling system for continuous real-time monitoring of trace elements in natural waters, *Electroanalysis*, Vol. 10, No. 6, 1998, pp. 355-363.
- [5] H. W. Jannasch, C. O. Wirsen, S. J. Molyneux, and T. A. Langworthy, Comparative Physiological-Studies on Hyperthermophilic Archaea Isolated from Deep-Sea Hot Vents with Emphasis on *Pyrococcus* Strain Gb-D, *Applied and Environmental Microbiology*, Vol. 58, No. 11, 1992, pp. 3472-3481.
- [6] European parliament, *EU mercury strategy*, [http://www.europarl.europa.eu/news/expert/infopress\\_page/064-6115-073-03-11-911-20060309IPR06021-14-03-2006-2006-false/default\\_en.htm](http://www.europarl.europa.eu/news/expert/infopress_page/064-6115-073-03-11-911-20060309IPR06021-14-03-2006-2006-false/default_en.htm), 14. 3. 2006.
- [7] J. Barek, J. Fischer, T. Navratil, K. Peckova, B. Yosypchuk, and J. Zima, Non-traditional Electrode Materials in Environmental Analysis of Biologically Active Organic Compounds, *Electroanalysis*, Vol. 19, No. 19-20, 2007, pp. 2003-2014.
- [8] B. Yosypchuk and I. Sestakova, Non-traditional Metal Electrode Materials in Electrochemical Environmental Analysis of Biologically Active Compounds, in *5th WSEAS International Conference on ENVIRONMENT, ECOSYSTEMS and DEVELOPMENT*, WSEAS, Puerto De La Cruz 2007.
- [9] R. Selesovska-Fadrna, M. Fojta, T. Navratil, and J. Chylkova, Brdicka-type processes of cysteine and cysteine-containing peptides on silver amalgam electrodes, *Analytica Chimica Acta*, Vol. 582, No. 2, 2007, pp. 344-352.
- [10] L. Novotny, L. Havran, B. Josypchuk, and M. Fojta, Adsorptive stripping voltammetry of denatured DNA on Hg/Ag electrode, *Electroanalysis*, Vol. 12, No. 12, 2000, pp. 960-962.
- [11] B. Yosypchuk, M. Heyrovsky, E. Palecek, and L. Novotny, Use of solid amalgam electrodes in nucleic acid analysis, *Electroanalysis*, Vol. 14, No. 21, 2002, pp. 1488-1493.
- [12] B. Yosypchuk and L. Novotny, The arrangement of a combined voltammetric-potentiometric sensor with the solid silver amalgam bridge, *Chemicke Listy*, Vol. 96, No. 11, 2002, pp. 886-888.
- [13] B. Yosypchuk and L. Novotny, Electrodes of nontoxic solid amalgams for electrochemical measurements, *Electroanalysis*, Vol. 14, No. 24, 2002, pp. 1733-1738.
- [14] B. Yosypchuk and L. Novotny, Combined voltammetric-potentiometric sensor with silver solid amalgam link for electroanalytical measurements, *Electroanalysis*, Vol. 14, No. 24, 2002, pp. 1739-1741.
- [15] B. Yosypchuk and L. Novotny, Voltammetric determination of Cu, Pb, Cd, Zn and Tl using the silver solid amalgam electrode, *Chemicke Listy*, Vol. 96, No. 9, 2002, pp. 756-760.
- [16] B. Yosypchuk and L. Novotny, Determination of iodates using silver solid amalgam electrodes, *Electroanalysis*, Vol. 14, No. 15-16, 2002, pp. 1138-1142.
- [17] B. Yosypchuk and L. Novotny, Nontoxic electrodes of solid amalgams, *Critical Reviews in Analytical Chemistry*, Vol. 32, No. 2, 2002, pp. 141-151.
- [18] B. Yosypchuk and L. Novotny, Cathodic stripping voltammetry of cysteine using silver and copper solid amalgam electrodes, *Talanta*, Vol. 56, No. 5, 2002, pp. 971-976.
- [19] B. Yosypchuk and L. Novotny, Mercurous sulfate reference electrode based on solid silver amalgam, *Chemicke Listy*, Vol. 97, No. 11, 2003, pp. 1083-1086.
- [20] B. Yosypchuk and L. Novotny, Copper solid amalgam electrodes, *Electroanalysis*, Vol. 15, No. 2, 2003, pp. 121-125.
- [21] R. Fadrna, Polished silver solid amalgam electrode: Further characterization and applications in voltammetric measurements, *Analytical Letters*, Vol. 37, No. 15, 2004, pp. 3255-3270.
- [22] R. Fadrna, K. Cahova-Kucharikova, L. Havran, B. Yosypchuk, and M. Fojta, Use of polished and mercury film-modified silver solid amalgam electrodes in electrochemical analysis of DNA, *Electroanalysis*, Vol. 17, No. 5-6, 2005, pp. 452-459.
- [23] R. Fadrna, B. Yosypchuk, M. Fojta, T. Navratil, and L. Novotny, Voltammetric determination of adenine, guanine, and DNA using liquid mercury free polished silver solid amalgam electrode, *Analytical Letters*, Vol. 37, No. 3, 2004, pp. 399-413.
- [24] A. Danhel, K. Peckova, K. Cizek, J. Barek, J. Zima, B. Yosypchuk, and T. Navratil, Voltammetric determination of genotoxic dinitronaphthalenes with meniscus-modified silver solid amalgam electrode, *Chemicke Listy*, Vol. 101, No. 2, 2007, pp. 144-149.
- [25] J. Barek, E. Dodova, T. Navratil, B. Yosypchuk, L. Novotny, and J. Zima, Voltammetric determination of N,N-dimethyl-4-amine-carboxyazobenzene at a silver solid amalgam electrode, *Electroanalysis*, Vol. 15, No. 22, 2003, pp. 1778-1781.
- [26] B. Yosypchuk, I. Sestakova, and L. Novotny, Voltammetric determination of phytochelatin

- using copper solid amalgam electrode, *Talanta*, Vol. 59, No. 6, 2003, pp. 1253-1258.
- [27] D. E. Tallman and S. L. Petersen, Composite Electrodes For Electroanalysis - Principles And Applications, *Electroanalysis*, Vol. 2, No. 7, 1990, pp. 499-510.
- [28] S. L. Petersen and D. E. Tallman, Silver Composite Electrode for Voltammetry, *Analytical Chemistry*, Vol. 60, No. 1, 1988, pp. 82-86.
- [29] T. Navratil, J. Barek, and M. Kopanica, Anodic Stripping Voltammetry Using Graphite Composite Electrode, *Central European Journal of Chemistry*, Submitted 2007.
- [30] T. Navratil and M. Kopanica, Analytical application of silver composite electrode, *Critical Reviews in Analytical Chemistry*, Vol. 32, No. 2, 2002, pp. 153-166.
- [31] J. Navarro-Laboulais, J. Trijueque, J. J. Garcia-Jareno, D. Benito, and F. Vicente, Electrochemical impedance spectroscopy of conductor-insulator composite electrodes: properties in the blocking and diffusive regimes, *Journal of Electroanalytical Chemistry*, Vol. 444, No. 2, 1998, pp. 173-186.
- [32] T. Navratil and M. Kopanica, Lead determination on silver composite electrodes using the effect of underpotential deposition, *Chemické Listy*, Vol. 96, No. 2, 2002, pp. 111-116.
- [33] T. Navratil, M. Kopanica, and J. Krista, Anodic stripping voltammetry for arsenic determination on composite gold electrode, *Chemia Analityczna*, Vol. 48, No. 2, 2003, pp. 265-272.
- [34] T. Navratil, S. Sebkova, and M. Kopanica, Voltammetry of lead cations on a new type of silver composite electrode in the presence of other cations, *Analytical and Bioanalytical Chemistry*, Vol. 379, No. 2, 2004, pp. 294-301.
- [35] T. Navratil, Z. Senholdova, K. Shanmugam, and J. Barek, Voltammetric determination of phenylglyoxylic acid in urine using graphite composite electrode, *Electroanalysis*, Vol. 18, No. 2, 2006, pp. 201-206.
- [36] T. Navratil, Kompozitní elektrody, in *Možnosti inovací v elektroanalytické chemii, projekt "Pražské analytické centrum inovací" (Prague Centre for Innovations in Analytical Chemistry)* (Ed: J. Barek), VŠCHT, Prague 2006, pp. 113-118.
- [37] T. Navratil and M. Kopanica, Indirect voltammetric determination of thiocyanate ions in electroplating solutions, *Chemia Analityczna*, Vol. 48, No. 1, 2003, pp. 127-138.
- [38] S. Sebkova, T. Navratil, and M. Kopanica, Comparison of different types of silver composite electrodes to varied amount of silver on example of determination of 2-nitronaphtalene, *Analytical Letters*, Vol. 36, No. 13, 2003, pp. 2767-2782.
- [39] S. Sebkova, T. Navratil, and M. Kopanica, Silver composite electrode for voltammetric determination of halogenides, *Analytical Letters*, Vol. 37, No. 4, 2004, pp. 603-628.
- [40] S. Sebkova, T. Navratil, and M. Kopanica, Graphite composite electrode in voltammetry, *Analytical Letters*, Vol. 38, No. 11, 2005, pp. 1747-1758.
- [41] I. Sestakova and T. Navratil, Voltammetric methods in metallothionein research, *Bioinorganic Chemistry and Applications*, Vol. 3, No. 1-2, 2005, pp. 43-53.
- [42] P. Herasymenko, Adsorption processes in anodic oxidation of formic acid, *Ukrainskii Khimicheskii Zhurnal*, Vol. 4, 1929, pp. 439-452.
- [43] M. Drevinek and F. Trojanek, A voltammetric system for simultaneous measurement of several samples, *Chemické Listy*, Vol. 98, No. 4, 2004, pp. 188-190.
- [44] PalmSensens, *PalmSens - Handheld Electrochemical Sensor Interface*, <http://www.palmsens.com/>.
- [45] W. Markle and B. Speiser, Combinatorial microelectrochemistry - Part 3. On-line monitoring of electrolyses by steady-state cyclic voltammetry at microelectrodes, *Electrochimica Acta*, Vol. 50, No. 25-26, 2005, pp. 4916-4925.
- [46] W. Markle, B. Speiser, C. Tittel, and M. Vollmer, Combinatorial micro electrochemistry - Part 1. Automated micro electrosynthesis of iminoquinol ether and [1,2,4]triazolo[4,3- $\alpha$ ]pyridinium perchlorate collections in the wells of microtiter plates, *Electrochimica Acta*, Vol. 50, No. 14, 2005, pp. 2753-2762.
- [47] T. Navratil and B. Yosypchuk, Automation of Electrochemical Experiments Using Multichannel Device for Sequential Autonomous Measurements, *Chemia Analityczna*, Submitted 2007.
- [48] T. Navratil, B. Yosypchuk, and M. Fojta, The way of automated measurement of electrochemical signal on number sets electrodes and apparatus for the realization of this way, Application No. PV 2007-40, 2007.
- [49] O. Dracka, Theory of current elimination in linear scan voltammetry, *Journal of Electroanalytical Chemistry*, Vol. 402, No. 1-2, 1996, pp. 19-28.
- [50] S. Sander, T. Navratil, and L. Novotny, Study of the complexation, adsorption and electrode reaction mechanisms of chromium(VI) and (III) with DTPA under adsorptive stripping voltammetric conditions, *Electroanalysis*, Vol. 15, No. 19, 2003, pp. 1513-1521.